CHAPTER 1

Introduction to Design

1.1. INTRODUCTION

This chapter is an introduction to the nature and methodology of the design process, and its application to the design of chemical manufacturing processes.

1.2. NATURE OF DESIGN

This section is a general, somewhat philosophical, discussion of the design process; how a designer works. The subject of this book is chemical engineering design, but the methodology of design described in this section applies equally to other branches of engineering design.

Design is a creative activity, and as such can be one of the most rewarding and satisfying activities undertaken by an engineer. It is the synthesis, the putting together, of ideas to achieve a desired purpose. The design does not exist at the commencement of the project. The designer starts with a specific objective in mind, a need, and by developing and evaluating possible designs, arrives at what he considers the best way of achieving that objective; be it a better chair, a new bridge, or for the chemical engineer, a new chemical product or a stage in the design of a production process.

When considering possible ways of achieving the objective the designer will be constrained by many factors, which will narrow down the number of possible designs; but, there will rarely be just one possible solution to the problem, just one design. Several alternative ways of meeting the objective will normally be possible, even several best designs, depending on the nature of the constraints.

These constraints on the possible solutions to a problem in design arise in many ways. Some constraints will be fixed, invariable, such as those that arise from physical laws, government regulations, and standards. Others will be less rigid, and will be capable of relaxation by the designer as part of his general strategy in seeking the best design. The constraints that are outside the designer's influence can be termed the external constraints. These set the outer boundary of possible designs; as shown in Figure 1.1. Within this boundary there will be a number of plausible designs bounded by the other constraints, the internal constraints, over which the designer has some control; such as, choice of process, choice of process conditions, materials, equipment.

Economic considerations are obviously a major constraint on any engineering design: plants must make a profit.

Time will also be a constraint. The time available for completion of a design will usually limit the number of alternative designs that can be considered.

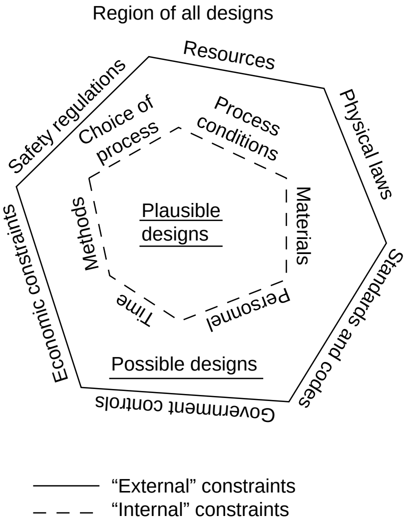

Figure 1.1. Design constraints

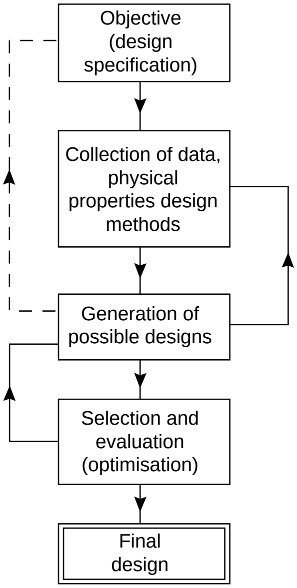

Figure 1.2. The design process

The stages in the development of a design, from the initial identification of the objective to the final design, are shown diagrammatically in Figure 1.2. Each stage is discussed in the following sections.

Figure 1.2 shows design as an iterative procedure; as the design develops the designer will be aware of more possibilities and more constraints, and will be constantly seeking new data and ideas, and evaluating possible design solutions.

1.2.1. The design objective (the need)

Chaddock (1975) defined design as, the conversion of an ill-defined requirement into a satisfied customer.

The designer is creating a design for an article, or a manufacturing process, to fulfil a particular need. In the design of a chemical process, the need is the public need for the product, the commercial opportunity, as foreseen by the sales and marketing organisation. Within this overall objective the designer will recognise sub-objectives; the requirements of the various units that make up the overall process.

Before starting work the designer should obtain as complete, and as unambiguous, a statement of the requirements as possible. If the requirement (need) arises from outside the design group, from a client or from another department, then he will have to elucidate the real requirements through discussion. It is important to distinguish between the real needs and the wants. The wants are those parts of the initial specification that may be thought desirable, but which can be relaxed if required as the design develops. For example, a particular product specification may be considered desirable by the sales department, but may be difficult and costly to obtain, and some relaxation of the specification may be possible, producing a saleable but cheaper product. Whenever he is in a position to do so, the designer should always question the design requirements (the project and equipment specifications) and keep them under review as the design progresses.

Where he writes specifications for others, such as for the mechanical design or purchase of a piece of equipment, he should be aware of the restrictions (constraints) he is placing on other designers. A tight, well-thought-out, comprehensive, specification of the requirements defines the external constraints within which the other designers must work.

1.2.2. Data collection

To proceed with a design, the designer must first assemble all the relevant facts and data required. For process design this will include information on possible processes, equipment performance, and physical property data. This stage can be one of the most time consuming, and frustrating, aspects of design. Sources of process information and physical properties are reviewed in Chapter 8.

Many design organisations will prepare a basic data manual, containing all the process "know-how" on which the design is to be based. Most organisations will have design manuals covering preferred methods and data for the more frequently used, routine, design procedures.

The national standards are also sources of design methods and data; they are also design constraints.

The constraints, particularly the external constraints, should be identified early in the design process.

1.2.3. Generation of possible design solutions

The creative part of the design process is the generation of possible solutions to the problem (ways of meeting the objective) for analysis, evaluation and selection. In this activity the designer will largely rely on previous experience, his own and that of others.

It is doubtful if any design is entirely novel. The antecedence of most designs can usually be easily traced. The first motor cars were clearly horse-drawn carriages without the horse; and the development of the design of the modern car can be traced step by step from these early prototypes. In the chemical industry, modern distillation processes have developed from the ancient stills used for rectification of spirits; and the packed columns used for gas absorption have developed from primitive, brushwood-packed towers. So, it is not often that a process designer is faced with the task of producing a design for a completely novel process or piece of equipment.

The experienced engineer will wisely prefer the tried and tested methods, rather than possibly more exciting but untried novel designs. The work required to develop new processes, and the cost, is usually underestimated. Progress is made more surely in small steps. However, whenever innovation is wanted, previous experience, through prejudice, can inhibit the generation and acceptance of new ideas; the “not invented here” syndrome.

The amount of work, and the way it is tackled, will depend on the degree of novelty in a design project.

Chemical engineering projects can be divided into three types, depending on the novelty involved:

1. Modifications, and additions, to existing plant; usually carried out by the plant design group.
2. New production capacity to meet growing sales demand, and the sale of established processes by contractors. Repetition of existing designs, with only minor design changes.
3. New processes, developed from laboratory research, through pilot plant, to a commercial process. Even here, most of the unit operations and process equipment will use established designs.

The first step in devising a new process design will be to sketch out a rough block diagram showing the main stages in the process; and to list the primary function (objective) and the major constraints for each stage. Experience should then indicate what types of unit operations and equipment should be considered.

Jones (1970) discusses the methodology of design, and reviews some of the special techniques, such as brainstorming sessions and synectics, that have been developed to help generate ideas for solving intractable problems. A good general reference on the art of problem solving is the classical work by Polya (1957); see also Chittenden (1987). Some techniques for problem solving in the Chemical Industry are covered in a short text by Casey and Frazer (1984).

The generation of ideas for possible solutions to a design problem cannot be separated from the selection stage of the design process; some ideas will be rejected as impractical as soon as they are conceived.

1.2.4. Selection

The designer starts with the set of all possible solutions bounded by the external constraints, and by a process of progressive evaluation and selection, narrows down the range of candidates to find the “best” design for the purpose.

The selection process can be considered to go through the following stages:

Possible designs (credible) — within the external constraints.
Plausible designs (feasible) — within the internal constraints.
Probable designs — likely candidates.
Best design (optimum) — judged the best solution to the problem.

The selection process will become more detailed and more refined as the design progresses from the area of possible to the area of probable solutions. In the early stages a coarse screening based on common sense, engineering judgement, and rough costings will usually suffice. For example, it would not take many minutes to narrow down the choice of raw materials for the manufacture of ammonia from the possible candidates of, say, wood, peat, coal, natural gas, and oil, to a choice of between gas and oil, but a more detailed study would be needed to choose between oil and gas. To select the best design from the probable designs, detailed design work and costing will usually be necessary. However, where the performance of candidate designs is likely to be close the cost of this further refinement, in time and money, may not be worthwhile, particularly as there will usually be some uncertainty in the accuracy of the estimates.

The mathematical techniques that have been developed to assist in the optimisation of designs, and plant performance, are discussed briefly in Section 1.10.

Rudd and Watson (1968) and Wells (1973) describe formal techniques for the preliminary screening of alternative designs.

1.3. THE ANATOMY OF A CHEMICAL MANUFACTURING PROCESS

The basic components of a typical chemical process are shown in Figure 1.3, in which each block represents a stage in the overall process for producing a product from the raw materials. Figure 1.3 represents a generalised process; not all the stages will be needed for any particular process, and the complexity of each stage will depend on the nature of the process. Chemical engineering design is concerned with the selection and arrangement of the stages, and the selection, specification and design of the equipment required to perform the stage functions.

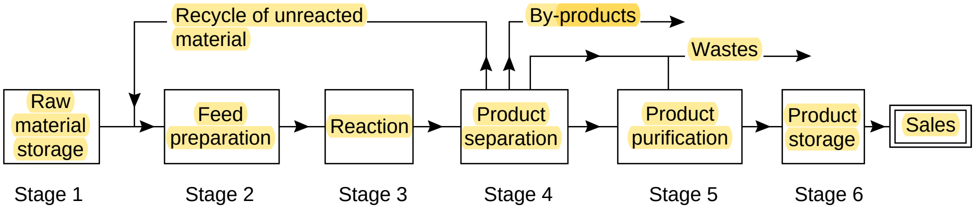

Figure 1.3. Anatomy of a chemical process

Stage 1. Raw material storage

Unless the raw materials (also called essential materials, or feed stocks) are supplied as intermediate products (intermediates) from a neighbouring plant, some provision will have to be made to hold several days, or weeks, storage to smooth out fluctuations and interruptions in supply. Even when the materials come from an adjacent plant some provision is usually made to hold a few hours, or even days, supply to decouple the processes. The storage required will depend on the nature of the raw materials, the method of delivery, and what assurance can be placed on the continuity of supply. If materials are delivered by ship (tanker or bulk carrier) several weeks stocks may be necessary; whereas if they are received by road or rail, in smaller lots, less storage will be needed.

Stage 2. Feed preparation

Some purification, and preparation, of the raw materials will usually be necessary before they are sufficiently pure, or in the right form, to be fed to the reaction stage. For example, acetylene generated by the carbide process contains arsenical and sulphur compounds, and other impurities, which must be removed by scrubbing with concentrated sulphuric acid (or other processes) before it is sufficiently pure for reaction with hydrochloric acid to produce dichloroethane. Liquid feeds will need to be vaporised before being fed to gas-phase reactors, and solids may need crushing, grinding and screening.

Stage 3. Reactor

The reaction stage is the heart of a chemical manufacturing process. In the reactor the raw materials are brought together under conditions that promote the production of the desired product; invariably, by-products and unwanted compounds (impurities) will also be formed.

Stage 4. Product separation

In this first stage after the reactor the products and by-products are separated from any unreacted material. If in sufficient quantity, the unreacted material will be recycled to the reactor. They may be returned directly to the reactor, or to the feed purification and preparation stage. The by-products may also be separated from the products at this stage.

Stage 5. Purification

Before sale, the main product will usually need purification to meet the product specification. If produced in economic quantities, the by-products may also be purified for sale.

Stage 6. Product storage

Some inventory of finished product must be held to match production with sales. Provision for product packaging and transport will also be needed, depending on the nature of the product. Liquids will normally be dispatched in drums and in bulk tankers (road, rail and sea), solids in sacks, cartons or bales.

The stock held will depend on the nature of the product and the market.

Ancillary processes

In addition to the main process stages shown in Figure 1.3, provision will have to be made for the supply of the services (utilities) needed; such as, process water, cooling water, compressed air, steam. Facilities will also be needed for maintenance, firefighting, offices and other accommodation, and laboratories; see Chapter 14.

1.3.1. Continuous and batch processes

Continuous processes are designed to operate 24 hours a day, 7 days a week, throughout the year. Some down time will be allowed for maintenance and, for some processes, catalyst regeneration. The plant attainment; that is, the percentage of the available hours in a year that the plant operates, will usually be 90 to 95%.

$$\text{Attainment \%} = \frac{\text{hours operated}}{8760} \times 100$$

Batch processes are designed to operate intermittently. Some, or all, the process units being frequently shut down and started up.

Continuous processes will usually be more economical for large scale production. Batch processes are used where some flexibility is wanted in production rate or product specification.

Choice of continuous versus batch production

The choice between batch or continuous operation will not be clear cut, but the following rules can be used as a guide.

Continuous

1. Production rate greater than 5×10^6 kg/h
2. Single product
3. No severe fouling
4. Good catalyst life
5. Proven processes design
6. Established market

Batch

1. Production rate less than 5×10^6 kg/h
2. A range of products or product specifications
3. Severe fouling
4. Short catalyst life
5. New product
6. Uncertain design

1.4. THE ORGANISATION OF A CHEMICAL ENGINEERING PROJECT

The design work required in the engineering of a chemical manufacturing process can be divided into two broad phases.

Phase 1. Process design, which covers the steps from the initial selection of the process to be used, through to the issuing of the process flow-sheets; and includes the selection,

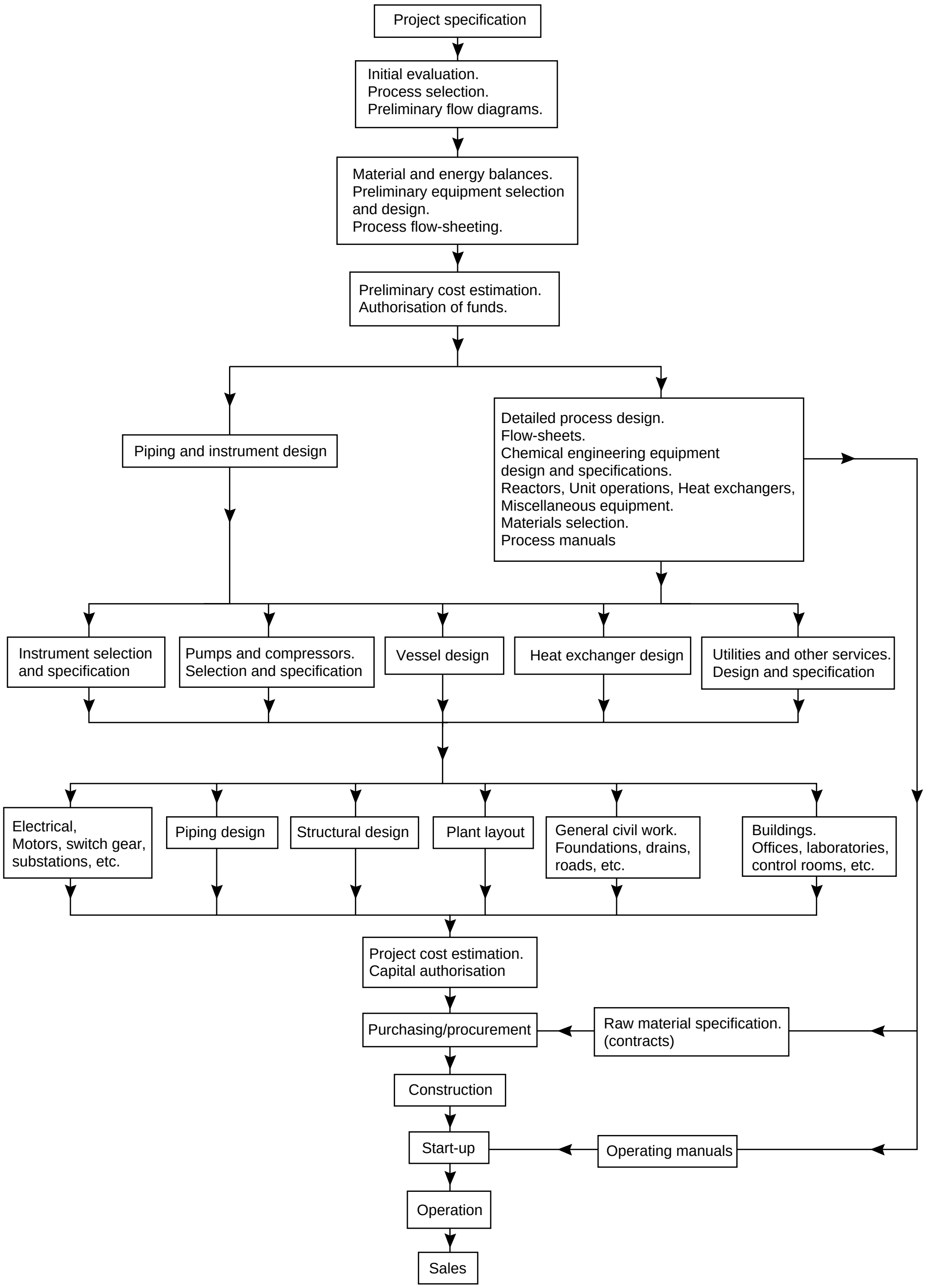

Figure 1.4. The structure of a chemical engineering project

specification and chemical engineering design of equipment. In a typical organisation, this phase is the responsibility of the Process Design Group, and the work will be mainly done by chemical engineers. The process design group may also be responsible for the preparation of the piping and instrumentation diagrams.

Phase 2. The detailed mechanical design of equipment; the structural, civil and electrical design; and the specification and design of the ancillary services. These activities will be the responsibility of specialist design groups, having expertise in the whole range of engineering disciplines.

Other specialist groups will be responsible for cost estimation, and the purchase and procurement of equipment and materials.

The sequence of steps in the design, construction and start-up of a typical chemical process plant is shown diagrammatically in Figure 1.4 and the organisation of a typical project group in Figure 1.5. Each step in the design process will not be as neatly separated from the others as is indicated in Figure 1.4; nor will the sequence of events be as clearly defined. There will be a constant interchange of information between the various design sections as the design develops, but it is clear that some steps in a design must be largely completed before others can be started.

A project manager, often a chemical engineer by training, is usually responsible for the co-ordination of the project, as shown in Figure 1.5.

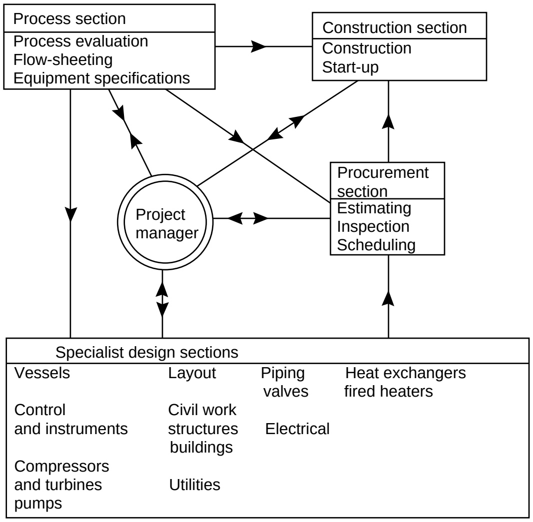

Figure 1.5. Project organisation

As was stated in Section 1.2.1, the project design should start with a clear specification defining the product, capacity, raw materials, process and site location. If the project is based on an established process and product, a full specification can be drawn up at the start of the project. For a new product, the specification will be developed from an economic evaluation of possible processes, based on laboratory research, pilot plant tests and product market research.

The organisation of chemical process design is discussed in more detail by Rase and Barrow (1964) and Baasel (1974).

Some of the larger chemical manufacturing companies have their own project design organisations and carry out the whole project design and engineering, and possibly construction, within their own organisation. More usually the design and construction, and possibly assistance with start-up, is entrusted to one of the international contracting firms.

The operating company will often provide the "know-how" for the process, and will work closely with the contractor throughout all stages of the project.

1.5. PROJECT DOCUMENTATION

As shown in Figure 1.5 and described in Section 1.4, the design and engineering of a chemical process requires the co-operation of many specialist groups. Effective co-operation depends on effective communications, and all design organisations have formal procedures for handling project information and documentation. The project documentation will include:

1. General correspondence	within the design group and with:
	government departments
	equipment vendors
	site personnel
	the client
2. Calculation sheets	design calculations
	costing
	computer print-out
3. Drawings	flow-sheets
	piping and instrumentation diagrams
	layout diagrams
	plot/site plans
	equipment details
	piping diagrams
	architectural drawings
	design sketches
4. Specification sheets	for equipment, such as:
	heat exchangers
	pumps
5. Purchase orders	quotations
	invoices

All documents should be assigned a code number for easy cross referencing, filing and retrieval.

Calculation sheets

The design engineer should develop the habit of setting out calculations so that they can be easily understood and checked by others. It is good practice to include on calculation sheets the basis of the calculations, and any assumptions and approximations made, in sufficient detail for the methods, as well as the arithmetic, to be checked. Design calculations are normally set out on standard sheets. The heading at the top of each sheet should include: the project title and identification number and, most importantly, the signature (or initials) of the person who checked the calculation.

Drawings

All project drawings are normally drawn on specially printed sheets, with the company name; project title and number; drawing title and identification number; draughtsman's name and person checking the drawing; clearly set out in a box in the bottom right-hand corner. Provision should also be made for noting on the drawing all modifications to the initial issue.

Drawings should conform to accepted drawing conventions, preferably those laid down by the national standards. The symbols used for flow-sheets and piping and instrument diagrams are discussed in Chapter 4. Drawings and sketches are normally made on detail paper (semi-transparent) in pencil, so modifications can be easily made, and prints taken.

In most design offices Computer Aided Design (CAD) methods are now used to produce the drawings required for all the aspects of a project: flow-sheets, piping and instrumentation, mechanical and civil work.

Specification sheets

Standard specification sheets are normally used to transmit the information required for the detailed design, or purchase, of equipment items; such as, heat exchangers, pumps, columns.

As well as ensuring that the information is clearly and unambiguously presented, standard specification sheets serve as check lists to ensure that all the information required is included.

Examples of equipment specification sheets are given in Appendix G.

Process manuals

Process manuals are often prepared by the process design group to describe the process and the basis of the design. Together with the flow-sheets, they provide a complete technical description of the process.

Operating manuals

Operating manuals give the detailed, step by step, instructions for operation of the process and equipment. They would normally be prepared by the operating company personnel, but may also be issued by a contractor as part of the contract package for a less experienced client. The operating manuals would be used for operator instruction and training, and for the preparation of the formal plant operating instructions.

1.6. CODES AND STANDARDS

The need for standardisation arose early in the evolution of the modern engineering industry; Whitworth introduced the first standard screw thread to give a measure of interchangeability between different manufacturers in 1841. Modern engineering standards cover a much wider function than the interchange of parts. In engineering practice they cover:

1. Materials, properties and compositions.
2. Testing procedures for performance, compositions, quality.
3. Preferred sizes; for example, tubes, plates, sections.
4. Design methods, inspection, fabrication.
5. Codes of practice, for plant operation and safety.

The terms STANDARD and CODE are used interchangeably, though CODE should really be reserved for a code of practice covering say, a recommended design or operating procedure; and STANDARD for preferred sizes, compositions, etc.

All of the developed countries, and many of the developing countries, have national standards organisations, responsible for the issue and maintenance of standards for the manufacturing industries, and for the protection of consumers. In the United Kingdom preparation and promulgation of national standards are the responsibility of the British Standards Institution (BSI). The Institution has a secretariat and a number of technical personnel, but the preparation of the standards is largely the responsibility of committees of persons from the appropriate industry, the professional engineering institutions and other interested organisations.

In the United States the government organisation responsible for coordinating information on standards is the National Bureau of Standards; standards are issued by Federal, State and various commercial organisations. The principal ones of interest to chemical engineers are those issued by the American National Standards Institute (ANSI), the American Petroleum Institute (API), the American Society for Testing Materials (ASTM), and the American Society of Mechanical Engineers (ASME) (pressure vessels). Burklin (1979) gives a comprehensive list of the American codes and standards.

The International Organization for Standardization (ISO) coordinates the publication of international standards.

All the published British standards are listed, and their scope and application described, in the *British Standards Institute Catalogue*; which the designer should consult. The catalogue is available online, go to the BSI group home page, www.bsi-global.com.

As well as the various national standards and codes, the larger design organisations will have their own (in-house) standards. Much of the detail in engineering design work is routine and repetitious, and it saves time and money, and ensures a conformity between projects, if standard designs are used whenever practicable.

Equipment manufacturers also work to standards to produce standardised designs and size ranges for commonly used items; such as electric motors, pumps, pipes and pipe fittings. They will conform to national standards, where they exist, or to those issued by trade associations. It is clearly more economic to produce a limited range of standard sizes than to have to treat each order as a special job.

For the designer, the use of a standardised component size allows for the easy integration of a piece of equipment into the rest of the plant. For example, if a standard range of centrifugal pumps is specified the pump dimensions will be known, and this facilitates the design of the foundations plates, pipe connections and the selection of the drive motors: standard electric motors would be used.

For an operating company, the standardisation of equipment designs and sizes increases interchangeability and reduces the stock of spares that have to be held in maintenance stores.

Though there are clearly considerable advantages to be gained from the use of standards in design, there are also some disadvantages. Standards impose constraints on the designer. The nearest standard size will normally be selected on completing a design calculation (rounding-up) but this will not necessarily be the optimum size; though as the standard size will be cheaper than a special size, it will usually be the best choice from the point of view of initial capital cost. Standard design methods must, of their nature, be historical, and do not necessarily incorporate the latest techniques.

The use of standards in design is illustrated in the discussion of the pressure vessel design standards (codes) in Chapter 13.

1.7. FACTORS OF SAFETY (DESIGN FACTORS)

Design is an inexact art; errors and uncertainties will arise from uncertainties in the design data available and in the approximations necessary in design calculations. To ensure that the design specification is met, factors are included to give a margin of safety in the design; safety in the sense that the equipment will not fail to perform satisfactorily, and that it will operate safely: will not cause a hazard. “Design factor” is a better term to use, as it does not confuse safety and performance factors.

In mechanical and structural design, the magnitude of the design factors used to allow for uncertainties in material properties, design methods, fabrication and operating loads are well established. For example, a factor of around 4 on the tensile strength, or about 2.5 on the 0.1 per cent proof stress, is normally used in general structural design. The selection of design factors in mechanical engineering design is illustrated in the discussion of pressure vessel design in Chapter 13.

Design factors are also applied in process design to give some tolerance in the design. For example, the process stream average flows calculated from material balances are usually increased by a factor, typically 10 per cent, to give some flexibility in process operation. This factor will set the maximum flows for equipment, instrumentation, and piping design. Where design factors are introduced to give some contingency in a process design, they should be agreed within the project organisation, and clearly stated in the project documents (drawings, calculation sheets and manuals). If this is not done, there is a danger that each of the specialist design groups will add its own “factor of safety”; resulting in gross, and unnecessary, over-design.

When selecting the design factor to use a balance has to be made between the desire to make sure the design is adequate and the need to design to tight margins to remain competitive. The greater the uncertainty in the design methods and data, the bigger the design factor that must be used.

1.8. SYSTEMS OF UNITS

To be consistent with the other volumes in this series, SI units have been used in this book. However, in practice the design methods, data and standards which the designer will use are often only available in the traditional scientific and engineering units. Chemical engineering has always used a diversity of units; embracing the scientific CGS and MKS systems, and both the American and British engineering systems. Those engineers in the older industries will also have had to deal with some bizarre traditional units; such as degrees Twaddle (density) and barrels for quantity. Desirable as it may be for industry world-wide to adopt one consistent set of units, such as SI, this is unlikely to come about for many years, and the designer must contend with whatever system, or combination of systems, his organisation uses. For those in the contracting industry this will also mean working with whatever system of units the client requires.

It is usually the best practice to work through design calculations in the units in which the result is to be presented; but, if working in SI units is preferred, data can be converted to SI units, the calculation made, and the result converted to whatever units are required. Conversion factors to the SI system from most of the scientific and engineering units used in chemical engineering design are given in Appendix D.

Some license has been taken in the use of the SI system in this volume. Temperatures are given in degrees Celsius (°C); degrees Kelvin are only used when absolute temperature is required in the calculation. Pressures are often given in bar (or atmospheres) rather than in the Pascals (N/m^2), as this gives a better feel for the magnitude of the pressures. In technical calculations the bar can be taken as equivalent to an atmosphere, whatever definition is used for atmosphere. The abbreviations bara and barg are often used to denote bar absolute and bar gauge; analogous to psia and psig when the pressure is expressed in pound force per square inch. When bar is used on its own, without qualification, it is normally taken as absolute.

For stress, N/mm^2 have been used, as these units are now generally accepted by engineers, and the use of a small unit of area helps to indicate that stress is the intensity of force at a point (as is also pressure). For quantity, kmol are generally used in preference to mol, and for flow, kmol/h instead of mol/s, as this gives more sensibly sized figures, which are also closer to the more familiar lb/h.

For volume and volumetric flow, m^3 and m^3/h are used in preference to m^3/s, which gives ridiculously small values in engineering calculations. Litres per second are used for small flow-rates, as this is the preferred unit for pump specifications.

Where, for convenience, other than SI units have been used on figures or diagrams, the scales are also given in SI units, or the appropriate conversion factors are given in the text. The answers to some examples are given in British engineering units as well as SI, to help illustrate the significance of the values.

Some approximate conversion factors to SI units are given in Table 1.1. These are worth committing to memory, to give some feel for the units for those more familiar with the traditional engineering units. The exact conversion factors are also shown in the table. A more comprehensive table of conversion factors is given in Appendix D.

Engineers need to be aware of the difference between US gallons and imperial gallons (UK) when using American literature and equipment catalogues. Equipment quoted in an

Table 1.1. Approximate conversion units

Quantity	British Eng. unit	SI unit approx.	exact
Energy	1 Btu	1 kJ	1.05506
Specific enthalpy	1 Btu/lb	2 kJ/kg	2.326
Specific heat capacity	1 Btu/lb°F (CHU/lb°C)	4 kJ/kg°C	4.1868
Heat transfer coeff.	1 $\text{Btu/ft}^2\text{h°F}$ $(\text{CHU/ft}^2\text{h°C})$	6 $\text{W/m}^2\,°\text{C}$	5.678
Viscosity	1 centipoise 1 lb_f/ft h	1 mNs/m^2 0.4 mNs/m^2	1.000 0.4134
Surface tension	1 dyne/cm	1 mN/m	1.000
Pressure	1 lb_f/in^2 1 atm	7 kN/m^2 1 bar 10^5 N/m^2	6.894 1.01325
Density	1 lb/ft^3 1 g/cm^3	16 kg/m^3 1 kg/m^3	16.0190
Volume	1 imp gal.	4.5×10^{-3} m^3	4.5461×10^{-3}
Flow-rate	1 imp gal/m	16 m^3/h	16.366

Note:
1 US gallon = 0.84 imperial gallons (UK)
1 barrel (oil) = 50 US gall ≈ 0.19 m^3 (exact 0.1893)
1 kWh = 3.6 MJ

American catalogue in US gallons or gpm (gallons per minute) will have only 80 per cent of the rated capacity when measured in imperial gallons.

The electrical supply frequency in these two countries is also different: 60 Hz in the US and 50 Hz in the UK. So a pump specified as 50 gpm (US gallons), running at 1750 rpm (revolutions per second) in the US would only deliver 35 imp gpm if operated in the UK; where the motor speed would be reduced to 1460 rpm: so beware.

1.9. DEGREES OF FREEDOM AND DESIGN VARIABLES. THE MATHEMATICAL REPRESENTATION OF THE DESIGN PROBLEM

In Section 1.2 it was shown that the designer in seeking a solution to a design problem works within the constraints inherent in the particular problem.

In this section the structure of design problems is examined by representing the general design problem in a mathematical form.

1.9.1. Information flow and design variables

A process unit in a chemical process plant performs some operation on the inlet material streams to produce the desired outlet streams. In the design of such a unit the design calculations model the operation of the unit. A process unit and the design equations

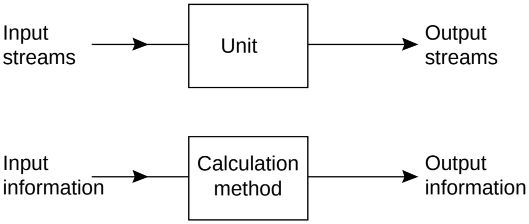

Figure 1.6. The "design unit"

representing the unit are shown diagrammatically in Figure 1.6. In the "design unit" the flow of material is replaced by a flow of information into the unit and a flow of derived information from the unit.

The information flows are the values of the variables which are involved in the design; such as, stream compositions, temperatures, pressure, stream flow-rates, and stream enthalpies. Composition, temperature and pressure are intensive variables: independent of the quantity of material (flow-rate). The constraints on the design will place restrictions on the possible values that these variables can take. The values of some of the variables will be fixed directly by process specifications. The values of other variables will be determined by "design relationships" arising from constraints. Some of the design relationships will be in the form of explicit mathematical equations (design equations); such as those arising from material and energy balances, thermodynamic relationships, and equipment performance parameters. Other relationships will be less precise; such as those arising from the use of standards and preferred sizes, and safety considerations.

The difference between the number of variables involved in a design and the number of design relationships has been called the number of "degrees of freedom"; similar to the use of the term in the phase rule. The number of variables in the system is analogous to the number of variables in a set of simultaneous equations, and the number of relationships analogous to the number of equations. The difference between the number of variables and equations is called the variance of the set of equations.

If N_v is the number of possible variables in a design problem and N_r the number of design relationships, then the "degrees of freedom" N_d is given by:

$$N_d = N_v - N_r \tag{1.1}$$

N_d represents the freedom that the designer has to manipulate the variables to find the best design.

If $N_v = N_r, N_d = 0$ and there is only one, unique, solution to the problem. The problem is not a true design problem, no optimisation is possible.

If $N_v < N_r, N_d < 0$, and the problem is over defined; only a trivial solution is possible.

If $N_v > N_r, N_d > 0$, and there is an infinite number of possible solutions. However, for a practical problem there will be only a limited number of feasible solutions. The value of N_d is the number of variables which the designer must assign values to solve the problem.

How the number of process variables, design relationships, and design variables defines a system can be best illustrated by considering the simplest system; a single-phase, process stream.

Process stream

Consider a single-phase stream, containing C components.

Variable	Number
Stream flow-rate	1
Composition (component concentrations)	C
Temperature	1
Pressure	1
Stream enthalpy	1
	Total, $N_v = C + 4$
Relationships between variables	**Number**
Composition$^{(1)}$	1
Enthalpy$^{(2)}$	1
	Total, $N_r = 2$

Degrees of freedom $N_d = N_v - N_r = (C + 4) - 2 = \underline{\underline{C + 2}}$

(1) The sum of the mass or mol, fractions, must equal one.
(2) The enthalpy is a function of stream composition, temperature and pressure.

Specifying $(C + 2)$ variables completely defines the stream.

Flash distillation

The idea of degrees of freedom in the design process can be further illustrated by considering a simple process unit, a flash distillation. (For a description of flash distillation see Volume 2, Chapter 11).

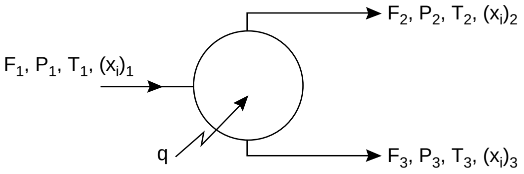

Figure 1.7. Flash distillation

The unit is shown in Figure 1.7, where:
F = stream flow rate,
P = pressure,
T = temperature,
x_i = concentration, component i,
q = heat input.
Suffixes, 1 = inlet, 2 = outlet vapour, 3 = outlet liquid.

Variable	Number
Streams (free variables)(1)	$3(C+2)^1$
Still	
pressure	1
temperature	1
heat input	1
	$N_r = 3C + 9$

Relationship	Number
Material balances (each component)	C
Heat balance, overall	1
v–l–e relationships(2)	C
Equilibrium still restriction(3)	4
	$2C + 5$

Degrees of freedom $N_d = (3C + 9) - (2C + 5) = \underline{\underline{C + 4}}$

(1) The degrees of freedom for each stream. The total variables in each stream could have been used, and the stream relationships included in the count of relationships.

This shows how the degrees of freedom for a complex unit can be built up from the degrees of freedom of its components. For more complex examples see Kwauk (1956).

(2) Given the temperature and pressure, the concentration of any component in the vapour phase can be obtained from the concentration in the liquid phase, from the vapour–liquid equilibrium data for the system.

(3) The concept (definition) of an equilibrium separation implies that the outlet streams and the still are at the same temperature and pressure. This gives four equations:

$$P_2 = P_3 = P$$

$$T_2 = T_3 = T$$

Though the total degrees of freedom is seen to be $(C + 4)$ some of the variables will normally be fixed by general process considerations, and will not be free for the designer to select as "design variables". The flash distillation unit will normally be one unit in a process system and the feed composition and feed conditions will be fixed by the upstream processes; the feed will arise as an outlet stream from some other unit. Defining the feed fixes $(C + 2)$ variables, so the designer is left with:

$$(C + 4) - (C + 2) = 2$$

as design variables.

Summary

The purpose of this discussion was to show that in a design there will be a certain number of variables that the designer must specify to define the problem, and which he can manipulate to seek the best design. In manual calculations the designer will rarely need to calculate the degrees of freedom in a formal way. He will usually have intuitive feel for the problem, and can change the calculation procedure, and select the design variables, as he works through the design. He will know by experience if the problem is correctly specified. A computer, however, has no intuition, and for computer-aided design calculations it is essential to ensure that the necessary number of variables is specified to define the problem correctly. For complex processes the number of variables and relating equations will be very large, and the calculation of the degrees of freedom very involved. Kwauk (1956) has shown how the degrees of freedom can be calculated for separation processes by building up the complex unit from simpler units. Smith (1963) uses Kwauk's method, and illustrates how the idea of "degrees of freedom" can be used in the design of separation processes.

1.9.2. Selection of design variables

In setting out to solve a design problem the designer has to decide which variables are to be chosen as "design variables"; the ones he will manipulate to produce the best design. The choice of design variables is important; careful selection can simplify the design calculations. This can be illustrated by considering the choice of design variables for a simple binary flash distillation.

For a flash distillation the total degrees of freedom was shown to be $(C + 4)$, so for two components $N_d = 6$. If the feed stream flow, composition, temperature and pressure are fixed by upstream conditions, then the number of design variables will be:

$$N'_d = 6 - (C + 2) = 6 - 4 = 2$$

So the designer is free to select two variables from the remaining variables in order to proceed with the calculation of the outlet stream compositions and flows.

If he selects the still pressure (which for a binary system will determine the vapour–liquid–equilibrium relationship) and one outlet stream flow-rate, then the outlet compositions can be calculated by simultaneous solution of the mass balance and equilibrium relationships (equations). A graphical method for the simultaneous solution is given in Volume 2, Chapter 11.

However, if he selects an outlet stream composition (say the liquid stream) instead of a flow-rate, then the simultaneous solution of the mass balance and v–l–e relationships would not be necessary. The stream compositions could be calculated by the following step-by-step (sequential) procedure:

1. Specifying P determines the v–l–e relationship (equilibrium) curve from experimental data.
2. Knowing the outlet liquid composition, the outlet vapour composition can be calculated from the v–l–e relationship.
3. Knowing the feed and outlet compositions, and the feed flow-rate, the outlet stream flows can be calculated from a material balance.
4. An enthalpy balance then gives the heat input required.

The need for simultaneous solution of the design equations implies that there is a recycle of information. Choice of an outlet stream composition as a design variable in

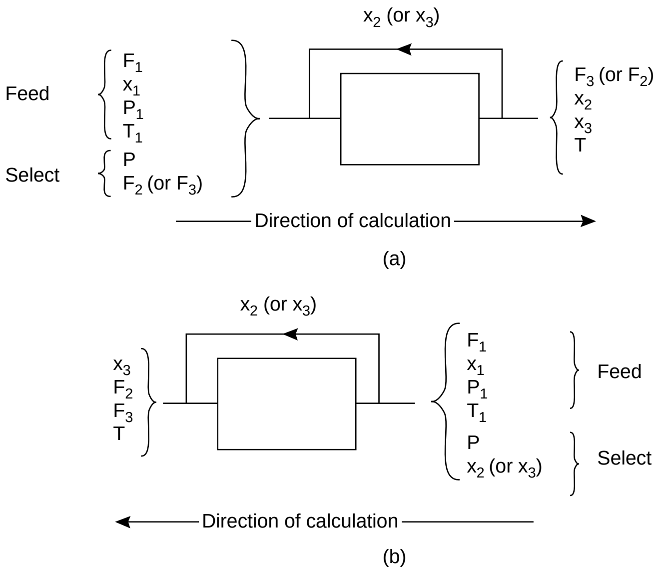

Figure 1.8. Information flow, binary flash distillation calculation (*a*) Information recycle (*b*) Information flow reversal

effect reverses the flow of information through the problem and removes the recycle; this is shown diagrammatically in Figure 1.8.

1.9.3. Information flow and the structure of design problems

It was shown in Section 1.9.2. by studying a relatively simple problem, that the way in which the designer selects his design variables can determine whether the design calculations will prove to be easy or difficult. Selection of one particular set of variables can lead to a straightforward, step-by-step, procedure, whereas selection of another set can force the need for simultaneous solution of some of the relationships; which often requires an iterative procedure (cut-and-try method). How the choice of design variables, inputs to the calculation procedure, affects the ease of solution for the general design problem can be illustrated by studying the flow of information, using simple information flow diagrams. The method used will be that given by Lee *et al*. (1966) who used a form of directed graph; a biparte graph, see Berge (1962).

The general design problem can be represented in mathematical symbolism as a series of equations:

$$\mathrm{f}_i(v_j) = 0$$

where $j = 1, 2, 3, \ldots, N_v$,
$i = 1, 2, 3, \ldots, N_r$

Consider the following set of such equations:

$$\mathrm{f}_1(v_1, v_2) = 0$$

$$\mathrm{f}_2(v_1, v_2, v_3, v_5) = 0$$

$$f_3(v_1, v_3, v_4) = 0$$

$$f_4(v_2, v_4, v_5, v_6) = 0$$

$$f_5(v_5, v_6, v_7) = 0$$

There are seven variables, $N_v = 7$, and five equations (relationships) $N_r = 5$, so the number of degrees of freedom is:

$$N_d = N_v - N_r = 7 - 5 = \underline{\underline{2}}$$

The task is to select two variables from the total of seven in such a way as to give the simplest, most efficient, method of solution to the seven equations. There are twenty-one ways of selecting two items from seven.

In Lee's method the equations and variables are represented by nodes on the biparte graph (circles), connected by edges (lines), as shown in Figure 1.9.

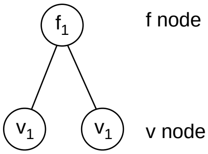

Figure 1.9. Nodes and edges on a biparte graph

Figure 1.9 shows that equation f_1 contains (is connected to) variables v_1 and v_2. The complete graph for the set of equations is shown in Figure 1.10.

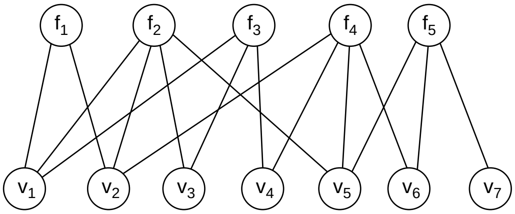

Figure 1.10. Biparte graph for the complete set of equations

The number of edges connected to a node defines the local degree of the node p. For example, the local degree of the f_1 node is 2, $p(f_1) = 2$, and at the v_5 node it is 3, $p(v_5) = 3$. Assigning directions to the edges of Figure 1.10 (by putting arrows on the lines) identifies one possible order of solution for the equations. If a variable v_j is defined as an output variable from an equation f_i, then the direction of information flow is from the node f_i to the node v_j and all other edges will be oriented into f_i. What this means, mathematically, is that assigning v_j as an output from f_i rearranges that equation so that:

$$f_i(v_1, v_2, \ldots, v_n) = v_j$$

v_j is calculated from equation f_i.

The variables selected as design variables (fixed by the designer) cannot therefore be assigned as output variables from an f node. They are inputs to the system and their edges must be oriented into the system of equations.

If, for instance, variables v_3 and v_4 are selected as design variables, then Figure 1.11 shows one possible order of solution of the set of equations. Different types of arrows are used to distinguish between input and output variables, and the variables selected as design variables are enclosed in a double circle.

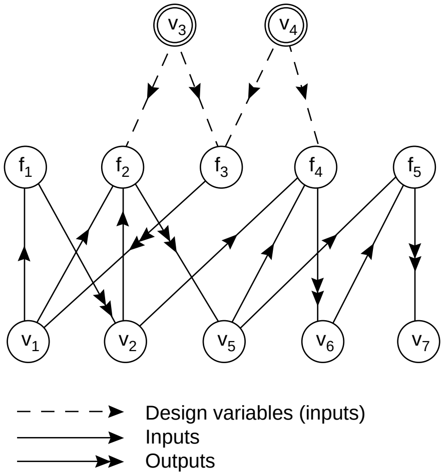

Figure 1.11. An order of solution

Tracing the order of the solution of the equations as shown in Figure 1.11 shows how the information flows through the system of equations:

1. Fixing v_3 and v_4 enables f_3 to be solved, giving v_1 as the output. v_1 is an input to f_1 and f_2.
2. With v_1 as an input, f_1 can be solved giving v_2; v_2 is an input to f_2 and f_4.
3. Knowing v_3, v_1 and v_2, f_2 can be solved to give v_5; v_5 is an input to f_4 and f_5.
4. Knowing v_4, v_2 and v_5, f_4 can be solved to give v_6; v_6 is an input to f_5.
5. Knowing v_6 and v_5, f_5 can be solved to give v_7; which completes the solution.

This order of calculation can be shown more clearly by redrawing Figure 1.11 as shown in Figure 1.12.

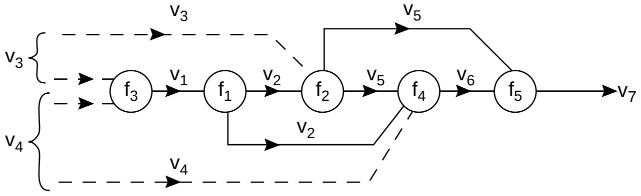

Figure 1.12. Figure 1.11 redrawn to show order of solution

With this order, the equations can be solved sequentially, with no need for the simultaneous solution of any of the equations. The fortuitous selection of v_3 and v_4 as design variables has given an efficient order of solution of the equations.

If for a set of equations an order of solution exists such that there is no need for the simultaneous solution of any of the equations, the system is said to be "acyclic", no recycle of information.

If another pair of variables had been selected, for instance v_5 and v_7, an acyclic order of solution for the set of equations would not necessarily have been obtained.

For many design calculations it will not be possible to select the design variables so as to eliminate the recycle of information and obviate the need for iterative solution of the design relationships.

For example, the set of equations given below will be cyclic for all choices of the two possible design variables.

$$\mathrm{f}_1(x_1, x_2) = 0$$

$$\mathrm{f}_2(x_1, x_3, x_4) = 0$$

$$\mathrm{f}_3(x_2, x_3, x_4, x_5, x_6) = 0$$

$$\mathrm{f}_4(x_4, x_5, x_6) = 0$$

$$N_d = 6 - 4 = 2$$

The biparte graph for this example, with x_3 and x_5 selected as the design variables (inputs), is shown in Figure 1.13.

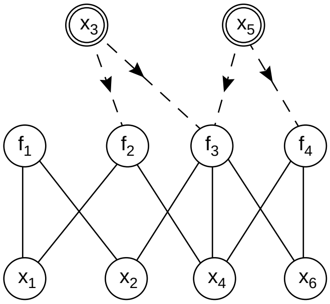

Figure 1.13.

One strategy for the solution of this cyclic set of equations would be to guess (assign a value to) x_6. The equations could then be solved sequentially, as shown in Figure 1.14, to produce a calculated value for x_6, which could be compared with the assumed value and the procedure repeated until a satisfactory convergence of the assumed and calculated value had been obtained. Assigning a value to x_6 is equivalent to "tearing" the recycle loop at x_6 (Figure 1.15). Iterative methods for the solution of equations are discussed by Henley and Rosen (1969).

When a design problem cannot be reduced to an acyclic form by judicious selection of the design variables, the design variables should be chosen so as to reduce the recycle of

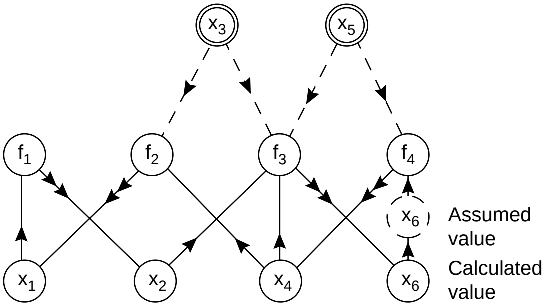

Figure 1.14.

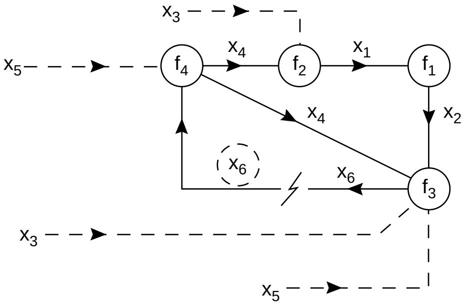

Figure 1.15.

information to a minimum. Lee and Rudd (1966) and Rudd and Watson (1968) give an algorithm that can be used to help in the selection of the best design variables in manual calculations.

The recycle of information, often associated with the actual recycle of process material, will usually occur in any design problem involving large sets of equations; such as in the computer simulation of chemical processes. Efficient methods for the solution of sets of equations are required in computer-aided design procedures to reduce the computer time needed. Several workers have published algorithms for the efficient ordering of recycle loops for iterative solution procedures, and some references to this work are given in the chapter on flow-sheeting, Chapter 4.

1.10. OPTIMISATION

Design is optimisation: the designer seeks the best, the optimum, solution to a problem.

Much of the selection and choice in the design process will depend on the intuitive judgement of the designer; who must decide when more formal optimisation techniques can be used to advantage.

The task of formally optimising the design of a complex processing plant involving several hundred variables, with complex interactions, is formidable, if not impossible. The task can be reduced by dividing the process into more manageable units, identifying the key variables and concentrating work where the effort involved will give the greatest benefit. Sub-division, and optimisation of the sub-units rather than the whole, will not necessarily give the optimum design for the whole process. The optimisation of one unit may be at the expense of another. For example, it will usually be satisfactory to optimise the reflux ratio for a fractionating column independently of the rest of the plant; but if the column is part of a separation stage following a reactor, in which the product is separated from the unreacted materials, then the design of the column will interact with, and may well determine, the optimisation of the reactor design.

In this book the discussion of optimisation methods will, of necessity, be limited to a brief review of the main techniques used in process and equipment design. The extensive literature on the subject should be consulted for full details of the methods available, and their application and limitations; see Beightler and Wilde (1967), Beveridge and Schechter (1970), Stoecker (1989), Rudd and Watson (1968), Edgar and Himmelblau (2001). The books by Rudd and Watson (1968) and Edgar and Himmelblau (2001) are particularly recommended to students.

1.10.1. General procedure

When setting out to optimise any system, the first step is clearly to identify the objective: the criterion to be used to judge the system performance. In engineering design the objective will invariably be an economic one. For a chemical process, the overall objective for the operating company will be to maximise profits. This will give rise to sub-objectives, which the designer will work to achieve. The main sub-objective will usually be to minimise operating costs. Other sub-objectives may be to reduce investment, maximise yield, reduce labour requirements, reduce maintenance, operate safely.

When choosing his objectives the designer must keep in mind the overall objective. Minimising cost per unit of production will not necessarily maximise profits per unit time; market factors, such as quality and delivery, may determine the best overall strategy.

The second step is to determine the objective function: the system of equations, and other relationships, which relate the objective with the variables to be manipulated to optimise the function. If the objective is economic, it will be necessary to express the objective function in economic terms (costs).

Difficulties will arise in expressing functions that depend on value judgements; for example, the social benefits and the social costs that arise from pollution.

The third step is to find the values of the variables that give the optimum value of the objective function (maximum or minimum). The best techniques to be used for this step will depend on the complexity of the system and on the particular mathematical model used to represent the system.

A mathematical model represents the design as a set of equations (relationships) and, as was shown in Section 1.9.1, it will only be possible to optimise the design if the number of variables exceeds the number of relationships; there is some degree of freedom in the system.

1.10.2. Simple models

If the objective function can be expressed as a function of one variable (single degree of freedom) the function can be differentiated, or plotted, to find the maximum or minimum.

This will be possible for only a few practical design problems. The technique is illustrated in Example 1.1, and in the derivation of the formula for optimum pipe diameter in Chapter 5. The determination of the economic reflux ratio for a distillation column, which is discussed in Volume 2, Chapter 11, is an example of the use of a graphical procedure to find the optimum value.

Example 1.1

The optimum proportions for a cylindrical container. A classical example of the optimisation of a simple function.

The surface area, A, of a closed cylinder is:

$$A = \pi \times D \times L + 2\frac{\pi}{4}D^2$$

where D = vessel diameter
L = vessel length (or height)

This will be the objective function which is to be minimised; simplified:

$$f(D \times L) = D \times L + \frac{D^2}{2} \qquad \text{(equation A)}$$

For a given volume, V, the diameter and length are related by:

$$V = \frac{\pi}{4}D^2 \times L$$

and

$$L = \frac{4V}{\pi D^2} \qquad \text{(equation B)}$$

and the objective function becomes

$$f(D) = \frac{4V}{\pi D} + \frac{D^2}{2}$$

Setting the differential of this function zero will give the optimum value for D

$$\frac{-4V}{\pi D^2} + D = 0$$

$$D = \sqrt[3]{\frac{4V}{\pi}}$$

From equation B, the corresponding length will be:

$$L = \sqrt[3]{\frac{4V}{\pi}}$$

So for a cylindrical container the minimum surface area to enclose a given volume is obtained when the length is made equal to the diameter.

In practice, when cost is taken as the objective function, the optimum will be nearer $L = 2D$; the proportions of the ubiquitous tin can, and oil drum. This is because the cost will include that of forming the vessel and making the joints, in addition to cost of the material (the surface area); see Wells (1973).

If the vessel is a pressure vessel the optimum length to diameter ratio will be even greater, as the thickness of plate required is a direct function of the diameter; see Chapter 13. Urbaniec (1986) gives procedures for the optimisation of tanks and vessel, and other process equipment.

1.10.3. Multiple variable problems

The general optimisation problem can be represented mathematically as:

$$\mathrm{f} = \mathrm{f}(v_1, v_2, v_3, \ldots, v_n) \tag{1.2}$$

where f is the objective function and $v_1, v_2, v_3, \ldots, v_n$ are the variables.

In a design situation there will be constraints on the possible values of the objective function, arising from constraints on the variables; such as, minimum flow-rates, maximum allowable concentrations, and preferred sizes and standards.

Some may be equality constraints, expressed by equations of the form:

$$\Phi_m = \Phi_m(v_1, v_2, v_3, \ldots, v_n) = 0 \tag{1.3}$$

Others as inequality constraints:

$$\Psi_p = \Psi_p(v_1, v_2, v_3, \ldots, v_n) \leq P_p \tag{1.4}$$

The problem is to find values for the variables v_1 to v_n that optimise the objective function: that give the maximum or minimum value, within the constraints.

Analytical methods

If the objective function can be expressed as a mathematical function the classical methods of calculus can be used to find the maximum or minimum. Setting the partial derivatives to zero will produce a set of simultaneous equations that can be solved to find the optimum values. For the general, unconstrained, objective function, the derivatives will give the critical points; which may be maximum or minimum, or ridges or valleys. As with single variable functions, the nature of the first derivative can be found by taking the second derivative. For most practical design problems the range of values that the variables can take will be subject to constraints (equations 1.3 and 1.4), and the optimum of the constrained objective function will not necessarily occur where the partial derivatives of the objective function are zero. This situation is illustrated in Figure 1.16 for a two-dimensional problem. For this problem, the optimum will lie on the boundary defined by the constraint $y = a$.

The method of Lagrange's undetermined multipliers is a useful analytical technique for dealing with problems that have equality constraints (fixed design values). Examples of the use of this technique for simple design problems are given by Stoecker (1989), Peters and Timmerhaus (1991) and Boas (1963a).

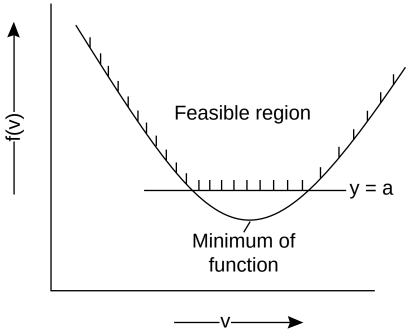

Figure 1.16. Effect of constraints on optimum of a function

Search methods

The nature of the relationships and constraints in most design problems is such that the use of analytical methods is not feasible. In these circumstances search methods, that require only that the objective function can be computed from arbitrary values of the independent variables, are used. For single variable problems, where the objective function is unimodal, the simplest approach is to calculate the value of the objective function at uniformly spaced values of the variable until a maximum (or minimum) value is obtained. Though this method is not the most efficient, it will not require excessive computing time for simple problems. Several more efficient search techniques have been developed, such as the method of the golden section; see Boas (1963b) and Edgar and Himmelblau (2001).

Efficient search methods will be needed for multi-dimensional problems, as the number of calculations required and the computer time necessary will be greatly increased, compared with single variable problems; see Himmelblau (1963), Stoecker (1971), Beveridge and Schechter (1970), and Baasel (1974).

Two variable problems can be plotted as shown in Figure 1.17. The values of the objective function are shown as contour lines, as on a map, which are slices through the three-dimensional model of the function. Seeking the optimum of such a function can be

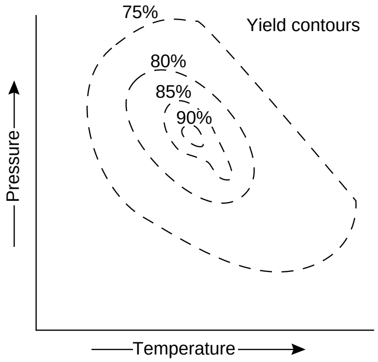

Figure 1.17. Yield as a function of reactor temperature and pressure

likened to seeking the top of a hill (or bottom of a valley), and a useful technique for this type of problem is the *gradient method* (*method of steepest ascent, or descent*), see Edgar and Himmelblau (2001).

1.10.4. Linear programming

Linear programming is an optimisation technique that can be used when the objective function and constraints can be expressed as a linear function of the variables; see Driebeek (1969), Williams (1967) and Dano (1965).

The technique is useful where the problem is to decide the optimum utilisation of resources. Many oil companies use linear programming to determine the optimum schedule of products to be produced from the crude oils available. Algorithms have been developed for the efficient solution of linear programming problems and the SIMPLEX algorithm, Dantzig (1963), is the most commonly used.

Examples of the application of linear programming in chemical process plant design and operation are given by Allen (1971), Rudd and Watson (1968), Stoecker (1991), and Urbaniec (1986).

1.10.5. Dynamic programming

Dynamic programming is a technique developed for the optimisation of large systems; see Nemhauser (1966), Bellman (1957) and Aris (1963).

The basic approach used is to divide the system into convenient sub-systems and optimise each sub-system separately, while taking into account the interactions between the sub-systems. The decisions made at each stage contribute to the overall systems objective function, and to optimise the overall objective function an appropriate combination of the individual stages has to be found. In a typical process plant system the possible number of combinations of the stage decisions will be very large. The dynamic programming approach uses Bellman's "Principle of Optimality",[†] which enables the optimum policy to be found systematically and efficiently by calculating only a fraction of the possible combinations of stage decisions. The method converts the problem from the need to deal with "*N*" optimisation decisions simultaneously to a sequential set of "*N*" problems. The application of dynamic programming to design problems is well illustrated in Rudd and Watson's book; see also Wells (1973) and Edgar and Himmelblau (2001).

1.10.6. Optimisation of batch and semicontinuous processes

In batch operation there will be periods when product is being produced, followed by non-productive periods when the product is discharged and the equipment prepared for the next batch. The rate of production will be determined by the total batch time, productive

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[†] Bellman's (1957) principle of optimality: "An optimal policy has the property that, whatever the initial state and the initial decision are, the remaining decisions must constitute an optimal policy with regard to the state resulting from the first decision."

plus non-productive periods.

$$\text{Batches per year} = \frac{8760 \times \text{plant attainment}}{\text{batch cycle time}} \tag{1.5}$$

where the "plant attainment" is the fraction of the total hours in a year (8760) that the plant is in operation.

$$\text{Annual production} = \text{quantity produced per batch} \times \text{batches per year.}$$

$$\text{Cost per unit of production} = \frac{\text{annual cost of production}}{\text{annual production rate}} \tag{1.6}$$

With many batch processes, the production rate will decrease during the production period; for example, batch reactors and plate and frame filter presses, and there will be an optimum batch size, or optimum cycle time, that will give the minimum cost per unit of production.

For some processes, though they would not be classified as batch processes, the period of continuous production will be limited by gradual changes in process conditions; such as, the deactivation of catalysts or the fouling of heat-exchange surfaces. Production will be lost during the periods when the plant is shut down for catalyst renewal or equipment clean-up, and, as with batch process, there will be an optimum cycle time to give the minimum production cost.

The optimum time between shut-downs can be found by determining the relationship between cycle time and cost per unit of production (the objective function) and using one of the optimisation techniques outlined in this section to find the minimum.

With discontinuous processes, the period between shut-downs will usually be a function of equipment size. Increasing the size of critical equipment will extend the production period, but at the expense of increased capital cost. The designer must strike a balance between the savings gained by reducing the non-productive period and the increased investment required.

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1.12. NOMENCLATURE

		Dimensions in **MLTθ**
C	Number of components	—
D	Diameter	**L**
F	Stream flow rate	$\mathbf{MT}^{-1}$
f	General function	—
f_i	General function (design relationship)	—
$\mathrm{f}_1, \mathrm{f}_2 \ldots$	General functions (design relationships)	—
L	Length	**L**
N_d	Degrees of freedom in a design problem	—
N'_d	Degrees of freedom (variables free to be selected as design variables)	—
N_r	Number of design relationships	—
N_v	Number of variables	—
P	Pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
P_p	Inequality constraints	—
q	Heat input, flash distillation	$\mathbf{ML}^{2}\mathbf{T}^{-3}$
T	Temperature	$\boldsymbol{\theta}$
v_j	Variables	—
$v_1, v_2 \ldots$	Variables	—
$x_1, x_2 \ldots$	Variables	—
Φ	Equality constraint function	—
Ψ	Inequality constraint function	—

Suffixes

1	Inlet, flash distillation
2	Vapour outlet, flash distillation
3	Liquid outlet, flash distillation

1.13 PROBLEMS

1.1. Given that 1 in = 25.4 mm; 1 lbm = 0.4536 kg; 1 °F = 0.556 °C; 1 cal = 4.1868 J; g = 9.807 m s^{-2}, calculate conversion factors to SI units for the following terms:

- i. feet
- ii. pounds mass
- iii. pounds force
- iv. horse power (1 HP = 550 foot pounds per second)
- v. psi (pounds per square inch)
- vi. lb ft^{-1} s^{-1} (viscosity)
- vii. poise (gm cm^{-1} s^{-1})
- viii. Btu (British Thermal Unit)
- ix. CHU (Centigrade Heat Unit) also known as PCU (Pound Centigrade Unit)
- x. Btu ft^{-2} h^{-1} $°F^{-1}$ (heat transfer coefficient).

1.2. Determine the degrees of freedom available in the design of a simple heat exchanger. Take the exchanger as a double-pipe exchanger transferring heat between two single-phase streams.

1.3. A separator divides a process stream into three phases: a liquid organic stream, a liquid aqueous stream, and a gas stream. The feed stream contains three components, all of which are present to some extent in the separated steams. The composition and flowrate of the feed stream are known. All the streams will be at the same temperature and pressure. The phase equilibria for the three phases is available.

How many design variables need to be specified in order to calculate the output stream compositions and flow rates?

1.4. A rectangular tank with a square base is constructed from 5 mm steel plates. If the capacity required is eight cubic metres determine the optimum dimensions if the tank has:

- i. a closed top
- ii. an open top.

1.5. Estimate the optimum thickness of insulation for the roof of a house, given the following information. The insulation will be installed flat on the attic floor.

Overall heat transfer coefficient for the insulation as a function of thickness, U values (see Chapter 12):

thickness, mm	0	25	50	100	150	200	250
U, Wm^{-2} $°C^{-1}$	20	0.9	0.7	0.3	0.25	0.20	0.15

Average temperature difference between inside and outside of house 10 °C; heating period 200 days in a year.

Cost of insulation, including installation, £70/m^3. Capital charges (see Chapter 6) 15 per cent per year. Cost of fuel, allowing for the efficiency of the heating system, 6p/MJ.

Note: the rate at which heat is being lost is given by $U \times \Delta T$, W/m^2, where U is the overall coefficient and ΔT the temperature difference; see Chapter 12.

1.6. (US version) Estimate the optimum thickness of insulation for the roof of a house given the following information. The insulation will be installed flat on the attic floor.

Overall heat transfer coefficient for the insulation as a function of thickness, U values (see Chapter 12):

thickness, mm	0	25	50	100	150	200	250
U, $\mathrm{Wm^{-2}\ ^{\circ}C^{-1}}$	20	0.9	0.7	0.3	0.25	0.20	0.15

Average temperature difference between inside and outside of house 12 °C; heating period 250 days in a year. Cost of insulation, including installation, $\$120/\mathrm{m}^3$. Capital charges (see chapter 6) 20 per cent per year. Cost of fuel, allowing for the efficiency of the heating system, 9c/MJ.

Note: the rate at which heat is being lost is given by $U \times \Delta T$, $\mathrm{W/m^2}$, where U is the overall coefficient and ΔT the temperature difference; see Chapter 12.

1.7. What is the optimum practical shape for a dwelling, to minimise the heat losses through the building fabric?

Why is this optimum shape seldom used?

What people do use the optimum shape for their winter dwellings? Is heat retention their only consideration in their selection of this shape?

1.8. You are part of the design team working on a project for the manufacture of cyclohexane.

The chief engineer calls you into his office and asks you to prepare an outline design for an inert gas purging and blanketing system for the reactors and other equipment, on shutdown. This request arises from a report into an explosion and fire at another site manufacturing a similar product.

Following the steps given in Figure 1.2, find what you consider the best solution to this design problem.

CHAPTER 2

Fundamentals of Material Balances

2.1. INTRODUCTION

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions.

A good understanding of material balance calculations is essential in process design.

In this chapter the fundamentals of the subject are covered, using simple examples to illustrate each topic. Practice is needed to develop expertise in handling what can often become very involved calculations. More examples and a more detailed discussion of the subject can be found in the numerous specialist books written on material and energy balance computations. Several suitable texts are listed under the heading of "Further Reading" at the end of this chapter.

The application of material balances to more complex problems is discussed in "Flow-sheeting", Chapter 4.

Material balances are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss.

2.2. THE EQUIVALENCE OF MASS AND ENERGY

Einstein showed that mass and energy are equivalent. Energy can be converted into mass, and mass into energy. They are related by Einstein's equation:

$$E = mc^2 \tag{2.1}$$

where E = energy, J,
m = mass, kg,
c = the speed of light *in vacuo*, 3×10^8 m/s.

The loss of mass associated with the production of energy is significant only in nuclear reactions. Energy and matter are always considered to be separately conserved in chemical reactions.

2.3. CONSERVATION OF MASS

The general conservation equation for any process system can be written as:

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady-state process the accumulation term will be zero. Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place a particular chemical species may be formed or consumed in the process. If there is no chemical reaction the steady-state balance reduces to

$$\text{Material out} = \text{Material in}$$

A balance equation can be written for each separately identifiable species present, elements, compounds or radicals; and for the total material.

Example 2.1

2000 kg of a 5 per cent slurry of calcium hydroxide in water is to be prepared by diluting a 20 per cent slurry. Calculate the quantities required. The percentages are by weight.

Solution

Let the unknown quantities of the 20% slurry and water be X and Y respectively.

Material balance on $Ca(OH)_2$

$$\begin{array}{ccc} \textit{In} & & \textit{Out} \\ X\dfrac{20}{100} & = & 2000 \times \dfrac{5}{100} \end{array} \qquad (a)$$

Balance on water

$$X\frac{(100-20)}{100} + Y = 2000\frac{(100-5)}{100} \qquad (b)$$

From equation (a) $X = 500$ kg.

Substituting into equation (b) gives $Y = \underline{\underline{1500\text{ kg}}}$

Check material balance on total quantity:

$$X + Y = 2000$$

$$500 + 1500 = 2000, \text{ correct}$$

2.4. UNITS USED TO EXPRESS COMPOSITIONS

When specifying a composition as a percentage it is important to state clearly the basis: weight, molar or volume.

The abbreviations w/w and v/v are used to designate weight basis and volume basis.

Example 2.2

Technical grade hydrochloric acid has a strength of 28 per cent w/w, express this as a mol fraction.

Solution

Basis of calculation 100 kg of 28 per cent w/w acid.

$$\begin{aligned}
&\text{Molecular mass: water 18, HCl 36.5}\\
\text{Mass HCl} &= 100 \times 0.28 = 28\text{ kg}\\
\text{Mass water} &= 100 \times 0.72 = 72\text{ kg}\\
\text{kmol HCl} &= \frac{28}{36.5} = 0.77\\
\text{kmol water} &= \frac{72}{18} \quad = \underline{4.00}\\
\text{Total mols} &\qquad\quad = 4.77\\
\text{mol fraction HCl} &= \frac{0.77}{4.77} = 0.16\\
\text{mol fraction water} &= \frac{4.00}{4.77} = \underline{0.84}\\
\text{Check total} &\qquad\quad\;\; 1.00
\end{aligned}$$

Within the accuracy needed for technical calculations, volume fractions can be taken as equivalent to mol fractions for gases, up to moderate pressures (say 25 bar).

Trace quantities are often expressed as parts per million (ppm). The basis, weight or volume, needs to be stated.

$$\text{ppm} = \frac{\text{quantity of component}}{\text{total quantity}} \times 10^6$$

Note. 1 ppm $= 10^{-4}$ per cent.

Minute quantities are sometimes quoted in ppb, parts per billion. Care is needed here, as the billion is usually an American billion (10^9), not the UK billion (10^{12}).

2.5. STOICHIOMETRY

Stoichiometry (from the Greek *stoikeion* — element) is the practical application of the law of multiple proportions. The stoichiometric equation for a chemical reaction states unambiguously the number of molecules of the reactants and products that take part; from which the quantities can be calculated. The equation must balance.

With simple reactions it is usually possible to balance the stoichiometric equation by inspection, or by trial and error calculations. If difficulty is experienced in balancing complex equations, the problem can always be solved by writing a balance for each element present. The procedure is illustrated in Example 2.3.

Example 2.3

Write out and balance the overall equation for the manufacture of vinyl chloride from ethylene, chlorine and oxygen.

Solution

Method: write out the equation using letters for the unknown number of molecules of each reactant and product. Make a balance on each element. Solve the resulting set of equations.

$$A(C_2H_4) + B(Cl_2) + C(O_2) = D(C_2H_3Cl) + E(H_2O)$$

Balance on carbon

$$2A = 2D, \quad A = D$$

on hydrogen

$$4A = 3D + 2E$$

$$\text{substituting } D = A \text{ gives } E = \frac{A}{2}$$

on chlorine

$$2B = D, \text{hence } B = \frac{A}{2}$$

on oxygen

$$2C = E, \qquad C = \frac{E}{2} = \frac{A}{4}$$

putting $A = 1$, the equation becomes

$$C_2H_4 + \tfrac{1}{2}Cl_2 + \tfrac{1}{4}O_2 = C_2H_3Cl + \tfrac{1}{2}H_2O$$

multiplying through by the largest denominator to remove the fractions

$$4C_2H_4 + 2Cl_2 + O_2 = 4C_2H_3Cl + 2H_2O$$

2.6. CHOICE OF SYSTEM BOUNDARY

The conservation law holds for the complete process and any sub-division of the process. The system boundary defines the part of the process being considered. The flows into and out of the system are those crossing the boundary and must balance with material generated or consumed within the boundary.

Any process can be divided up in an arbitrary way to facilitate the material balance calculations. The judicious choice of the system boundaries can often greatly simplify what would otherwise be difficult and tortuous calculations.

No hard and fast rules can be given on the selection of suitable boundaries for all types of material balance problems. Selection of the best sub-division for any particular process is a matter of judgement, and depends on insight into the structure of the problem, which can only be gained by practice. The following general rules will serve as a guide:

1. With complex processes, first take the boundary round the complete process and if possible calculate the flows in and out. Raw materials in, products and by-products out.
2. Select the boundaries to sub-divide the process into simple stages and make a balance over each stage separately.
3. Select the boundary round any stage so as to reduce the number of unknown streams to as few as possible.

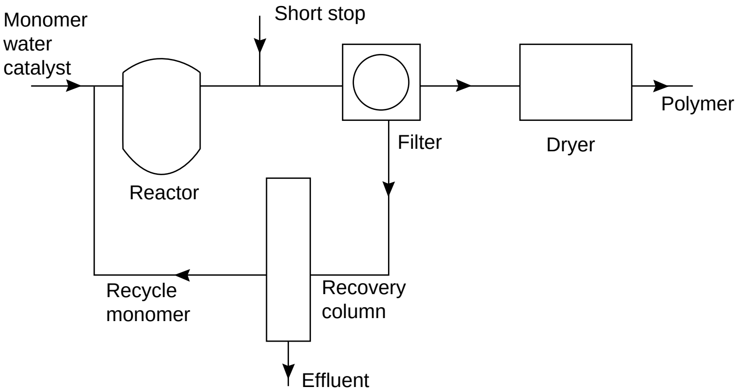
4. As a first step, include any recycle streams within the system boundary (see Section 2.14).

Example 2.4

Selection of system boundaries and organisation of the solution.
The diagram shows the main steps in a process for producing a polymer. From the following data, calculate the stream flows for a production rate of 10,000 kg/h.

Reactor,	yield on polymer	100 per cent
	slurry polymerisation	20 per cent monomer/water
	conversion	90 per cent
	catalyst 1 kg/1000 kg monomer	
	short stopping agent	0.5 kg/1000 kg unreacted monomer

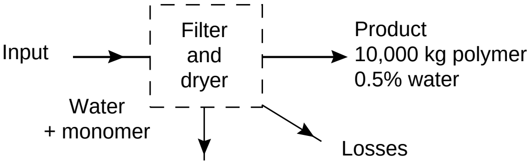
Filter, wash water approx. 1 kg/1 kg polymer
Recovery column, yield 98 per cent (percentage recovered)
Dryer, feed ~5 per cent water, product specification 0.5 per cent H_2O
Polymer losses in filter and dryer ~1 per cent



Solution

Only those flows necessary to illustrate the choice of system boundaries and method of calculation are given in the Solution.

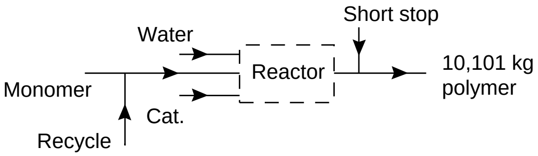
Basis: 1 hour
Take the first system boundary round the filter and dryer.



With 1 per cent loss, polymer entering sub-system

$$= \frac{10{,}000}{0.99} = \underline{\underline{10{,}101\ \text{kg}}}$$

Take the next boundary round the reactor system; the feeds to the reactor can then be calculated.



At 90 per cent conversion, monomer feed

$$= \frac{10{,}101}{0.9} = \underline{\underline{11{,}223\ \text{kg}}}$$

Unreacted monomer $= 11{,}223 - 10{,}101 = \underline{\underline{1122\ \text{kg}}}$

Short-stop, at 0.5 kg/1000 kg unreacted monomer

$$= 1122 \times 0.5 \times 10^{-3} = \underline{\underline{0.6\ \text{kg}}}$$

Catalyst, at 1 kg/1000 kg monomer

$$= 11{,}223 \times 1 \times 10^{-3} = \underline{\underline{11\ \text{kg}}}$$

Let water feed to reactor be F_1, then for 20 per cent monomer

$$0.2 = \frac{11{,}223}{F_1 + 11{,}223}$$

$$F_1 = \frac{11{,}223(1 - 0.2)}{0.2} = \underline{\underline{44{,}892\ \text{kg}}}$$

Now consider filter-dryer sub-system again.
Water in polymer to dryer, at 5 per cent (neglecting polymer loss)

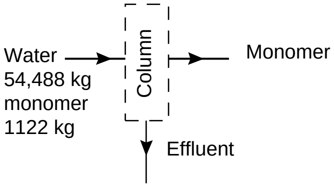
$$= 10{,}101 \times 0.05 = \underline{\underline{505\ \text{kg}}}$$

Balance over reactor-filter-dryer sub-system gives flows to recovery column.

$$\text{water, } 44{,}892 + 10{,}101 - 505 = \underline{\underline{54{,}448\ \text{kg}}}$$

$$\text{monomer, unreacted monomer, } = \underline{\underline{1122\ \text{kg}}}$$

Now consider recovery system

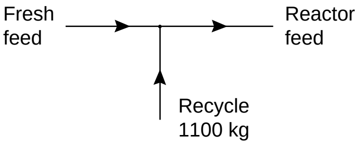


With 98 per cent recovery, recycle to reactor

$$= 0.98 \times 1122 = \underline{\underline{1100 \text{ kg}}}$$

Composition of effluent 23 kg monomer, 54,488 kg water.

Consider reactor monomer feed



Balance round tee gives fresh monomer required

$$= 11{,}223 - 1100 = \underline{\underline{10{,}123 \text{ kg}}}$$

2.7. CHOICE OF BASIS FOR CALCULATIONS

The correct choice of the basis for a calculation will often determine whether the calculation proves to be simple or complex. As with the choice of system boundaries, no all-embracing rules or procedures can be given for the selection of the right basis for any problem. The selection depends on judgement gained by experience. Some guide rules that will help in the choice are:

1. Time: choose the time basis in which the results are to be presented; for example kg/h, tonne/y.
2. For batch processes use one batch.
3. Choose as the mass basis the stream flow for which most information is given.
4. It is often easier to work in mols, rather than weight, even when no reaction is involved.
5. For gases, if the compositions are given by volume, use a volume basis, remembering that volume fractions are equivalent to mol fractions up to moderate pressures.

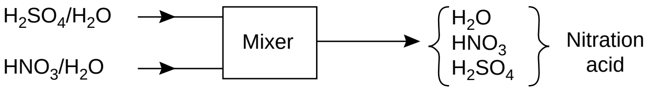
2.8. NUMBER OF INDEPENDENT COMPONENTS

A balance equation can be written for each independent component. Not all the components in a material balance will be independent.

Physical systems, no reaction

If there is no chemical reaction the number of independent components is equal to the number of distinct chemical species present.

Consider the production of a nitration acid by mixing 70 per cent nitric and 98 per cent sulphuric acid. The number of distinct chemical species is 3; water, sulphuric acid, nitric acid.



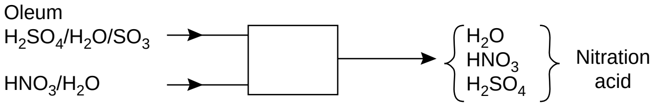
Chemical systems, reaction

If the process involves chemical reaction the number of independent components will not necessarily be equal to the number of chemical species, as some may be related by the chemical equation. In this situation the number of independent components can be calculated by the following relationship:

$$\text{Number of independent components} = \text{Number of chemical species} - \text{Number of independent chemical equations} \tag{2.2}$$

Example 2.5

If nitration acid is made up using oleum in place of the 98 per cent sulphuric acid, there will be four distinct chemical species: sulphuric acid, sulphur trioxide, nitric acid, water. The sulphur trioxide will react with the water producing sulphuric acid so there are only three independent components



Reaction equation $SO_3 + H_2O \rightarrow H_2SO_4$

No. of chemical species	4
No. of reactions	1
No. of independent equations	3

2.9. CONSTRAINTS ON FLOWS AND COMPOSITIONS

It is obvious, but worth emphasising, that the sum of the individual component flows in any stream cannot exceed the total stream flow. Also, that the sum of the individual molar or weight fractions must equal 1. Hence, the composition of a stream is completely defined if all but one of the component concentrations are given.

The component flows in a stream (or the quantities in a batch) are completely defined by any of the following:

1. Specifying the flow (or quantity) of each component.
2. Specifying the total flow (or quantity) and the composition.
3. Specifying the flow (or quantity) of one component and the composition.

Example 2.6

The feed stream to a reactor contains: ethylene 16 per cent, oxygen 9 per cent, nitrogen 31 per cent, and hydrogen chloride. If the ethylene flow is 5000 kg/h, calculate the individual component flows and the total stream flow. All percentages are by weight.

Solution

$$\text{Percentage HCl} = 100 - (16 + 9 + 31) = \underline{\underline{44}}$$

$$\text{Percentage ethylene} = \frac{5000}{\text{total}} \times 100 = \underline{\underline{16}}$$

$$\text{hence total flow} = 5000 \times \frac{100}{16} = \underline{\underline{31{,}250\ \text{kg/h}}}$$

$$\text{so, oxygen flow} = \frac{9}{100} \times 31{,}250 = \underline{\underline{2813\ \text{kg/h}}}$$

$$\text{nitrogen} = 31{,}250 \times \frac{31}{100} = \underline{\underline{9687\ \text{kg/h}}}$$

$$\text{hydrogen chloride} = 31{,}250 \times \frac{44}{100} = \underline{\underline{13{,}750\ \text{kg/h}}}$$

General rule: the ratio of the flow of any component to the flow of any other component is the same as the ratio of the compositions of the two components.

The flow of any component in Example 2.6 could have been calculated directly from the ratio of the percentage to that of ethylene, and the ethylene flow.

$$\text{Flow of hydrogen chloride} = \frac{44}{16} \times 5000 = \underline{\underline{13{,}750\ \text{kg/h}}}$$

2.10. GENERAL ALGEBRAIC METHOD

Simple material-balance problems involving only a few streams and with a few unknowns can usually be solved by simple direct methods. The relationship between the unknown quantities and the information given can usually be clearly seen. For more complex problems, and for problems with several processing steps, a more formal algebraic approach can be used. The procedure is involved, and often tedious if the calculations have to be done manually, but should result in a solution to even the most intractable problems, providing sufficient information is known.

Algebraic symbols are assigned to all the unknown flows and compositions. Balance equations are then written around each sub-system for the independent components (chemical species or elements).

Material-balance problems are particular examples of the general design problem discussed in Chapter 1. The unknowns are compositions or flows, and the relating equations arise from the conservation law and the stoichiometry of the reactions. For any problem to have a unique solution it must be possible to write the same number of independent equations as there are unknowns.

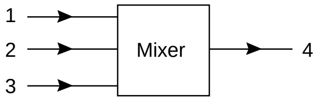
Consider the general material balance problem where there are N_s streams each containing N_c independent components. Then the number of variables, N_v, is given by:

$$N_v = N_c \times N_s \tag{2.3}$$

If N_e independent balance equations can be written, then the number of variables, N_d, that must be specified for a unique solution, is given by:

$$N_d = (N_s \times N_c) - N_e \tag{2.4}$$

Consider a simple mixing problem



Let F_n be the total flow in stream n, and $x_{n,m}$ the concentration of component m in stream n. Then the general balance equation can be written

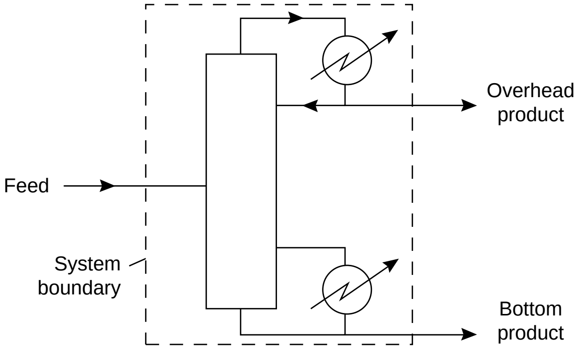
$$F_1x_{1,m} + F_2x_{2,m} + F_3x_{3,m} = F_4x_{4,m} \tag{2.5}$$

A balance equation can also be written for the total of each stream:

$$F_1 + F_2 + F_3 = F_4 \tag{2.6}$$

but this could be obtained by adding the individual component equations, and so is not an additional independent equation. There are m independent equations, the number of independent components.

Consider a separation unit, such as a distillation column, which divides a process stream into two product streams. Let the feed rate be 10,000 kg/h; composition benzene 60 per cent, toluene 30 per cent, xylene 10 per cent.



There are three streams, feed, overheads and bottoms, and three independent components in each stream.

Number of variables (component flow rates) $= 9$
Number of independent material balance equations $= 3$
Number of variables to be specified for a unique solution $= 9 - 3 = 6$

Three variables are specified; the feed flow and composition fixes the flow of each component in the feed.

Number of variables to be specified by designer $= 6 - 3 = 3$. Any three component flows can be chosen.

Normally the top composition and flow or the bottom composition and flow would be chosen.

If the primary function of the column is to separate the benzene from the other components, the maximum toluene and xylene in the overheads would be specified; say, at 5 kg/h and 3 kg/h, and the loss of benzene in the bottoms also specified; say, at not greater than 5 kg/h. Three flows are specified, so the other flows can be calculated.

Benzene in overheads = benzene in feed − benzene in bottoms.

$$0.6 \times 10{,}000 - 5 = \underline{\underline{5995\ \text{kg/h}}}$$

Toluene in bottoms = toluene in feed − toluene in overheads

$$0.3 \times 10{,}000 - 5 = \underline{\underline{2995\ \text{kg/h}}}$$

Xylene in bottoms = xylene in feed − xylene in overheads

$$0.1 \times 10{,}000 - 3 = \underline{\underline{997\ \text{kg/h}}}$$

2.11. TIE COMPONENTS

In Section 2.9 it was shown that the flow of any component was in the same ratio to the flow of any other component, as the ratio of the concentrations of the two components. If one component passes unchanged through a process unit it can be used to tie the inlet and outlet compositions.

This technique is particularly useful in handling combustion calculations where the nitrogen in the combustion air passes through unreacted and is used as the tie component. This is illustrated in Example 2.8.

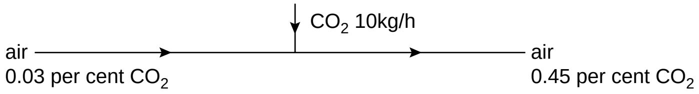
This principle can also be used to measure the flow of a process stream by introducing a measured flow of some easily analysed (compatible) material.

Example 2.7

Carbon dioxide is added at a rate of 10 kg/h to an air stream and the air is sampled at a sufficient distance downstream to ensure complete mixing. If the analysis shows 0.45 per cent v/v CO_2, calculate the air-flow rate.

Solution

Normal carbon dioxide content of air is 0.03 per cent



Basis: kmol/h, as percentages are by volume.

$$\text{kmol/h } CO_2 \text{ introduced} = \frac{10}{44} = 0.2273$$

Let X be the air flow.
Balance on CO_2, the tie component

$$\begin{aligned}
CO_2 \text{ in} &= 0.0003\ X + 0.2273 \\
CO_2 \text{ out} &= 0.0045\ X \\
X(0.0045 - 0.0003) &= 0.2273 \\
X = 0.2273/0.0042 &= 54\ \text{kmol/h} \\
&= 54 \times 29 = \underline{\underline{1560\ \text{kg/h}}}
\end{aligned}$$

Example 2.8

In a test on a furnace fired with natural gas (composition 95 per cent methane, 5 per cent nitrogen) the following flue gas analysis was obtained: carbon dioxide 9.1 per cent, carbon monoxide 0.2 per cent, oxygen 4.6 per cent, nitrogen 86.1 per cent, all percentages by volume.

Calculate the percentage excess air flow (percentage above stoichiometric).

Solution

$$\text{Reaction: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Note: the flue gas analysis is reported on the dry basis, any water formed having been condensed out.

Nitrogen is the tie component.

Basis: 100 mol, dry flue gas; as the analysis of the flue gas is known, the mols of each element in the flue gas (flow out) can be easily calculated and related to the flow into the system.

Let the quantity of fuel (natural gas) per 100 mol dry flue gas be X.

Balance on carbon, mols in fuel = mols in flue gas

$$0.95\ X = 9.1 + 0.2, \ \text{hence } X = \underline{\underline{9.79\ \text{mol}}}$$

Balance on nitrogen (composition of air O_2 21 per cent, N_2 79 per cent).

Let Y be the flow of air per 100 mol dry flue gas.

$$N_2 \text{ in air} + N_2 \text{ in fuel} = N_2 \text{ in flue gas}$$

$$0.79\ Y + 0.05 \times 9.79 = 86.1, \ \text{hence } Y = \underline{\underline{108.4\ \text{mol}}}$$

Stoichiometric air; from the reaction equation 1 mol methane requires 2 mol oxygen,

$$\text{so, stoichiometric air} = 9.79 \times 0.95 \times 2 \times \frac{100}{21} = \underline{\underline{88.6\ \text{mol}}}$$

$$\text{Percentage excess air} = \frac{(\text{air supplied} - \text{stoichiometric air})}{\text{stoichiometric air}} \times 100$$

$$= \frac{108.4 - 88.6}{88.6} = \underline{\underline{22\ \text{per cent}}}$$

2.12. EXCESS REAGENT

In industrial reactions the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess to promote the desired reaction; to maximise the use of an expensive reagent; or to ensure complete reaction of a reagent, as in combustion.

The percentage excess reagent is defined by the following equation:

$$\text{Per cent excess} = \frac{\text{quantity supplied} - \text{stoichiometric}}{\text{stoichiometric quantity}} \times 100 \qquad (2.7)$$

It is necessary to state clearly to which reagent the excess refers. This is often termed the limiting reagent.

Example 2.9

To ensure complete combustion, 20 per cent excess air is supplied to a furnace burning natural gas. The gas composition (by volume) is methane 95 per cent, ethane 5 per cent.

Calculate the mols of air required per mol of fuel.

Solution

Basis: 100 mol gas, as the analysis is volume percentage.

$$\text{Reactions: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\text{Stoichiometric mols } O_2 \text{ required} = 95 \times 2 + 5 \times 3\tfrac{1}{2} = \underline{\underline{207.5}}$$

$$\text{With 20 per cent excess, mols } O_2 \text{ required} = 207.5 \times \frac{120}{100} = \underline{\underline{249}}$$

$$\text{Mols air (21 per cent } O_2) = 249 \times \frac{100}{21} = 1185.7$$

$$\text{Air per mol fuel} = \frac{1185.7}{100} = \underline{\underline{11.86\ \text{mol}}}$$

2.13. CONVERSION AND YIELD

It is important to distinguish between conversion and yield (see Volume 3, Chapter 1). Conversion is to do with reactants (reagents); yield with products.

Conversion

Conversion is a measure of the fraction of the reagent that reacts.

To optimise reactor design and to minimise by-product formation, the conversion of a particular reagent is often less than 100 per cent. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

$$\begin{aligned}\text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}}\\ &= \frac{(\text{amount in feed stream}) - (\text{amount in product stream})}{(\text{amount in feed stream})} \qquad (2.8)\end{aligned}$$

This definition gives the total conversion of the particular reagent to all products. Sometimes figures given for conversion refer to one specific product, usually the desired product. In this instance the product must be specified as well as the reagent. This is really a way of expressing yield.

Example 2.10

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55 per cent to reduce carbon formation, which fouls the reactor tubes.

Calculate the quantity of DCE needed to produce 5000 kg/h VC.

Solution

Basis: 5000 kg/h VC (the required quantity).

Reaction: $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$
mol weights DCE 99, VC 62.5

$$\text{kmol/h VC produced} = \frac{5000}{62.5} = \underline{\underline{80}}$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let X be DCE feed kmol/h:

$$\text{Per cent conversion} = 55 = \frac{80}{X} \times 100$$

$$X = \frac{80}{0.55} = \underline{\underline{145.5 \text{ kmol/h}}}$$

In this example the small loss of DCE to carbon and other products has been neglected. All the DCE reacted has been assumed to be converted to VC.

Yield

Yield is a measure of the performance of a reactor or plant. Several different definitions of yield are used, and it is important to state clearly the basis of any yield figures. This is often not done when yield figures are quoted in the literature, and the judgement has to be used to decide what was intended.

For a reactor the yield (i.e. *relative yield*, Volume 3, Chapter 1) is defined by:

$$\text{Yield} = \frac{\text{mols of product produced} \times \text{stoichiometric factor}}{\text{mols of reagent converted}} \tag{2.9}$$

$$\text{Stoichiometric factor} = \text{Stoichiometric mols of reagent required per mol of product produced}$$

With industrial reactors it is necessary to distinguish between “Reaction yield” (chemical yield), which includes only chemical losses to side products; and the overall “Reactor yield” which will include physical losses.

If the conversion is near 100 per cent it may not be worth separating and recycling the unreacted material; the overall reactor yield would then include the loss of unreacted material. If the unreacted material is separated and recycled, the overall yield *taken over the reactor and separation step* would include any physical losses from the separation step.

Plant yield is a measure of the overall performance of the plant and includes all chemical and physical losses.

Plant yield (applied to the complete plant or any stage)

$$= \frac{\text{mols product produced} \times \text{stoichiometric factor}}{\text{mols reagent fed to the process}} \tag{2.10}$$

Where more than one reagent is used, or product produced, it is essential that product and reagent to which the yield figure refers is clearly stated.

Example 2.11

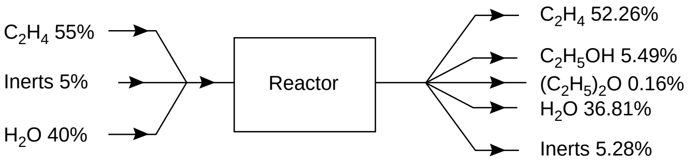
In the production of ethanol by the hydrolysis of ethylene, diethyl ether is produced as a by-product. A typical feed stream composition is: 55 per cent ethylene, 5 per cent inerts, 40 per cent water; and product stream: 52.26 per cent ethylene, 5.49 per cent ethanol, 0.16 per cent ether, 36.81 per cent water, 5.28 per cent inerts. Calculate the yield of ethanol and ether based on ethylene.

Solution

$$\text{Reactions:} \quad C_2H_4 + H_2O \rightarrow C_2H_5OH \tag{a}$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \tag{b}$$

Basis: 100 mols feed (easier calculation than using the product stream)



Note: the flow of inerts will be constant as they do not react, and it can be used to calculate the other flows from the compositions.

Feed stream	ethylene	55 mol
	inerts	5 mol
	water	40 mol

Product stream

$$\text{ethylene} = \frac{52.26}{5.28} \times 5 = 49.49 \text{ mol}$$
$$\text{ethanol} = \frac{5.49}{5.28} \times 5 = 5.20 \text{ mol}$$
$$\text{ether} = \frac{0.16}{5.28} \times 5 = 0.15 \text{ mol}$$
$$\text{Amount of ethylene reacted} = 55.0 - 49.49 = 5.51 \text{ mol}$$
$$\text{Yield of ethanol based on ethylene} = \frac{5.2 \times 1}{5.51} \times 100 = \underline{\underline{94.4 \text{ per cent}}}$$

As 1 mol of ethanol is produced per mol of ethylene the stoichiometric factor is 1.

$$\text{Yield of ether based on ethylene} = \frac{0.15 \times 2}{5.51} \times 100 = \underline{\underline{5.44 \text{ per cent}}}$$

The stoichiometric factor is 2, as 2 mol of ethylene produce 1 mol of ether.

Note: the conversion of ethylene, to all products, is given by:

$$\text{Conversion} = \frac{\text{mols fed} - \text{mols out}}{\text{mols fed}} = \frac{55 - 49.49}{55} \times 100$$
$$= \underline{\underline{10 \text{ per cent}}}$$

The yield based on water could also be calculated but is of no real interest as water is relatively inexpensive compared with ethylene. Water is clearly fed to the reactor in considerable excess.

Example 2.12

In the chlorination of ethylene to produce dichloroethane (DCE), the conversion of ethylene is reported as 99.0 per cent. If 94 mol of DCE are produced per 100 mol of ethylene fed, calculate the overall yield and the reactor (reaction) yield based on ethylene. The unreacted ethylene is not recovered.

Solution

$$\text{Reaction: } C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Stoichiometric factor 1.

$$\text{Overall yield (including physical losses)} = \frac{\text{mols DCE produced} \times 1}{\text{mols ethylene fed}} \times 100$$

$$= \frac{94}{100} \times 100 = \underline{\underline{94 \text{ per cent}}}$$

$$\text{Chemical yield (reaction yield)} = \frac{\text{mols DCE produced}}{\text{mols ethylene converted}} \times 100$$

$$= \frac{94}{99} \times 100 = \underline{\underline{94.5 \text{ per cent}}}$$

The principal by-product of this process is trichloroethane.

2.14. RECYCLE PROCESSES

Processes in which a flow stream is returned (recycled) to an earlier stage in the processing sequence are frequently used. If the conversion of a valuable reagent in a reaction process is appreciably less than 100 per cent, the unreacted material is usually separated and recycled. The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

In mass balance calculations the presence of recycle streams makes the calculations more difficult.

Without recycle, the material balances on a series of processing steps can be carried out sequentially, taking each unit in turn; the calculated flows out of one unit become the feeds to the next. If a recycle stream is present, then at the point where the recycle is returned the flow will not be known as it will depend on downstream flows not yet calculated. Without knowing the recycle flow, the sequence of calculations cannot be continued to the point where the recycle flow can be determined.

Two approaches to the solution of recycle problems are possible:

1. The cut and try method. The recycle stream flows can be estimated and the calculations continued to the point where the recycle is calculated. The estimated flows are then compared with the calculated and a better estimate made. The procedure is continued until the difference between the estimated and the calculated flows is within acceptable limits.
2. The formal, algebraic, method. The presence of recycle implies that some of the mass balance equations will have to be solved simultaneously. The equations are set up with the recycle flows as unknowns and solved using standard methods for the solution of simultaneous equations.

With simple problems, with only one or two recycle loops, the calculation can often be simplified by the careful selection of the basis of calculation and the system boundaries. This is illustrated in Examples 2.4 and 2.13.

The solution of more complex material balance problems involving several recycle loops is discussed in Chapter 4.

Example 2.13

The block diagram shows the main steps in the balanced process for the production of vinyl chloride from ethylene. Each block represents a reactor and several other processing units. The main reactions are:

Block A, chlorination

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2, \text{ yield on ethylene 98 per cent}$$

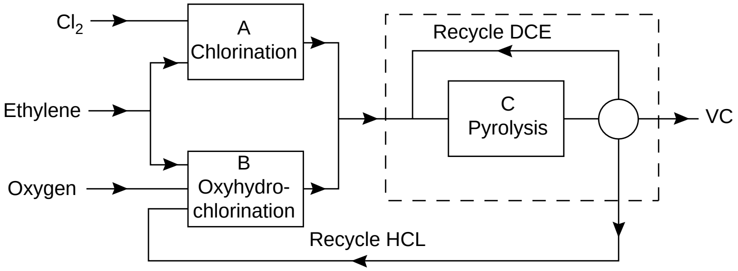
Block B, oxyhydrochlorination

$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O, \text{ yields: on ethylene 95 per cent, on HCl 90 per cent}$$

Block C, pyrolysis

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl, \text{ yields: on DCE 99 per cent, on HCl 99.5 per cent}$$

The HCl from the pyrolysis step is recycled to the oxyhydrochlorination step. The flow of ethylene to the chlorination and oxyhydrochlorination reactors is adjusted so that the production of HCl is in balance with the requirement. The conversion in the pyrolysis reactor is limited to 55 per cent, and the unreacted dichloroethane (DCE) separated and recycled.



Using the yield figures given, and neglecting any other losses, calculate the flow of ethylene to each reactor and the flow of DCE to the pyrolysis reactor, for a production rate of 12,500 kg/h vinyl chloride (VC).

Solution

Molecular weights: vinyl chloride 62.5, DCE 99.0, HCl 36.5.

$$\text{VC per hour} = \frac{12{,}500}{62.5} = 200 \text{ kmol/h}$$

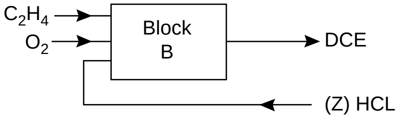
Draw a system boundary round each block, enclosing the DCE recycle within the boundary of step C.

Let flow of ethylene to block A be X and to block B be Y, and the HCl recycle be Z.

Then the total mols of DCE produced $= 0.98X + 0.95Y$, allowing for the yields, and the mols of HCl produced in block C

$$= (0.98X + 0.95Y)0.995 = Z \qquad (a)$$

Consider the flows to and product from block B



The yield of DCE based on HCl is 90 per cent, so the mols of DCE produced

$$= \frac{0.90Z}{2}$$

Note: the stoichiometric factor is 2 (2 mol HCl per mol DCE).

The yield of DCE based on ethylene is 95 per cent, so

$$\frac{0.9Z}{2} = 0.95Y$$

$$Z = \frac{0.95 \times 2Y}{0.9}$$

Substituting for Z into equation (a) gives

$$Y = (0.98X + 0.95Y)0.995 \times \frac{0.9}{2 \times 0.95}$$

$$Y = 0.837X \qquad (b)$$

Total VC produced $= 0.99 \times$ total DCE, so

$$0.99(0.98X + 0.95Y) = 200 \text{ kmol/h}$$

Substituting for Y from equation (b) gives $X = \underline{\underline{113.8 \text{ kmol/h}}}$

and $Y = 0.837 \times 113.8 = \underline{\underline{95.3 \text{ kmol/h}}}$

HCl recycle from equation (a)

$$Z = (0.98 \times 113.8 + 0.95 \times 95.3)0.995 = \underline{\underline{201.1 \text{ kmol/h}}}$$

Note: overall yield on ethylene $= \dfrac{200}{(113.8 + 95.3)} \times 100 = \underline{\underline{96 \text{ per cent}}}$

2.15. PURGE

It is usually necessary to bleed off a portion of a recycle stream to prevent the build-up of unwanted material. For example, if a reactor feed contains inert components that are not separated from the recycle stream in the separation units these inerts would accumulate in the recycle stream until the stream eventually consisted entirely of inerts. Some portion of the stream would have to be purged to keep the inert level within acceptable limits. A continuous purge would normally be used. Under steady-state conditions:

Loss of inert in the purge = Rate of feed of inerts into the system

The concentration of any component in the purge stream will be the same as that in the recycle stream at the point where the purge is taken off. So the required purge rate can be determined from the following relationship:

[Feed stream flow-rate] × [Feed stream inert concentration] =
[Purge stream flow-rate] × [Specified (desired) recycle inert concentration]

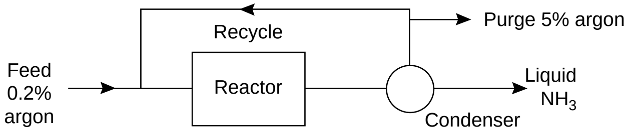
Example 2.14

In the production of ammonia from hydrogen and nitrogen the conversion, based on either raw material, is limited to 15 per cent. The ammonia produced is condensed from the reactor (converter) product stream and the unreacted material recycled. If the feed contains 0.2 per cent argon (from the nitrogen separation process), calculate the purge rate required to hold the argon in the recycle stream below 5.0 per cent. Percentages are by volume.

Solution

Basis: 100 mols feed (purge rate will be expressed as mols per 100 mol feed, as the production rate is not given).

Process diagram



Volume percentages are taken as equivalent to mol per cent.

Argon entering system with feed = 100 × 0.2/100 = 0.2 mol.

Let purge rate per 100 mol feed be F.

Argon leaving system in purge = $F \times 5/100 = 0.05F$.

At the steady state, argon leaving = argon entering

$$0.05F = 0.2$$

$$F = \frac{0.2}{0.05} = \underline{\underline{4}}$$

Purge required: 4 mol per 100 mol feed.

2.16. BY-PASS

A flow stream may be divided and some part diverted (by-passed) around some units. This procedure is often used to control stream composition or temperature.

Material balance calculations on processes with by-pass streams are similar to those involving recycle, except that the stream is fed forward instead of backward. This usually makes the calculations easier than with recycle.

2.17. UNSTEADY-STATE CALCULATIONS

All the previous material balance examples have been steady-state balances. The accumulation term was taken as zero, and the stream flow-rates and compositions did not vary with time. If these conditions are not met the calculations are more complex. Steady-state calculations are usually sufficient for the calculations of the process flow-sheet (Chapter 4). The unsteady-state behaviour of a process is important when considering the process start-up and shut-down, and the response to process upsets.

Batch processes are also examples of unsteady-state operation; though the total material requirements can be calculated by taking one batch as the basis for the calculation.

The procedure for the solution of unsteady-state balances is to set up balances over a small increment of time, which will give a series of differential equations describing the process. For simple problems these equations can be solved analytically. For more complex problems computer methods would be used.

The general approach to the solution of unsteady-state problems is illustrated in Example 2.15. Batch distillation is a further example of an unsteady-state material balance (see Volume 2, Chapter 11).

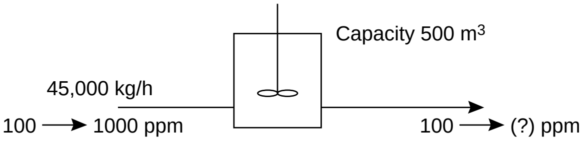
The behaviour of processes under non-steady-state conditions is a complex and specialised subject and beyond the scope of this book. It can be important in process design when assessing the behaviour of a process from the point of view of safety and control.

The use of material balances in the modelling of complex unsteady-state processes is discussed in the books by Myers and Seider (1976) and Henley and Rosen (1969).

Example 2.15

A hold tank is installed in an aqueous effluent-treatment process to smooth out fluctuations in concentration in the effluent stream. The effluent feed to the tank normally contains no more than 100 ppm of acetone. The maximum allowable concentration of acetone in the effluent discharge is set at 200 ppm. The surge tank working capacity is 500 m^3 and it can be considered to be perfectly mixed. The effluent flow is 45,000 kg/h. If the acetone concentration in the feed suddenly rises to 1000 ppm, due to a spill in the process plant, and stays at that level for half an hour, will the limit of 200 ppm in the effluent discharge be exceeded?

Solution



Basis: increment of time Δt.

To illustrate the general solution to this type of problem, the balance will be set up in terms of symbols for all the quantities and then actual values for this example substituted.

Let, Material in the tank $= M$,
Flow-rate $= F$,
Initial concentration in the tank $= C_0$,
Concentration at time t after the feed concentration is increased $= C$,
Concentration in the effluent feed $= C_1$,
Change in concentration over time increment $\Delta t = \Delta C$,
Average concentration in the tank during the time increment $= C_{\text{av}}$.

Then, as there is no generation in the system, the general material balance (Section 2.3) becomes:

$$\text{Input} - \text{Output} = \text{Accumulation}$$

Material balance on acetone.

Note: as the tank is considered to be perfectly mixed the outlet concentration will be the same as the concentration in the tank.

$$\text{Acetone in} - \text{Acetone out} = \text{Acetone accumulated in the tank}$$

$$FC_1\Delta t - FC_{\text{av}}\Delta t = M(C + \Delta C) - MC$$

$$F(C_1 - C_{\text{av}}) = M\frac{\Delta C}{\Delta t}$$

Taking the limit, as $\Delta t \to 0$

$$\frac{\Delta C}{\Delta t} = \frac{\mathrm{d}C}{\mathrm{d}t},\quad C_{\text{av}} = C$$

$$F(C_1 - C) = M\frac{\mathrm{d}C}{\mathrm{d}t}$$

Integrating

$$\int_0^t \mathrm{d}t = \frac{M}{F}\int_{C_0}^{C} \frac{\mathrm{d}C}{(C_1 - C)}$$

$$t = -\frac{M}{F}\ln\left[\frac{C_1 - C}{C_1 - C_0}\right]$$

Substituting the values for the example, noting that the maximum outlet concentration will occur at the end of the half-hour period of high inlet concentration.

$t = 0.5$ h
$C_1 = 1000$ ppm
$C_0 = 100$ ppm (normal value)
$M = 500\ \text{m}^3 = 500{,}000$ kg
$F = 45{,}000$ kg/h

$$0.5 = -\frac{500{,}000}{45{,}000}\ln\left[\frac{1000 - C}{1000 - 100}\right]$$

$$0.045 = -\ln\left[\frac{1000 - C}{900}\right]$$

$$e^{-0.045} \times 900 = 1000 - C$$

$$C = \underline{\underline{140 \text{ ppm}}}$$

So the maximum allowable concentration will not be exceeded.

2.18. GENERAL PROCEDURE FOR MATERIAL-BALANCE PROBLEMS

The best way to tackle a problem will depend on the information given; the information required from the balance; and the constraints that arise from the nature of the problem. No all embracing, best method of solution can be given to cover all possible problems. The following step-by-step procedure is given as an aid to the efficient solution of material balance problems. The same general approach can be usefully employed to organise the solution of energy balance, and other design problems.

Procedure

Step 1. Draw a block diagram of the process.
Show each significant step as a block, linked by lines and arrows to show the stream connections and flow direction.

Step 2. List all the available data.
Show on the block diagram the known flows (or quantities) and stream compositions.

Step 3. List all the information required from the balance.

Step 4. Decide the system boundaries (see Section 2.6).

Step 5. Write out all the chemical reactions involved for the main products and by-products.

Step 6. Note any other constraints,
such as: specified stream compositions,
azeotropes,
phase equilibria,
tie substances (see Section 2.11).

The use of phase equilibrium relationships and other constraints in determining stream compositions and flows is discussed in more detail in Chapter 4.

Step 7. Note any stream compositions and flows that can be approximated.

Step 8. Check the number of conservation (and other) equations that can be written, and compare with the number of unknowns. Decide which variables are to be design variables; see Section 2.10.
This step would be used only for complex problems.

Step 9. Decide the basis of the calculation; see Section 2.7.

The order in which the steps are taken may be varied to suit the problem.

2.19. REFERENCES (FURTHER READING)

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2.20. NOMENCLATURE

		Dimensions in **MLT**
C	Concentration after time t, Example 2.15	—
C_{av}	Average concentration, Example 2.15	—
C_0	Initial concentration, Example 2.15	—
C_1	Concentration in feed to tank, Example 2.15	—
ΔC	Incremental change in concentration, Example 2.15	—
F	Flow-rate	$\mathbf{MT^{-1}}$
F_n	Total flow in stream n	$\mathbf{MT^{-1}}$
F_1	Water feed to reactor, Example 2.4	$\mathbf{MT^{-1}}$
M	Quantity in hold tank, Example 2.15	**M**
N_c	Number of independent components	—
N_d	Number of variables to be specified	—
N_e	Number of independent balance equations	—
N_s	Number of streams	—
N_v	Number of variables	—
t	Time, Example 2.15	**T**
Δt	Incremental change in time, Example 2.15	**T**
X	Unknown flow, Examples 2.8, 2.10, 2.13	$\mathbf{MT^{-1}}$
$x_{n,m}$	Concentration of component m in stream n	—
Y	Unknown flow, Examples 2.8, 2.13	$\mathbf{MT^{-1}}$
Z	Unknown flow, Example 2.13	$\mathbf{MT^{-1}}$

2.21. PROBLEMS

2.1. The composition of a gas derived by the gasification of coal is, volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, benzene 2, balance nitrogen. If the gas is burnt in a furnace with 20 per cent excess air, calculate:

(a) the amount of air required per 100 kmol of gas,
(b) The amount of flue gas produced per 100 kmol of gas,

(c) the composition of the flue gases, on a dry basis.

Assume complete combustion.

2.2. Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20 °C. The air contains 5.0 per cent v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia air mixture to the column is 200 m^3/s and the stream leaving the column contains 0.05 per cent v/v ammonia, calculate:

(a) The flow-rate of gas leaving the column.
(b) The mass of ammonia absorbed.
(c) The flow-rate of water to the column, if the exit water contains 1% w/w ammonia.

2.3. The off-gases from a gasoline stabiliser are fed to a reforming plant to produce hydrogen.
The composition of the off-gas, molar per cent, is: CH_4 77.5, C_2H_6 9.5, C_3H_8 8.5, C_4H_{10} 4.5.
The gases entering the reformer are at a pressure of 2 bara and 35 °C and the feed rate is 2000 m^3/h.
The reactions in the reformer are:

1. $C_2H_{2n+2} + n(H_2O) \rightarrow n(CO) + (2_n + 1)H_2$
2. $CO + H_2O \rightarrow CO_2 + H_2$

The molar conversion of C_2H_{2n+2} in reaction (1) is 96 per cent and of CO in reaction (2) 92 per cent.
Calculate:

(a) the average molecular mass of the off-gas,
(b) the mass of gas fed to the reformer, kg/h,
(c) the mass of hydrogen produced, kg/h.

2.4. Allyl alcohol can be produced by the hydrolysis of allyl chloride. Together with the main product, allyl alcohol, di-ally ether is produced as a by-product. The conversion of allyl chloride is typically 97 per cent and the yield to alcohol 90 per cent, both on a molar basis. Assuming that there are no other significant side reactions, calculate masses of alcohol and ether produced, per 1000 kg of allyl chloride fed to the reactor.

2.5. Aniline is produced by the hydrogenation of nitrobenzene. A small amount of cyclo-hexylamine is produced as a by-product. The reactions are:

1. $C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$
2. $C_6H_5NO_2 + 6H_2 \rightarrow C_6H_{11}NH_2 + 2H_2O$

Nitrobenzene is fed to the reactor as a vapour, with three times the stoichiometric quantity of hydrogen. The conversion of the nitrobenzene, to all products, is 96 per cent, and the yield to aniline 95 per cent.
The unreacted hydrogen is separated from the reactor products and recycled to the reactor. A purge is taken from the recycle stream to maintain the inerts in the

recycle stream below 5 per cent. The fresh hydrogen feed is 99.5 per cent pure, the remainder being inerts. All percentages are molar.

For a feed rate of 100 kmol/h of nitrobenzene, calculate:

(a) the fresh hydrogen feed,
(b) the purge rate required,
(c) the composition of the reactor outlet stream.

2.6. In the manufacture of aniline by the hydrogenation of nitrobenzene, the off-gases from the reactor are cooled and the products and unreacted nitrobenzene condensed. The hydrogen and inerts, containing only traces of the condensed materials, are recycled.

Using the typical composition of the reactor off-gas given below, estimate the stream compositions leaving the condenser.

Composition, kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, hydrogen 5640, nitrobenzene 40, inerts 300.

2.7. In the manufacture of aniline, the condensed reactor products are separated in a decanter. The decanter separates the feed into an organic phase and an aqueous phase. Most of the aniline in the feed is contained in the organic phase and most of the water in the aqueous phase. Using the data given below, calculate the stream compositions.

Data:

Typical feed composition, including impurities and by-products, weight per cent: water 23.8, aniline 72.2, nitrobenzene 3.2, cyclo-hexylamine 0.8.

Density of aqueous layer 0.995, density of organic layer 1.006. Therefore, the organic layer will be at the bottom.

Solubility of aniline in water 3.2 per cent w/w, and water in aniline 5.15 per cent w/w.

Partition coefficient of nitrobenzene between the aqueous and organic phases: $C_{organic}/C_{water} = 300$

Solubility of cyclo-hexylamine in the water phase 0.12 per cent w/w and in the organic phase 1.0 per cent w/w.

2.8. In the manufacture of aniline from nitrobenzene the reactor products are condensed and separated into an aqueous and organic phases in a decanter. The organic phase is fed to a striping column to recover the aniline. Aniline and water form an azeotrope, composition 0.96 mol fraction aniline. For the feed composition given below, make a mass balance round the column and determine the stream compositions and flow-rates. Take as the basis for the balance 100 kg/h feed and a 99.9 percentage recovery of the aniline in the overhead product. Assume that the nitrobenzene leaves with the water stream from the base of the column.

Feed composition, weight percentage: water 2.4, aniline 73.0, nitrobenzene 3.2, cyclo-hexylamine trace.

Note: Problems 2.5 to 2.8 can be taken together as an exercise in the calculation of a preliminary material balance for the manufacture of aniline by the process described in detail in Appendix F, Problem F.8.

CHAPTER 2

Fundamentals of Material Balances

2.1. INTRODUCTION

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions.

A good understanding of material balance calculations is essential in process design.

In this chapter the fundamentals of the subject are covered, using simple examples to illustrate each topic. Practice is needed to develop expertise in handling what can often become very involved calculations. More examples and a more detailed discussion of the subject can be found in the numerous specialist books written on material and energy balance computations. Several suitable texts are listed under the heading of "Further Reading" at the end of this chapter.

The application of material balances to more complex problems is discussed in "Flowsheeting", Chapter 4.

Material balances are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss.

2.2. THE EQUIVALENCE OF MASS AND ENERGY

Einstein showed that mass and energy are equivalent. Energy can be converted into mass, and mass into energy. They are related by Einstein's equation:

$$E = mc^2 \tag{2.1}$$

where E = energy, J,
m = mass, kg,
c = the speed of light *in vacuo*, 3×10^8 m/s.

The loss of mass associated with the production of energy is significant only in nuclear reactions. Energy and matter are always considered to be separately conserved in chemical reactions.

2.3. CONSERVATION OF MASS

The general conservation equation for any process system can be written as:

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady-state process the accumulation term will be zero. Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place a particular chemical species may be formed or consumed in the process. If there is no chemical reaction the steady-state balance reduces to

$$\text{Material out} = \text{Material in}$$

A balance equation can be written for each separately identifiable species present, elements, compounds or radicals; and for the total material.

Example 2.1

2000 kg of a 5 per cent slurry of calcium hydroxide in water is to be prepared by diluting a 20 per cent slurry. Calculate the quantities required. The percentages are by weight.

Solution

Let the unknown quantities of the 20% slurry and water be X and Y respectively.

Material balance on $Ca(OH)_2$

$$\begin{array}{cc} \textit{In} & \textit{Out} \\ X\dfrac{20}{100} & = 2000 \times \dfrac{5}{100} \end{array} \qquad (a)$$

Balance on water

$$X\frac{(100-20)}{100} + Y = 2000\frac{(100-5)}{100} \qquad (b)$$

From equation (a) $X = 500$ kg.

Substituting into equation (b) gives $Y = \underline{\underline{1500 \text{ kg}}}$

Check material balance on total quantity:

$$X + Y = 2000$$

$$500 + 1500 = 2000, \text{ correct}$$

2.4. UNITS USED TO EXPRESS COMPOSITIONS

When specifying a composition as a percentage it is important to state clearly the basis: weight, molar or volume.

The abbreviations w/w and v/v are used to designate weight basis and volume basis.

Example 2.2

Technical grade hydrochloric acid has a strength of 28 per cent w/w, express this as a mol fraction.

Solution

Basis of calculation 100 kg of 28 per cent w/w acid.

$$\begin{aligned}
&\text{Molecular mass: water 18, HCl 36.5}\\
\text{Mass HCl} &= 100 \times 0.28 = 28\ \text{kg}\\
\text{Mass water} &= 100 \times 0.72 = 72\ \text{kg}\\
\text{kmol HCl} &= \frac{28}{36.5} = 0.77\\
\text{kmol water} &= \frac{72}{18} \quad = \underline{4.00}\\
\text{Total mols} &\qquad\quad = 4.77\\
\text{mol fraction HCl} &= \frac{0.77}{4.77} = 0.16\\
\text{mol fraction water} &= \frac{4.00}{4.77} = \underline{0.84}\\
\text{Check total} &\qquad\quad\ \ 1.00
\end{aligned}$$

Within the accuracy needed for technical calculations, volume fractions can be taken as equivalent to mol fractions for gases, up to moderate pressures (say 25 bar).

Trace quantities are often expressed as parts per million (ppm). The basis, weight or volume, needs to be stated.

$$\text{ppm} = \frac{\text{quantity of component}}{\text{total quantity}} \times 10^6$$

Note. 1 ppm $= 10^{-4}$ per cent.

Minute quantities are sometimes quoted in ppb, parts per billion. Care is needed here, as the billion is usually an American billion (10^9), not the UK billion (10^{12}).

2.5. STOICHIOMETRY

Stoichiometry (from the Greek *stoikeion*—element) is the practical application of the law of multiple proportions. The stoichiometric equation for a chemical reaction states unambiguously the number of molecules of the reactants and products that take part; from which the quantities can be calculated. The equation must balance.

With simple reactions it is usually possible to balance the stoichiometric equation by inspection, or by trial and error calculations. If difficulty is experienced in balancing complex equations, the problem can always be solved by writing a balance for each element present. The procedure is illustrated in Example 2.3.

Example 2.3

Write out and balance the overall equation for the manufacture of vinyl chloride from ethylene, chlorine and oxygen.

Solution

Method: write out the equation using letters for the unknown number of molecules of each reactant and product. Make a balance on each element. Solve the resulting set of equations.

$$A(C_2H_4) + B(Cl_2) + C(O_2) = D(C_2H_3Cl) + E(H_2O)$$

Balance on carbon

$$2A = 2D, \quad A = D$$

on hydrogen

$$4A = 3D + 2E$$

$$\text{substituting } D = A \text{ gives } E = \frac{A}{2}$$

on chlorine

$$2B = D, \text{ hence } B = \frac{A}{2}$$

on oxygen

$$2C = E, \qquad C = \frac{E}{2} = \frac{A}{4}$$

putting $A = 1$, the equation becomes

$$C_2H_4 + \tfrac{1}{2}Cl_2 + \tfrac{1}{4}O_2 = C_2H_3Cl + \tfrac{1}{2}H_2O$$

multiplying through by the largest denominator to remove the fractions

$$4C_2H_4 + 2Cl_2 + O_2 = 4C_2H_3Cl + 2H_2O$$

2.6. CHOICE OF SYSTEM BOUNDARY

The conservation law holds for the complete process and any sub-division of the process. The system boundary defines the part of the process being considered. The flows into and out of the system are those crossing the boundary and must balance with material generated or consumed within the boundary.

Any process can be divided up in an arbitrary way to facilitate the material balance calculations. The judicious choice of the system boundaries can often greatly simplify what would otherwise be difficult and tortuous calculations.

No hard and fast rules can be given on the selection of suitable boundaries for all types of material balance problems. Selection of the best sub-division for any particular process is a matter of judgement, and depends on insight into the structure of the problem, which can only be gained by practice. The following general rules will serve as a guide:

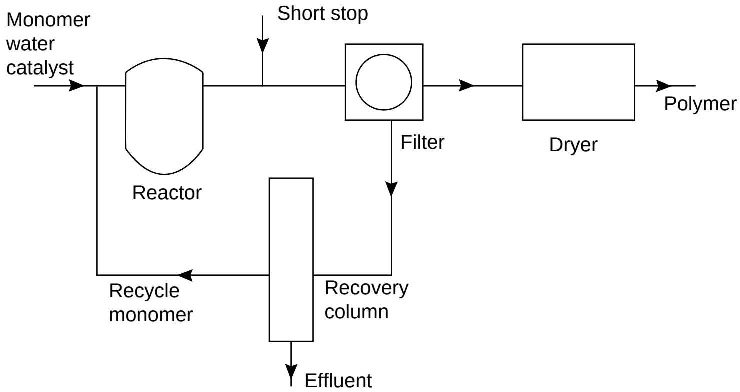
1. With complex processes, first take the boundary round the complete process and if possible calculate the flows in and out. Raw materials in, products and by-products out.
2. Select the boundaries to sub-divide the process into simple stages and make a balance over each stage separately.
3. Select the boundary round any stage so as to reduce the number of unknown streams to as few as possible.

4. As a first step, include any recycle streams within the system boundary (see Section 2.14).

Example 2.4

Selection of system boundaries and organisation of the solution.
The diagram shows the main steps in a process for producing a polymer. From the following data, calculate the stream flows for a production rate of 10,000 kg/h.

Reactor, yield on polymer 100 per cent
slurry polymerisation 20 per cent monomer/water
conversion 90 per cent
catalyst 1 kg/1000 kg monomer
short stopping agent 0.5 kg/1000 kg unreacted monomer
Filter, wash water approx. 1 kg/1 kg polymer
Recovery column, yield 98 per cent (percentage recovered)
Dryer, feed ~5 per cent water, product specification 0.5 per cent H_2O
Polymer losses in filter and dryer ~1 per cent

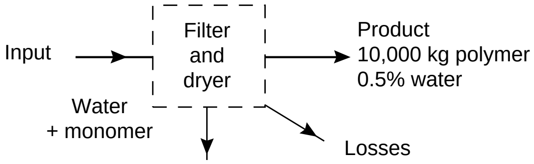


Solution

Only those flows necessary to illustrate the choice of system boundaries and method of calculation are given in the Solution.

Basis: 1 hour

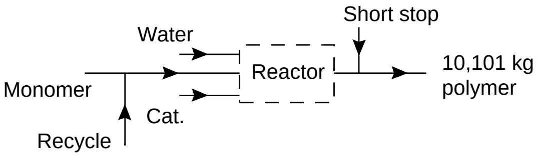
Take the first system boundary round the filter and dryer.



With 1 per cent loss, polymer entering sub-system

$$= \frac{10{,}000}{0.99} = \underline{\underline{10{,}101 \text{ kg}}}$$

Take the next boundary round the reactor system; the feeds to the reactor can then be calculated.



At 90 per cent conversion, monomer feed

$$= \frac{10{,}101}{0.9} = \underline{\underline{11{,}223 \text{ kg}}}$$

Unreacted monomer $= 11{,}223 - 10{,}101 = \underline{\underline{1122 \text{ kg}}}$

Short-stop, at 0.5 kg/1000 kg unreacted monomer

$$= 1122 \times 0.5 \times 10^{-3} = \underline{\underline{0.6 \text{ kg}}}$$

Catalyst, at 1 kg/1000 kg monomer

$$= 11{,}223 \times 1 \times 10^{-3} = \underline{\underline{11 \text{ kg}}}$$

Let water feed to reactor be F_1, then for 20 per cent monomer

$$0.2 = \frac{11{,}223}{F_1 + 11{,}223}$$

$$F_1 = \frac{11{,}223(1 - 0.2)}{0.2} = \underline{\underline{44{,}892 \text{ kg}}}$$

Now consider filter-dryer sub-system again.
Water in polymer to dryer, at 5 per cent (neglecting polymer loss)

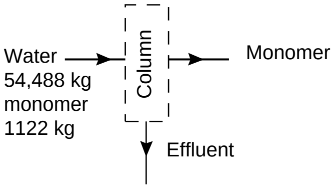
$$= 10{,}101 \times 0.05 = \underline{\underline{505 \text{ kg}}}$$

Balance over reactor-filter-dryer sub-system gives flows to recovery column.

$$\text{water, } 44{,}892 + 10{,}101 - 505 = \underline{\underline{54{,}448 \text{ kg}}}$$

$$\text{monomer, unreacted monomer, } = \underline{\underline{1122 \text{ kg}}}$$

Now consider recovery system

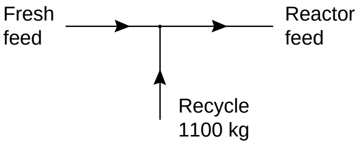


With 98 per cent recovery, recycle to reactor

$$= 0.98 \times 1122 = \underline{\underline{1100 \text{ kg}}}$$

Composition of effluent 23 kg monomer, 54,488 kg water.

Consider reactor monomer feed



Balance round tee gives fresh monomer required

$$= 11{,}223 - 1100 = \underline{\underline{10{,}123 \text{ kg}}}$$

2.7. CHOICE OF BASIS FOR CALCULATIONS

The correct choice of the basis for a calculation will often determine whether the calculation proves to be simple or complex. As with the choice of system boundaries, no all-embracing rules or procedures can be given for the selection of the right basis for any problem. The selection depends on judgement gained by experience. Some guide rules that will help in the choice are:

1. Time: choose the time basis in which the results are to be presented; for example kg/h, tonne/y.
2. For batch processes use one batch.
3. Choose as the mass basis the stream flow for which most information is given.
4. It is often easier to work in mols, rather than weight, even when no reaction is involved.
5. For gases, if the compositions are given by volume, use a volume basis, remembering that volume fractions are equivalent to mol fractions up to moderate pressures.

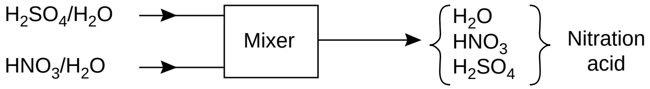
2.8. NUMBER OF INDEPENDENT COMPONENTS

A balance equation can be written for each independent component. Not all the components in a material balance will be independent.

Physical systems, no reaction

If there is no chemical reaction the number of independent components is equal to the number of distinct chemical species present.

Consider the production of a nitration acid by mixing 70 per cent nitric and 98 per cent sulphuric acid. The number of distinct chemical species is 3; water, sulphuric acid, nitric acid.



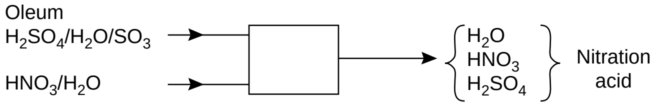
Chemical systems, reaction

If the process involves chemical reaction the number of independent components will not necessarily be equal to the number of chemical species, as some may be related by the chemical equation. In this situation the number of independent components can be calculated by the following relationship:

$$\text{Number of independent components} = \text{Number of chemical species} - \text{Number of independent chemical equations} \quad (2.2)$$

Example 2.5

If nitration acid is made up using oleum in place of the 98 per cent sulphuric acid, there will be four distinct chemical species: sulphuric acid, sulphur trioxide, nitric acid, water. The sulphur trioxide will react with the water producing sulphuric acid so there are only three independent components



Reaction equation $SO_3 + H_2O \rightarrow H_2SO_4$

No. of chemical species	4
No. of reactions	1
No. of independent equations	3

2.9. CONSTRAINTS ON FLOWS AND COMPOSITIONS

It is obvious, but worth emphasising, that the sum of the individual component flows in any stream cannot exceed the total stream flow. Also, that the sum of the individual molar or weight fractions must equal 1. Hence, the composition of a stream is completely defined if all but one of the component concentrations are given.

The component flows in a stream (or the quantities in a batch) are completely defined by any of the following:

1. Specifying the flow (or quantity) of each component.
2. Specifying the total flow (or quantity) and the composition.
3. Specifying the flow (or quantity) of one component and the composition.

Example 2.6

The feed stream to a reactor contains: ethylene 16 per cent, oxygen 9 per cent, nitrogen 31 per cent, and hydrogen chloride. If the ethylene flow is 5000 kg/h, calculate the individual component flows and the total stream flow. All percentages are by weight.

Solution

$$\begin{aligned}
\text{Percentage HCl} &= 100 - (16 + 9 + 31) = \underline{\underline{44}} \\
\text{Percentage ethylene} &= \frac{5000}{\text{total}} \times 100 = \underline{\underline{16}} \\
\text{hence total flow} &= 5000 \times \frac{100}{16} = \underline{\underline{31{,}250\ \text{kg/h}}} \\
\text{so, oxygen flow} &= \frac{9}{100} \times 31{,}250 = \underline{\underline{2813\ \text{kg/h}}} \\
\text{nitrogen} &= 31{,}250 \times \frac{31}{100} = \underline{\underline{9687\ \text{kg/h}}} \\
\text{hydrogen chloride} &= 31{,}250 \times \frac{44}{100} = \underline{\underline{13{,}750\ \text{kg/h}}}
\end{aligned}$$

General rule: the ratio of the flow of any component to the flow of any other component is the same as the ratio of the compositions of the two components.

The flow of any component in Example 2.6 could have been calculated directly from the ratio of the percentage to that of ethylene, and the ethylene flow.

$$\text{Flow of hydrogen chloride} = \frac{44}{16} \times 5000 = \underline{\underline{13{,}750\ \text{kg/h}}}$$

2.10. GENERAL ALGEBRAIC METHOD

Simple material-balance problems involving only a few streams and with a few unknowns can usually be solved by simple direct methods. The relationship between the unknown quantities and the information given can usually be clearly seen. For more complex problems, and for problems with several processing steps, a more formal algebraic approach can be used. The procedure is involved, and often tedious if the calculations have to be done manually, but should result in a solution to even the most intractable problems, providing sufficient information is known.

Algebraic symbols are assigned to all the unknown flows and compositions. Balance equations are then written around each sub-system for the independent components (chemical species or elements).

Material-balance problems are particular examples of the general design problem discussed in Chapter 1. The unknowns are compositions or flows, and the relating equations arise from the conservation law and the stoichiometry of the reactions. For any problem to have a unique solution it must be possible to write the same number of independent equations as there are unknowns.

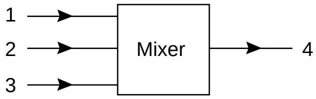
Consider the general material balance problem where there are N_s streams each containing N_c independent components. Then the number of variables, N_v, is given by:

$$N_v = N_c \times N_s \tag{2.3}$$

If N_e independent balance equations can be written, then the number of variables, N_d, that must be specified for a unique solution, is given by:

$$N_d = (N_s \times N_c) - N_e \tag{2.4}$$

Consider a simple mixing problem



Let F_n be the total flow in stream n, and $x_{n,m}$ the concentration of component m in stream n. Then the general balance equation can be written

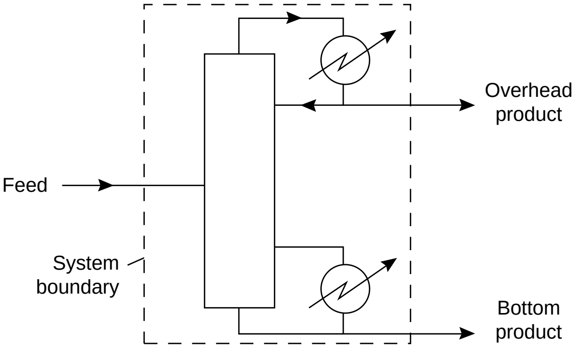
$$F_1 x_{1,m} + F_2 x_{2,m} + F_3 x_{3,m} = F_4 x_{4,m} \tag{2.5}$$

A balance equation can also be written for the total of each stream:

$$F_1 + F_2 + F_3 = F_4 \tag{2.6}$$

but this could be obtained by adding the individual component equations, and so is not an additional independent equation. There are m independent equations, the number of independent components.

Consider a separation unit, such as a distillation column, which divides a process stream into two product streams. Let the feed rate be 10,000 kg/h; composition benzene 60 per cent, toluene 30 per cent, xylene 10 per cent.



There are three streams, feed, overheads and bottoms, and three independent components in each stream.

Number of variables (component flow rates) = 9
Number of independent material balance equations = 3
Number of variables to be specified for a unique solution = 9 − 3 = 6

Three variables are specified; the feed flow and composition fixes the flow of each component in the feed.

Number of variables to be specified by designer = 6 − 3 = 3. Any three component flows can be chosen.

Normally the top composition and flow or the bottom composition and flow would be chosen.

If the primary function of the column is to separate the benzene from the other components, the maximum toluene and xylene in the overheads would be specified; say, at 5 kg/h and 3 kg/h, and the loss of benzene in the bottoms also specified; say, at not greater than 5 kg/h. Three flows are specified, so the other flows can be calculated.

Benzene in overheads = benzene in feed − benzene in bottoms.

$$0.6 \times 10{,}000 - 5 = \underline{\underline{5995\ \text{kg/h}}}$$

Toluene in bottoms = toluene in feed − toluene in overheads

$$0.3 \times 10{,}000 - 5 = \underline{\underline{2995\ \text{kg/h}}}$$

Xylene in bottoms = xylene in feed − xylene in overheads

$$0.1 \times 10{,}000 - 3 = \underline{\underline{997\ \text{kg/h}}}$$

2.11. TIE COMPONENTS

In Section 2.9 it was shown that the flow of any component was in the same ratio to the flow of any other component, as the ratio of the concentrations of the two components. If one component passes unchanged through a process unit it can be used to tie the inlet and outlet compositions.

This technique is particularly useful in handling combustion calculations where the nitrogen in the combustion air passes through unreacted and is used as the tie component. This is illustrated in Example 2.8.

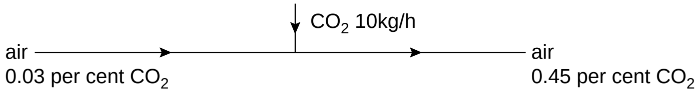
This principle can also be used to measure the flow of a process stream by introducing a measured flow of some easily analysed (compatible) material.

Example 2.7

Carbon dioxide is added at a rate of 10 kg/h to an air stream and the air is sampled at a sufficient distance downstream to ensure complete mixing. If the analysis shows 0.45 per cent v/v CO_2, calculate the air-flow rate.

Solution

Normal carbon dioxide content of air is 0.03 per cent



Basis: kmol/h, as percentages are by volume.

$$\text{kmol/h } CO_2 \text{ introduced} = \frac{10}{44} = 0.2273$$

Let X be the air flow.
Balance on CO_2, the tie component

$$\begin{aligned} CO_2 \text{ in} &= 0.0003\ X + 0.2273 \\ CO_2 \text{ out} &= 0.0045\ X \\ X(0.0045 - 0.0003) &= 0.2273 \\ X = 0.2273/0.0042 &= 54\ \text{kmol/h} \\ &= 54 \times 29 = \underline{\underline{1560\ \text{kg/h}}} \end{aligned}$$

Example 2.8

In a test on a furnace fired with natural gas (composition 95 per cent methane, 5 per cent nitrogen) the following flue gas analysis was obtained: carbon dioxide 9.1 per cent, carbon monoxide 0.2 per cent, oxygen 4.6 per cent, nitrogen 86.1 per cent, all percentages by volume.

Calculate the percentage excess air flow (percentage above stoichiometric).

Solution

$$\text{Reaction: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Note: the flue gas analysis is reported on the dry basis, any water formed having been condensed out.

Nitrogen is the tie component.

Basis: 100 mol, dry flue gas; as the analysis of the flue gas is known, the mols of each element in the flue gas (flow out) can be easily calculated and related to the flow into the system.

Let the quantity of fuel (natural gas) per 100 mol dry flue gas be X.

Balance on carbon, mols in fuel = mols in flue gas

$$0.95\ X = 9.1 + 0.2,\ \text{ hence } X = \underline{\underline{9.79\ \text{mol}}}$$

Balance on nitrogen (composition of air O_2 21 per cent, N_2 79 per cent).

Let Y be the flow of air per 100 mol dry flue gas.

$$N_2 \text{ in air} + N_2 \text{ in fuel} = N_2 \text{ in flue gas}$$

$$0.79\ Y + 0.05 \times 9.79 = 86.1,\ \text{ hence } Y = \underline{\underline{108.4\ \text{mol}}}$$

Stoichiometric air; from the reaction equation 1 mol methane requires 2 mol oxygen,

$$\text{so, stoichiometric air} = 9.79 \times 0.95 \times 2 \times \frac{100}{21} = \underline{\underline{88.6\ \text{mol}}}$$

$$\text{Percentage excess air} = \frac{(\text{air supplied} - \text{stoichiometric air})}{\text{stoichiometric air}} \times 100$$

$$= \frac{108.4 - 88.6}{88.6} = \underline{\underline{22\ \text{per cent}}}$$

2.12. EXCESS REAGENT

In industrial reactions the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess to promote the desired reaction; to maximise the use of an expensive reagent; or to ensure complete reaction of a reagent, as in combustion.

The percentage excess reagent is defined by the following equation:

$$\text{Per cent excess} = \frac{\text{quantity supplied} - \text{stoichiometric}}{\text{stoichiometric quantity}} \times 100 \qquad (2.7)$$

It is necessary to state clearly to which reagent the excess refers. This is often termed the limiting reagent.

Example 2.9

To ensure complete combustion, 20 per cent excess air is supplied to a furnace burning natural gas. The gas composition (by volume) is methane 95 per cent, ethane 5 per cent.

Calculate the mols of air required per mol of fuel.

Solution

Basis: 100 mol gas, as the analysis is volume percentage.

$$\text{Reactions: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\text{Stoichiometric mols } O_2 \text{ required} = 95 \times 2 + 5 \times 3\tfrac{1}{2} = \underline{\underline{207.5}}$$

$$\text{With 20 per cent excess, mols } O_2 \text{ required} = 207.5 \times \frac{120}{100} = \underline{\underline{249}}$$

$$\text{Mols air (21 per cent } O_2) = 249 \times \frac{100}{21} = 1185.7$$

$$\text{Air per mol fuel} = \frac{1185.7}{100} = \underline{\underline{11.86\ \text{mol}}}$$

2.13. CONVERSION AND YIELD

It is important to distinguish between conversion and yield (see Volume 3, Chapter 1). Conversion is to do with reactants (reagents); yield with products.

Conversion

Conversion is a measure of the fraction of the reagent that reacts.

To optimise reactor design and to minimise by-product formation, the conversion of a particular reagent is often less than 100 per cent. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

$$\begin{aligned}\text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}}\\ &= \frac{\text{(amount in feed stream)} - \text{(amount in product stream)}}{\text{(amount in feed stream)}} \qquad (2.8)\end{aligned}$$

This definition gives the total conversion of the particular reagent to all products. Sometimes figures given for conversion refer to one specific product, usually the desired product. In this instance the product must be specified as well as the reagent. This is really a way of expressing yield.

Example 2.10

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55 per cent to reduce carbon formation, which fouls the reactor tubes.

Calculate the quantity of DCE needed to produce 5000 kg/h VC.

Solution

Basis: 5000 kg/h VC (the required quantity).

Reaction: $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$

mol weights DCE 99, VC 62.5

$$\text{kmol/h VC produced} = \frac{5000}{62.5} = \underline{\underline{80}}$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let X be DCE feed kmol/h:

$$\text{Per cent conversion} = 55 = \frac{80}{X} \times 100$$

$$X = \frac{80}{0.55} = \underline{\underline{145.5 \text{ kmol/h}}}$$

In this example the small loss of DCE to carbon and other products has been neglected. All the DCE reacted has been assumed to be converted to VC.

Yield

Yield is a measure of the performance of a reactor or plant. Several different definitions of yield are used, and it is important to state clearly the basis of any yield figures. This is often not done when yield figures are quoted in the literature, and the judgement has to be used to decide what was intended.

For a reactor the yield (i.e. *relative yield*, Volume 3, Chapter 1) is defined by:

$$\text{Yield} = \frac{\text{mols of product produced} \times \text{stoichiometric factor}}{\text{mols of reagent converted}} \tag{2.9}$$

Stoichiometric factor = Stoichiometric mols of reagent required per mol of product produced

With industrial reactors it is necessary to distinguish between "Reaction yield" (chemical yield), which includes only chemical losses to side products; and the overall "Reactor yield" which will include physical losses.

If the conversion is near 100 per cent it may not be worth separating and recycling the unreacted material; the overall reactor yield would then include the loss of unreacted material. If the unreacted material is separated and recycled, the overall yield *taken over the reactor and separation step* would include any physical losses from the separation step.

Plant yield is a measure of the overall performance of the plant and includes all chemical and physical losses.

Plant yield (applied to the complete plant or any stage)

$$= \frac{\text{mols product produced} \times \text{stoichiometric factor}}{\text{mols reagent fed to the process}} \tag{2.10}$$

Where more than one reagent is used, or product produced, it is essential that product and reagent to which the yield figure refers is clearly stated.

Example 2.11

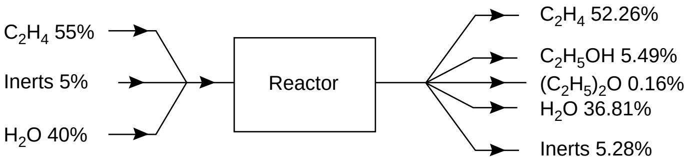
In the production of ethanol by the hydrolysis of ethylene, diethyl ether is produced as a by-product. A typical feed stream composition is: 55 per cent ethylene, 5 per cent inerts, 40 per cent water; and product stream: 52.26 per cent ethylene, 5.49 per cent ethanol, 0.16 per cent ether, 36.81 per cent water, 5.28 per cent inerts. Calculate the yield of ethanol and ether based on ethylene.

Solution

$$\text{Reactions:} \quad C_2H_4 + H_2O \rightarrow C_2H_5OH \tag{a}$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \tag{b}$$

Basis: 100 mols feed (easier calculation than using the product stream)



Note: the flow of inerts will be constant as they do not react, and it can be used to calculate the other flows from the compositions.

Feed stream	ethylene	55 mol
	inerts	5 mol
	water	40 mol

Product stream

$$\text{ethylene} = \frac{52.26}{5.28} \times 5 = 49.49\ \text{mol}$$

$$\text{ethanol} = \frac{5.49}{5.28} \times 5 = 5.20\ \text{mol}$$

$$\text{ether} = \frac{0.16}{5.28} \times 5 = 0.15\ \text{mol}$$

$$\text{Amount of ethylene reacted} = 55.0 - 49.49 = 5.51\ \text{mol}$$

$$\text{Yield of ethanol based on ethylene} = \frac{5.2 \times 1}{5.51} \times 100 = \underline{\underline{94.4\ \text{per cent}}}$$

As 1 mol of ethanol is produced per mol of ethylene the stoichiometric factor is 1.

$$\text{Yield of ether based on ethylene} = \frac{0.15 \times 2}{5.51} \times 100 = \underline{\underline{5.44\ \text{per cent}}}$$

The stoichiometric factor is 2, as 2 mol of ethylene produce 1 mol of ether.

Note: the conversion of ethylene, to all products, is given by:

$$\text{Conversion} = \frac{\text{mols fed} - \text{mols out}}{\text{mols fed}} = \frac{55 - 49.49}{55} \times 100$$
$$= \underline{\underline{10\ \text{per cent}}}$$

The yield based on water could also be calculated but is of no real interest as water is relatively inexpensive compared with ethylene. Water is clearly fed to the reactor in considerable excess.

Example 2.12

In the chlorination of ethylene to produce dichloroethane (DCE), the conversion of ethylene is reported as 99.0 per cent. If 94 mol of DCE are produced per 100 mol of ethylene fed, calculate the overall yield and the reactor (reaction) yield based on ethylene. The unreacted ethylene is not recovered.

Solution

$$\text{Reaction: } C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Stoichiometric factor 1.

$$\text{Overall yield (including physical losses)} = \frac{\text{mols DCE produced} \times 1}{\text{mols ethylene fed}} \times 100$$

$$= \frac{94}{100} \times 100 = \underline{\underline{94 \text{ per cent}}}$$

$$\text{Chemical yield (reaction yield)} = \frac{\text{mols DCE produced}}{\text{mols ethylene converted}} \times 100$$

$$= \frac{94}{99} \times 100 = \underline{\underline{94.5 \text{ per cent}}}$$

The principal by-product of this process is trichloroethane.

2.14. RECYCLE PROCESSES

Processes in which a flow stream is returned (recycled) to an earlier stage in the processing sequence are frequently used. If the conversion of a valuable reagent in a reaction process is appreciably less than 100 per cent, the unreacted material is usually separated and recycled. The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

In mass balance calculations the presence of recycle streams makes the calculations more difficult.

Without recycle, the material balances on a series of processing steps can be carried out sequentially, taking each unit in turn; the calculated flows out of one unit become the feeds to the next. If a recycle stream is present, then at the point where the recycle is returned the flow will not be known as it will depend on downstream flows not yet calculated. Without knowing the recycle flow, the sequence of calculations cannot be continued to the point where the recycle flow can be determined.

Two approaches to the solution of recycle problems are possible:

1. The cut and try method. The recycle stream flows can be estimated and the calculations continued to the point where the recycle is calculated. The estimated flows are then compared with the calculated and a better estimate made. The procedure is continued until the difference between the estimated and the calculated flows is within acceptable limits.
2. The formal, algebraic, method. The presence of recycle implies that some of the mass balance equations will have to be solved simultaneously. The equations are set up with the recycle flows as unknowns and solved using standard methods for the solution of simultaneous equations.

With simple problems, with only one or two recycle loops, the calculation can often be simplified by the careful selection of the basis of calculation and the system boundaries. This is illustrated in Examples 2.4 and 2.13.

The solution of more complex material balance problems involving several recycle loops is discussed in Chapter 4.

Example 2.13

The block diagram shows the main steps in the balanced process for the production of vinyl chloride from ethylene. Each block represents a reactor and several other processing units. The main reactions are:

Block A, chlorination

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2, \text{ yield on ethylene 98 per cent}$$

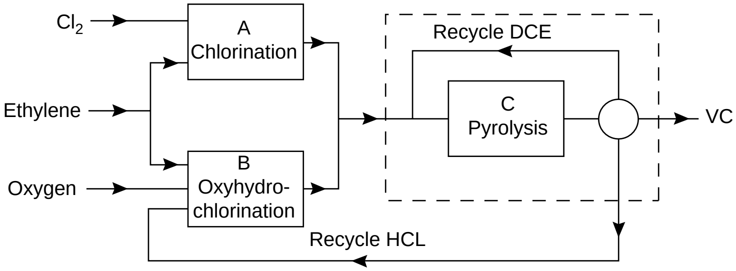
Block B, oxyhydrochlorination

$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O, \text{ yields: on ethylene 95 per cent, on HCl 90 per cent}$$

Block C, pyrolysis

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl, \text{ yields: on DCE 99 per cent, on HCl 99.5 per cent}$$

The HCl from the pyrolysis step is recycled to the oxyhydrochlorination step. The flow of ethylene to the chlorination and oxyhydrochlorination reactors is adjusted so that the production of HCl is in balance with the requirement. The conversion in the pyrolysis reactor is limited to 55 per cent, and the unreacted dichloroethane (DCE) separated and recycled.



Using the yield figures given, and neglecting any other losses, calculate the flow of ethylene to each reactor and the flow of DCE to the pyrolysis reactor, for a production rate of 12,500 kg/h vinyl chloride (VC).

Solution

Molecular weights: vinyl chloride 62.5, DCE 99.0, HCl 36.5.

$$\text{VC per hour} = \frac{12{,}500}{62.5} = 200 \text{ kmol/h}$$

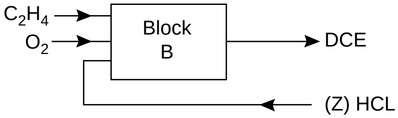
Draw a system boundary round each block, enclosing the DCE recycle within the boundary of step C.

Let flow of ethylene to block A be X and to block B be Y, and the HCl recycle be Z.

Then the total mols of DCE produced $= 0.98X + 0.95Y$, allowing for the yields, and the mols of HCl produced in block C

$$= (0.98X + 0.95Y)0.995 = Z \qquad (a)$$

Consider the flows to and product from block B



The yield of DCE based on HCl is 90 per cent, so the mols of DCE produced

$$= \frac{0.90Z}{2}$$

Note: the stoichiometric factor is 2 (2 mol HCl per mol DCE).

The yield of DCE based on ethylene is 95 per cent, so

$$\frac{0.9Z}{2} = 0.95Y$$

$$Z = \frac{0.95 \times 2Y}{0.9}$$

Substituting for Z into equation (a) gives

$$Y = (0.98X + 0.95Y)0.995 \times \frac{0.9}{2 \times 0.95}$$

$$Y = 0.837X \qquad (b)$$

Total VC produced $= 0.99 \times$ total DCE, so

$$0.99(0.98X + 0.95Y) = 200 \text{ kmol/h}$$

Substituting for Y from equation (b) gives $X = \underline{\underline{113.8 \text{ kmol/h}}}$

and $\qquad Y = 0.837 \times 113.8 = \underline{\underline{95.3 \text{ kmol/h}}}$

HCl recycle from equation (a)

$$Z = (0.98 \times 113.8 + 0.95 \times 95.3)0.995 = \underline{\underline{201.1 \text{ kmol/h}}}$$

Note: overall yield on ethylene $= \dfrac{200}{(113.8 + 95.3)} \times 100 = \underline{\underline{96 \text{ per cent}}}$

2.15. PURGE

It is usually necessary to bleed off a portion of a recycle stream to prevent the build-up of unwanted material. For example, if a reactor feed contains inert components that are not separated from the recycle stream in the separation units these inerts would accumulate in the recycle stream until the stream eventually consisted entirely of inerts. Some portion of the stream would have to be purged to keep the inert level within acceptable limits. A continuous purge would normally be used. Under steady-state conditions:

Loss of inert in the purge = Rate of feed of inerts into the system

The concentration of any component in the purge stream will be the same as that in the recycle stream at the point where the purge is taken off. So the required purge rate can be determined from the following relationship:

[Feed stream flow-rate] × [Feed stream inert concentration] =
[Purge stream flow-rate] × [Specified (desired) recycle inert concentration]

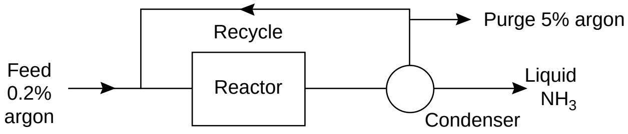
Example 2.14

In the production of ammonia from hydrogen and nitrogen the conversion, based on either raw material, is limited to 15 per cent. The ammonia produced is condensed from the reactor (converter) product stream and the unreacted material recycled. If the feed contains 0.2 per cent argon (from the nitrogen separation process), calculate the purge rate required to hold the argon in the recycle stream below 5.0 per cent. Percentages are by volume.

Solution

Basis: 100 mols feed (purge rate will be expressed as mols per 100 mol feed, as the production rate is not given).

Process diagram



Volume percentages are taken as equivalent to mol per cent.

Argon entering system with feed = 100 × 0.2/100 = 0.2 mol.

Let purge rate per 100 mol feed be F.

Argon leaving system in purge = $F \times 5/100 = 0.05F$.

At the steady state, argon leaving = argon entering

$$0.05F = 0.2$$

$$F = \frac{0.2}{0.05} = \underline{\underline{4}}$$

Purge required: 4 mol per 100 mol feed.

2.16. BY-PASS

A flow stream may be divided and some part diverted (by-passed) around some units. This procedure is often used to control stream composition or temperature.

Material balance calculations on processes with by-pass streams are similar to those involving recycle, except that the stream is fed forward instead of backward. This usually makes the calculations easier than with recycle.

2.17. UNSTEADY-STATE CALCULATIONS

All the previous material balance examples have been steady-state balances. The accumulation term was taken as zero, and the stream flow-rates and compositions did not vary with time. If these conditions are not met the calculations are more complex. Steady-state calculations are usually sufficient for the calculations of the process flow-sheet (Chapter 4). The unsteady-state behaviour of a process is important when considering the process start-up and shut-down, and the response to process upsets.

Batch processes are also examples of unsteady-state operation; though the total material requirements can be calculated by taking one batch as the basis for the calculation.

The procedure for the solution of unsteady-state balances is to set up balances over a small increment of time, which will give a series of differential equations describing the process. For simple problems these equations can be solved analytically. For more complex problems computer methods would be used.

The general approach to the solution of unsteady-state problems is illustrated in Example 2.15. Batch distillation is a further example of an unsteady-state material balance (see Volume 2, Chapter 11).

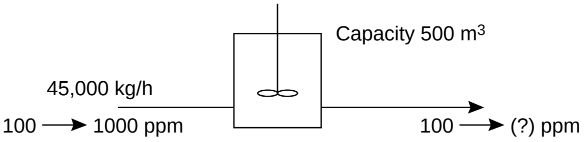
The behaviour of processes under non-steady-state conditions is a complex and specialised subject and beyond the scope of this book. It can be important in process design when assessing the behaviour of a process from the point of view of safety and control.

The use of material balances in the modelling of complex unsteady-state processes is discussed in the books by Myers and Seider (1976) and Henley and Rosen (1969).

Example 2.15

A hold tank is installed in an aqueous effluent-treatment process to smooth out fluctuations in concentration in the effluent stream. The effluent feed to the tank normally contains no more than 100 ppm of acetone. The maximum allowable concentration of acetone in the effluent discharge is set at 200 ppm. The surge tank working capacity is 500 m^3 and it can be considered to be perfectly mixed. The effluent flow is 45,000 kg/h. If the acetone concentration in the feed suddenly rises to 1000 ppm, due to a spill in the process plant, and stays at that level for half an hour, will the limit of 200 ppm in the effluent discharge be exceeded?

Solution



Basis: increment of time Δt.

To illustrate the general solution to this type of problem, the balance will be set up in terms of symbols for all the quantities and then actual values for this example substituted.

Let, Material in the tank $= M$,
Flow-rate $= F$,
Initial concentration in the tank $= C_0$,
Concentration at time t after the feed concentration is increased $= C$,
Concentration in the effluent feed $= C_1$,
Change in concentration over time increment $\Delta t = \Delta C$,
Average concentration in the tank during the time increment $= C_{av}$.

Then, as there is no generation in the system, the general material balance (Section 2.3) becomes:

$$\text{Input} - \text{Output} = \text{Accumulation}$$

Material balance on acetone.

Note: as the tank is considered to be perfectly mixed the outlet concentration will be the same as the concentration in the tank.

$$\text{Acetone in} - \text{Acetone out} = \text{Acetone accumulated in the tank}$$

$$FC_1\Delta t - FC_{av}\Delta t = M(C + \Delta C) - MC$$

$$F(C_1 - C_{av}) = M\frac{\Delta C}{\Delta t}$$

Taking the limit, as $\Delta t \to 0$

$$\frac{\Delta C}{\Delta t} = \frac{dC}{dt}, \quad C_{av} = C$$

$$F(C_1 - C) = M\frac{dC}{dt}$$

Integrating

$$\int_0^t dt = \frac{M}{F}\int_{C_0}^{C}\frac{dC}{(C_1 - C)}$$

$$t = -\frac{M}{F}\ln\left[\frac{C_1 - C}{C_1 - C_0}\right]$$

Substituting the values for the example, noting that the maximum outlet concentration will occur at the end of the half-hour period of high inlet concentration.

$t = 0.5$ h
$C_1 = 1000$ ppm
$C_0 = 100$ ppm (normal value)
$M = 500\ \text{m}^3 = 500{,}000$ kg
$F = 45{,}000$ kg/h

$$0.5 = -\frac{500{,}000}{45{,}000}\ln\left[\frac{1000 - C}{1000 - 100}\right]$$

$$0.045 = -\ln\left[\frac{1000 - C}{900}\right]$$

$$e^{-0.045} \times 900 = 1000 - C$$

$$C = \underline{\underline{140\text{ ppm}}}$$

So the maximum allowable concentration will not be exceeded.

2.18. GENERAL PROCEDURE FOR MATERIAL-BALANCE PROBLEMS

The best way to tackle a problem will depend on the information given; the information required from the balance; and the constraints that arise from the nature of the problem. No all embracing, best method of solution can be given to cover all possible problems. The following step-by-step procedure is given as an aid to the efficient solution of material balance problems. The same general approach can be usefully employed to organise the solution of energy balance, and other design problems.

Procedure

Step 1. Draw a block diagram of the process.
Show each significant step as a block, linked by lines and arrows to show the stream connections and flow direction.

Step 2. List all the available data.
Show on the block diagram the known flows (or quantities) and stream compositions.

Step 3. List all the information required from the balance.

Step 4. Decide the system boundaries (see Section 2.6).

Step 5. Write out all the chemical reactions involved for the main products and by-products.

Step 6. Note any other constraints,
such as: specified stream compositions,
azeotropes,
phase equilibria,
tie substances (see Section 2.11).

The use of phase equilibrium relationships and other constraints in determining stream compositions and flows is discussed in more detail in Chapter 4.

Step 7. Note any stream compositions and flows that can be approximated.

Step 8. Check the number of conservation (and other) equations that can be written, and compare with the number of unknowns. Decide which variables are to be design variables; see Section 2.10.
This step would be used only for complex problems.

Step 9. Decide the basis of the calculation; see Section 2.7.

The order in which the steps are taken may be varied to suit the problem.

2.19. REFERENCES (FURTHER READING)

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HENLEY, E. J. and ROSEN, E. M. (1969) *Material and Energy Balance Computations* (Wiley).
MYERS, A. L. and SEIDER, W. D. (1976) *Introduction to Chemical Engineering and Computer Calculations* (Prentice-Hall).

2.20. NOMENCLATURE

		Dimensions in **MLT**
C	Concentration after time t, Example 2.15	—
C_{av}	Average concentration, Example 2.15	—
C_0	Initial concentration, Example 2.15	—
C_1	Concentration in feed to tank, Example 2.15	—
ΔC	Incremental change in concentration, Example 2.15	—
F	Flow-rate	$\mathbf{MT}^{-1}$
F_n	Total flow in stream n	$\mathbf{MT}^{-1}$
F_1	Water feed to reactor, Example 2.4	$\mathbf{MT}^{-1}$
M	Quantity in hold tank, Example 2.15	**M**
N_c	Number of independent components	—
N_d	Number of variables to be specified	—
N_e	Number of independent balance equations	—
N_s	Number of streams	—
N_v	Number of variables	—
t	Time, Example 2.15	**T**
Δt	Incremental change in time, Example 2.15	**T**
X	Unknown flow, Examples 2.8, 2.10, 2.13	$\mathbf{MT}^{-1}$
$x_{n,m}$	Concentration of component m in stream n	—
Y	Unknown flow, Examples 2.8, 2.13	$\mathbf{MT}^{-1}$
Z	Unknown flow, Example 2.13	$\mathbf{MT}^{-1}$

2.21. PROBLEMS

2.1. The composition of a gas derived by the gasification of coal is, volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, benzene 2, balance nitrogen. If the gas is burnt in a furnace with 20 per cent excess air, calculate:

(a) the amount of air required per 100 kmol of gas,
(b) The amount of flue gas produced per 100 kmol of gas,

(c) the composition of the flue gases, on a dry basis.

Assume complete combustion.

2.2. Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20 °C. The air contains 5.0 per cent v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia air mixture to the column is 200 m^3/s and the stream leaving the column contains 0.05 per cent v/v ammonia, calculate:

(a) The flow-rate of gas leaving the column.
(b) The mass of ammonia absorbed.
(c) The flow-rate of water to the column, if the exit water contains 1% w/w ammonia.

2.3. The off-gases from a gasoline stabiliser are fed to a reforming plant to produce hydrogen.
The composition of the off-gas, molar per cent, is: CH_4 77.5, C_2H_6 9.5, C_3H_8 8.5, C_4H_{10} 4.5.
The gases entering the reformer are at a pressure of 2 bara and 35 °C and the feed rate is 2000 m^3/h.
The reactions in the reformer are:

1. $C_2H_{2n+2} + n(H_2O) \rightarrow n(CO) + (2_n + 1)H_2$
2. $CO + H_2O \rightarrow CO_2 + H_2$

The molar conversion of C_2H_{2n+2} in reaction (1) is 96 per cent and of CO in reaction (2) 92 per cent.
Calculate:

(a) the average molecular mass of the off-gas,
(b) the mass of gas fed to the reformer, kg/h,
(c) the mass of hydrogen produced, kg/h.

2.4. Allyl alcohol can be produced by the hydrolysis of allyl chloride. Together with the main product, allyl alcohol, di-ally ether is produced as a by-product. The conversion of allyl chloride is typically 97 per cent and the yield to alcohol 90 per cent, both on a molar basis. Assuming that there are no other significant side reactions, calculate masses of alcohol and ether produced, per 1000 kg of allyl chloride fed to the reactor.

2.5. Aniline is produced by the hydrogenation of nitrobenzene. A small amount of cyclo-hexylamine is produced as a by-product. The reactions are:

1. $C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$
2. $C_6H_5NO_2 + 6H_2 \rightarrow C_6H_{11}NH_2 + 2H_2O$

Nitrobenzene is fed to the reactor as a vapour, with three times the stoichiometric quantity of hydrogen. The conversion of the nitrobenzene, to all products, is 96 per cent, and the yield to aniline 95 per cent.
The unreacted hydrogen is separated from the reactor products and recycled to the reactor. A purge is taken from the recycle stream to maintain the inerts in the

recycle stream below 5 per cent. The fresh hydrogen feed is 99.5 per cent pure, the remainder being inerts. All percentages are molar.

For a feed rate of 100 kmol/h of nitrobenzene, calculate:

(a) the fresh hydrogen feed,
(b) the purge rate required,
(c) the composition of the reactor outlet stream.

2.6. In the manufacture of aniline by the hydrogenation of nitrobenzene, the off-gases from the reactor are cooled and the products and unreacted nitrobenzene condensed. The hydrogen and inerts, containing only traces of the condensed materials, are recycled.

Using the typical composition of the reactor off-gas given below, estimate the stream compositions leaving the condenser.

Composition, kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, hydrogen 5640, nitrobenzene 40, inerts 300.

2.7. In the manufacture of aniline, the condensed reactor products are separated in a decanter. The decanter separates the feed into an organic phase and an aqueous phase. Most of the aniline in the feed is contained in the organic phase and most of the water in the aqueous phase. Using the data given below, calculate the stream compositions.

Data:

Typical feed composition, including impurities and by-products, weight per cent: water 23.8, aniline 72.2, nitrobenzene 3.2, cyclo-hexylamine 0.8.

Density of aqueous layer 0.995, density of organic layer 1.006. Therefore, the organic layer will be at the bottom.

Solubility of aniline in water 3.2 per cent w/w, and water in aniline 5.15 per cent w/w.

Partition coefficient of nitrobenzene between the aqueous and organic phases: $C_{\text{organic}}/C_{\text{water}} = 300$

Solubility of cyclo-hexylamine in the water phase 0.12 per cent w/w and in the organic phase 1.0 per cent w/w.

2.8. In the manufacture of aniline from nitrobenzene the reactor products are condensed and separated into an aqueous and organic phases in a decanter. The organic phase is fed to a striping column to recover the aniline. Aniline and water form an azeotrope, composition 0.96 mol fraction aniline. For the feed composition given below, make a mass balance round the column and determine the stream compositions and flow-rates. Take as the basis for the balance 100 kg/h feed and a 99.9 percentage recovery of the aniline in the overhead product. Assume that the nitrobenzene leaves with the water stream from the base of the column.

Feed composition, weight percentage: water 2.4, aniline 73.0, nitrobenzene 3.2, cyclo-hexylamine trace.

Note: Problems 2.5 to 2.8 can be taken together as an exercise in the calculation of a preliminary material balance for the manufacture of aniline by the process described in detail in Appendix F, Problem F.8.

CHAPTER 3

Fundamentals of Energy Balances (and Energy Utilisation)

3.1. INTRODUCTION

As with mass, energy can be considered to be separately conserved in all but nuclear processes.

The conservation of energy, however, differs from that of mass in that energy can be generated (or consumed) in a chemical process. Material can change form, new molecular species can be formed by chemical reaction, but the total mass flow into a process unit must be equal to the flow out at the steady state. The same is not true of energy. The total enthalpy of the outlet streams will not equal that of the inlet streams if energy is generated or consumed in the processes; such as that due to heat of reaction.

Energy can exist in several forms: heat, mechanical energy, electrical energy, and it is the total energy that is conserved.

In process design, energy balances are made to determine the energy requirements of the process: the heating, cooling and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy usage, and suggest areas for conservation and savings.

In this chapter the fundamentals of energy balances are reviewed briefly, and examples given to illustrate the use of energy balances in process design. The methods used for energy recovery and conservation are also discussed.

More detailed accounts of the principles and applications of energy balances are given in the texts covering material and energy balance calculations which are cited at the end of Chapter 2.

3.2. CONSERVATION OF ENERGY

As for material (Section 2.3), a general equation can be written for the conservation of energy:

$$\text{Energy out} = \text{Energy in} + \text{generation} - \text{consumption} - \text{accumulation}$$

This is a statement of the first law of thermodynamics.

An energy balance can be written for any process step.

Chemical reaction will evolve energy (exothermic) or consume energy (endothermic).

For steady-state processes the accumulation of both mass and energy will be zero.

Energy can exist in many forms and this, to some extent, makes an energy balance more complex than a material balance.

3.3. FORMS OF ENERGY (PER UNIT MASS OF MATERIAL)

3.3.1. Potential energy

Energy due to position:

$$\text{Potential energy} = gz \tag{3.1}$$

where z = height above some arbitrary datum, m,
g = gravitational acceleration (9.81 m/s^2).

3.3.2. Kinetic energy

Energy due to motion:

$$\text{Kinetic energy} = \frac{u^2}{2} \tag{3.2}$$

where u = velocity, m/s.

3.3.3. Internal energy

The energy associated with molecular motion. The temperature T of a material is a measure of its internal energy U:

$$U = \mathrm{f}(T) \tag{3.3}$$

3.3.4. Work

Work is done when a force acts through a distance:

$$W = \int_0^1 F\,\mathrm{d}x \tag{3.4}$$

where F = force, N,
x and l = distance, m.

Work done on a system by its surroundings is conventionally taken as negative; work done by the system on the surroundings as positive.

Where the work arises from a change in pressure or volume:

$$W = \int_1^2 P\,\mathrm{d}v \tag{3.5}$$

where P = pressure, Pa (N/m^2),
v = volume per unit mass, m^3/kg.

To integrate this function the relationship between pressure and volume must be known. In process design an estimate of the work done in compressing or expanding a gas is often required. A rough estimate can be made by assuming either reversible adiabatic (isentropic) or isothermal expansion, depending on the nature of the process.

For isothermal expansion (expansion at constant temperature):

$$Pv = \text{constant}$$

For reversible adiabatic expansion (no heat exchange with the surroundings):

$$Pv^{\gamma} = \text{constant}$$

where γ = ratio of the specific heats, C_p/C_v.

The compression and expansion of gases is covered more fully in Section 3.13.

3.3.5. Heat

Energy is transferred either as heat or work. A system does not contain "heat", but the transfer of heat or work to a system changes its internal energy.

Heat taken in by a system from its surroundings is conventionally taken as positive and that given out as negative.

3.3.6. Electrical energy

Electrical, and the mechanical forms of energy, are included in the work term in an energy balance. Electrical energy will only be significant in energy balances on electrochemical processes.

3.4. THE ENERGY BALANCE

Consider a steady-state process represented by Figure 3.1. The conservation equation can be written to include the various forms of energy.

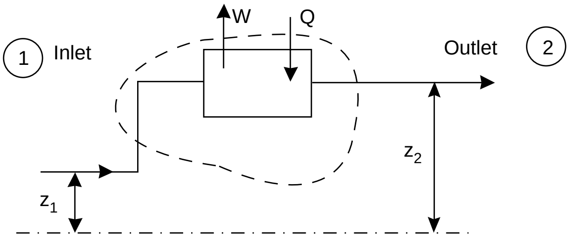


Figure 3.1. General steady-state process

For unit mass of material:

$$U_1 + P_1v_1 + u_1^2/2 + z_1g + Q = U_2 + P_2v_2 + u_2^2/2 + z_2g + W \tag{3.6}$$

The suffixes 1 and 2 represent the inlet and outlet points respectively. Q is the heat transferred across the system boundary; positive for heat entering the system, negative for heat leaving the system. W is the work done by the system; positive for work going from the system to the surroundings, and negative for work entering the system from the surroundings.

Equation 3.6 is a general equation for steady-state systems with flow.

In chemical processes, the kinetic and potential energy terms are usually small compared with the heat and work terms, and can normally be neglected.

It is convenient, and useful, to take the terms U and Pv together; defining the term enthalpy, usual symbol H, as:

$$H = U + Pv$$

Enthalpy is a function of temperature and pressure. Values for the more common substances have been determined experimentally and are given in the various handbooks (see Chapter 8).

Enthalpy can be calculated from specific and latent heat data; see Section 3.5.

If the kinetic and potential energy terms are neglected equation 3.6 simplifies to:

$$H_2 - H_1 = Q - W \tag{3.7}$$

This simplified equation is usually sufficient for estimating the heating and cooling requirements of the various unit operations involved in chemical processes.

As the flow-dependent terms have been dropped, the simplified equation is applicable to both static (non-flow) systems and flow systems. It can be used to estimate the energy requirement for batch processes.

For many processes the work term will be zero, or negligibly small, and equation 3.7 reduces to the simple heat balance equation:

$$Q = H_2 - H_1 \tag{3.8}$$

Where heat is generated in the system; for example, in a chemical reactor:

$$Q = Q_p + Q_s \tag{3.9}$$

Q_s = heat generated in the system. If heat is evolved (exothermic processes) Q_s is taken as *positive*, and if heat is absorbed (endothermic processes) it is taken as *negative*.
Q_p = process heat added to the system to maintain required system temperature.

Hence:

$$Q_p = H_2 - H_1 - Q_s \tag{3.10}$$

H_1 = enthalpy of the inlet stream,
H_2 = enthalpy of the outlet stream.

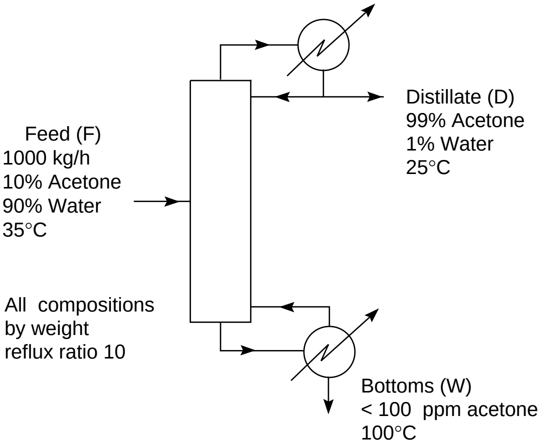
Example 3.1

Balance with no chemical reaction. Estimate the steam and the cooling water required for the distillation column shown in the figure.

Steam is available at 25 psig (274 kN/m^2 abs), dry saturated.

The rise in cooling water temperature is limited to 30°C.

Column operates at 1 bar.



Solution

Material balance

It is necessary to make a material balance to determine the top and bottoms product flow rates.

Balance on acetone, acetone loss in bottoms neglected.

$$1000 \times 0.1 = D \times 0.99$$

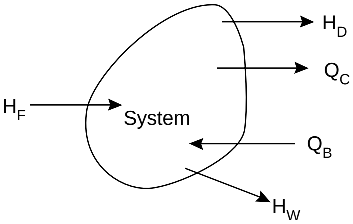
$$\text{Distillate, } D = 101 \text{ kg/h}$$

$$\text{Bottoms, } W = 1000 - 101 = 899 \text{ kg/h}$$

Energy balance

The kinetic and potential energy of the process streams will be small and can be neglected.

Take the first system boundary to include the reboiler and condenser.



Inputs: reboiler heat input Q_B + feed sensible heat H_F.

Outputs: condenser cooling Q_C + top and bottom product sensible heats $H_D + H_W$.

The heat losses from the system will be small if the column and exchangers are properly lagged (typically less than 5 per cent) and will be neglected.

Basis 25°C, 1h.

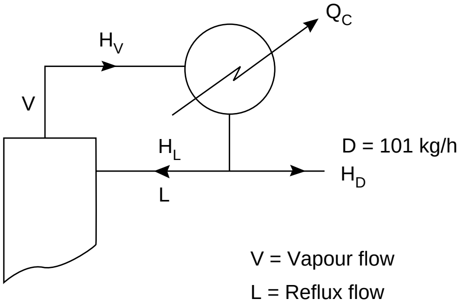
Heat capacity data, from Volume 1, average values.

Acetone:	25°C to 35°C	2.2 kJ/kg K
Water:	25°C to 100°C	4.2 kJ/kg K

Heat capacities can be taken as additive.

Feed, 10 per cent acetone $= 0.1 \times 2.2 + 0.9 \times 4.2 = 4.00$ kJ/kg K
Tops, 99 per cent acetone, taken as acetone, 2.2 kJ/kg K
Bottoms, as water, 4.2 kJ/kg K.

Q_C must be determined by taking a balance round the condenser.



V = Vapour flow
L = Reflux flow
H = Enthalpy

Reflux ratio (see Chapter 11)

$$R = \frac{L}{D} = 10$$

$$L = 10 \times 101 = 1010 \text{ kg/h}$$

$$V = L + D = 1111 \text{ kg/h}$$

From vapour–liquid equilibrium data:

boiling point of 99 per cent acetone/water = 56.5°C

At steady state:

$$\text{input} = \text{output}$$

$$H_V = H_D + H_L + Q_C,$$

Hence $$Q_C = H_V - H_D - H_L$$

Assume complete condensation.

Enthalpy of vapour H_V = latent + sensible heat.

There are two ways of calculating the specific enthalpy of the vapour at its boiling point.

(1) Latent heat of vaporisation at the base temperature + sensible heat to heat the vapour to the boiling point.
(2) Latent heat of vaporisation at the boiling point + sensible heat to raise liquid to the boiling point.

Values of the latent heat of acetone and water as functions of temperature are given in Volume 1, so the second method will be used.

$$\text{Latent heat acetone at } 56.5^\circ\text{C (330 K)} = 620 \text{ kJ/kg}$$

$$\text{Water at } 56.5^\circ\text{C (330 K)} = 2500 \text{ kJ/kg}$$

Taking latent heats as additive:

$$\begin{aligned} H_V &= 1111[(0.01 \times 2500 + 0.99 \times 620) + (56.5 - 25)2.2] \\ &= 786{,}699 \text{ kJ/h} \end{aligned}$$

The enthalpy of the top product and reflux are zero, as they are both at the base temperature. Both are liquid, and the reflux will be at the same temperature as the product.

Hence $$Q_C = H_V = \underline{\underline{786{,}699 \text{ kJ/h}}} \quad (218.5 \text{ kW})$$

Q_B is determined from a balance over complete system

$$\begin{gathered} \text{Input} \qquad\qquad \text{Output} \\ Q_B + H_F = Q_C + H_D + H_W \end{gathered}$$

$$\begin{aligned} H_F &= 1000 \times 4.00(35 - 25) = 40{,}000 \text{ kJ/h} \\ H_W &= 899 \times 4.2(100 - 25) = 283{,}185 \text{ kJ/h} \end{aligned}$$

(boiling point of bottom product taken as 100°C).

hence $$\begin{aligned} Q_B &= Q_C + H_W + H_D - H_F \\ &= 786{,}699 + 283{,}185 + 0 - 40{,}000 \\ &= \underline{\underline{1{,}029{,}884 \text{ kJ/h}}} \quad (286.1 \text{ kW}) \end{aligned}$$

Q_B is supplied by condensing steam.

$$\text{Latent heat of steam (Volume 1)} = 2174 \text{ kJ/kg at } 274 \text{ kN/m}^2$$

$$\text{Steam required} = \frac{1{,}029{,}884}{2174} = \underline{\underline{473.7 \text{ kg/h}}}$$

Q_C is removed by cooling water with a temperature rise of 30°C

$$Q_C = \text{water flow} \times 30 \times 4.2$$

$$\text{Water flow} = \frac{786{,}699}{4.2 \times 30} = \underline{\underline{6244 \text{ kg/h}}}$$

3.5. CALCULATION OF SPECIFIC ENTHALPY

Tabulated values of enthalpy are available only for the more common materials. In the absence of published data the following expressions can be used to estimate the specific enthalpy (enthalpy per unit mass).

For pure materials, with no phase change:

$$H_T = \int_{T_d}^{T} C_p \, \mathrm{d}T \tag{3.11}$$

where H_T = specific enthalpy at temperature T,
C_p = specific heat capacity of the material, constant pressure,
T_d = the datum temperature.

If a phase transition takes place between the specified and datum temperatures, the latent heat of the phase transition is added to the sensible-heat change calculated by equation 3.11. The sensible-heat calculation is then split into two parts:

$$H_T = \int_{T_d}^{T_p} C_{p1} \, \mathrm{d}T + \int_{T_p}^{T} C_{p2} \, \mathrm{d}T \tag{3.12}$$

where T_p = phase transition temperature,
C_{p1} = specific heat capacity first phase, below T_p,
C_{p2} = specific heat capacity second phase, above T_p.

The specific heat at constant pressure will vary with temperature and to use equations 3.11 and 3.12, values of C_p must be available as a function of temperature. For solids and gases C_p is usually expressed as an empirical power series equation:

$$C_p = a + bT + cT^2 + \mathrm{d}T^3 \tag{3.13a}$$

or

$$C_p = a + bT + cT^{-1/2} \tag{3.13b}$$

Absolute (K) or relative (°C) temperature scales may be specified when the relationship is in the form given in equation 3.13*a*. For equation 3.13*b* absolute temperatures must be used.

Example 3.2

Estimate the specific enthalpy of ethyl alcohol at 1 bar and 200°C, taking the datum temperature as 0°C.

C_p liquid 0°C 24.65 cal/mol°C
100°C 37.96 cal/mol°C

C_p gas (t°C) $14.66 + 3.758 \times 10^{-2}t - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3$ cal/mol

Boiling point of ethyl alcohol at 1 bar = 78.4°C.
Latent heat of vaporisation = 9.22 kcal/mol.

Solution

Note: as the data taken from the literature are given in cal/mol the calculation is carried out in these units and the result converted to SI units.

As no data are given on the exact variation of the C_p of the liquid with temperature, use an equation of the form $C_p = a + bt$, calculating a and b from the data given; this will be accurate enough over the range of temperature needed.

$$a = \text{value of } C_p \text{ at } 0^\circ\text{C}, \quad b = \frac{37.96 - 24.65}{100} = 0.133$$

$$\begin{aligned} H_{200^\circ\text{C}} &= \int_0^{78.4} (24.65 + 0.133t)\,\mathrm{d}t + 9.22 \times 10^3 + \int_{78.4}^{200} (14.66 + 3.758 \times 10^{-2}t \\ &\qquad - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3)\,\mathrm{d}t \\ &= \overset{78.4}{\underset{0}{[}} 24.65t + 0.133t^2/2] + 9.22 \times 10^3 + \overset{200}{\underset{78.4}{[}} 14.66t + 3.758 \times 10^{-2}t^2/2 - 2.091 \\ &\qquad \times 10^{-5}t^3/3 + 4.740 \times 10^{-9}t^4/4] \\ &= 13.95 \times 10^3 \text{ cal/mol} \\ &= 13.95 \times 10^3 \times 4.18 = \underline{\underline{58.31 \times 10^3 \text{ J/mol}}} \end{aligned}$$

Specific enthalpy = $\underline{\underline{58.31 \text{ kJ/mol}}}$.

Molecular weight of ethyl alcohol, $C_2H_5OH = 46$
Specific enthalpy = $58.31 \times 10^3/46 = \underline{\underline{1268 \text{ kJ/kg}}}$

3.6. MEAN HEAT CAPACITIES

The use of mean heat capacities often facilitates the calculation of sensible-heat changes; mean heat capacity over the temperature range t_1 to t_2 is defined by the following equation:

$$C_{pm} = \int_{t_1}^{t_2} C_p\,\mathrm{d}t \div \int_{t_1}^{t_2} \mathrm{d}t \tag{3.14}$$

Mean specific heat values are tabulated in various handbooks. If the values are for unit mass, calculated from some standard reference temperature, t_r, then the change in enthalpy between temperatures t_1 and t_2 is given by:

$$\Delta H = C_{pm,t_2}(t_2 - t_r) - C_{pm,t_1}(t_1 - t_r) \tag{3.15}$$

where t_r is the reference temperature from which the values of C_{pm} were calculated.

If C_p is expressed as a polynomial of the form: $C_p = a + bt + ct^2 + dt^3$, then the integrated form of equation 3.14 will be:

$$C_{pm} = \frac{a(t - t_r) + \dfrac{b}{2}(t^2 - t_r^2) + \dfrac{c}{3}(t^3 - t_r^3) + \dfrac{d}{4}(t^4 - t_r^4)}{t - t_r} \tag{3.16}$$

where t is the temperature at which C_{pm} is required.

If the reference temperature is taken at 0°C, equation 3.16 reduces to:

$$C_{p_m} = a + \frac{bt}{2} + \frac{ct^2}{3} + \frac{dt^3}{4} \tag{3.17}$$

and the enthalpy change from t_1 to t_2 becomes

$$\Delta H = C_{p_{m,t_2}} t_2 - C_{p_{m,t_1}} t_1 \tag{3.18}$$

The use of mean heat capacities is illustrated in Example 3.3.

Example 3.3

The gas leaving a combustion chamber has the following composition: CO_2 7.8, CO 0.6, O_2 3.4, H_2O 15.6, N_2 72.6, all volume percentage. Calculate the heat removed if the gas is cooled from 800 to 200°C.

Solution

Mean heat capacities for the combustion gases are readily available in handbooks and texts on heat and material balances. The following values are taken from K. A. Kobe, *Thermochemistry of Petrochemicals*, reprint No. 44, Pet. Ref. 1958; converted to SI units, J/mol°C, reference temperature 0°C.

°C	N_2	O_2	CO_2	CO	H_2O
200	29.24	29.95	40.15	29.52	34.12
800	30.77	32.52	47.94	31.10	37.38

Heat extracted from the gas in cooling from 800 to 200°C, for each component:

$$= M_c(C_{p_{m,800}} \times 800 - C_{p_{m,200}} \times 200)$$

where M_c = mols of that component.

Basis 100 mol gas (as analysis is by volume), substitution gives:

$$\begin{array}{lrl}
CO_2 & 7.8(47.94 \times 800 - 40.15 \times 200) = & 236.51 \times 10^3 \\
CO & 0.6(31.10 \times 800 - 29.52 \times 200) = & 11.39 \times 10^3 \\
O_2 & 3.4(32.52 \times 800 - 29.95 \times 200) = & 68.09 \times 10^3 \\
H_2O & 15.6(37.38 \times 800 - 34.12 \times 200) = & 360.05 \times 10^3 \\
N_2 & 72.6(30.77 \times 800 - 29.24 \times 200) = & \underline{1362.56 \times 10^3} \\
 & = & \underline{\underline{2038.60 \text{ kJ/100 mol}}} \\
 & = & \underline{\underline{20.39 \text{ kJ/mol}}}
\end{array}$$

3.7. THE EFFECT OF PRESSURE ON HEAT CAPACITY

The data on heat capacities given in the handbooks, and in Appendix A, are, usually for the ideal gas state. Equation 3.13*a* should be written as:

$$C_p^\circ = a + bT + cT^2 + dT^3 \tag{3.19}$$

where the superscript ° refers to the ideal gas state.

The ideal gas values can be used for the real gases at low pressures. At high pressures the effect of pressure on the specific heat may be appreciable.

Edmister (1948) published a generalised plot showing the isothermal pressure correction for real gases as a function of the reduced pressure and temperature. His chart, converted

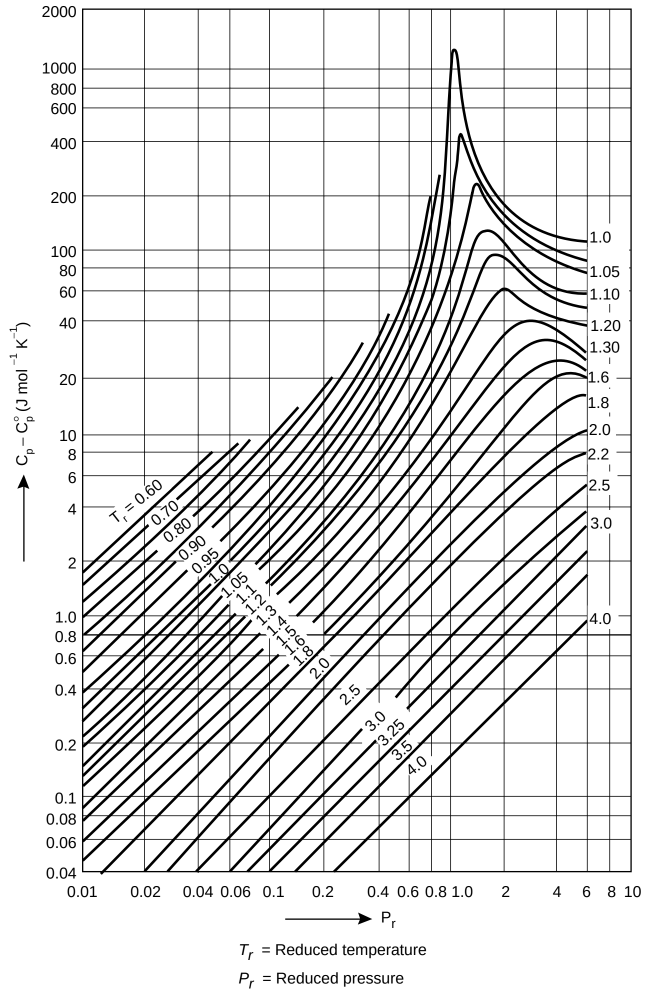


Figure 3.2. Excess heat capacity chart (reproduced from Sterbacek *et al*. (1979), with permission)

to SI units, is shown as Figure 3.2. Edmister's chart was based on hydrocarbons, but can be used for other materials to give an indication of the likely error if the ideal gas specific heat values are used without corrections.

The method is illustrated in Example 3.4.

Example 3.4

The ideal state heat capacity of ethylene is given by the equation:

$$C_p^\circ = 3.95 + 15.6 \times 10^{-2}T - 8.3 \times 10^{-5}T^2 + 17.6 \times 10^{-9}T^3 \text{ J/mol K}$$

Estimate the value at 10 bar and 300 K.

Solution

Ethylene: critical pressure 50.5 bar
critical temperature 283 K

$$C_p^\circ = 3.95 + 15.6 \times 10^{-2} \times 300 - 8.3 \times 10^{-5} \times 300^2 + 17.6 \times 10^{-9} \times 300^3$$

$$= \underline{\underline{43.76 \text{ J/mol K}}}$$

$$P_r = \frac{10}{50.5} = \underline{\underline{0.20}}$$

$$T_r = \frac{300}{283} = \underline{\underline{1.06}}$$

From Figure 3.2:

$$C_p - C_p^\circ \simeq \underline{\underline{5 \text{ J/mol K}}}$$

So

$$C_p = 43.76 + 5 = \underline{\underline{\approx 49 \text{ J/mol K}}}$$

The error in C_p if the ideal gas value were used uncorrected would be approximately 10 per cent.

3.8. ENTHALPY OF MIXTURES

For gases, the heats of mixing are usually negligible and the heat capacities and enthalpies can be taken as additive without introducing any significant error into design calculations; as was done in Example 3.3.

$$C_p(\text{mixture}) = x_a C_{p_a} + x_b C_{p_b} + x_c C_{p_c} + \cdots . \tag{3.20}$$

where x_a, x_b, x_c, etc., are the mol fractions of the components a, b, c.

For mixtures of liquids and for solutions, the heat of mixing (heat of solution) may be significant, and so must be included when calculating the enthalpy of the mixture.

For binary mixtures, the specific enthalpy of the mixture at temperature t is given by:

$$H_{\text{mixture},t} = x_a H_{a,t} + x_b H_{b,t} + \Delta H_{m,t} \tag{3.21}$$

where $H_{a,t}$ and $H_{b,t}$ are the specific enthalpies of the components a and b and $-\Delta H_{m,t}$ is the heat of mixing when 1 mol of solution is formed, at temperature t.

Heats of mixing and heats of solution are determined experimentally and are available in the handbooks for the more commonly used solutions.

If no values are available, judgement must be used to decide if the heat of mixing for the system is likely to be significant.

For organic solutions the heat of mixing is usually small compared with the other heat quantities, and can usually be neglected when carrying out a heat balance to determine the process heating or cooling requirements.

The heats of solution of organic and inorganic compounds in water can be large, particularly for the strong mineral acids and alkalies.

3.8.1. Integral heats of solution

Heats of solution are dependent on concentration. The integral heat of solution at any given concentration is the cumulative heat released, or absorbed, in preparing the solution from pure solvent and solute. The integral heat of solution at infinite dilution is called the *standard integral heat of solution*.

Tables of the integral heat of solution over a range of concentration, and plots of the integral heat of solution as a function of concentration, are given in the handbooks for many of the materials for which the heat of solution is likely to be significant in process design calculations.

The integral heat of solution can be used to calculate the heating or cooling required in the preparation of solutions, as illustrated in Example 3.5.

Example 3.5

A solution of NaOH in water is prepared by diluting a concentrated solution in an agitated, jacketed, vessel. The strength of the concentrated solution is 50 per cent w/w and 2500 kg of 5 per cent w/w solution is required per batch. Calculate the heat removed by the cooling water if the solution is to be discharged at a temperature of 25°C. The temperature of the solutions fed to the vessel can be taken to be 25°C.

Solution

Integral heat of solution of $NaOH - H_2O$, at 25°C

mols H_2O/mol NaOH	$-\Delta H^{\circ}_{\text{soln}}$ kJ/mol NaOH
2	22.9
4	34.4
5	37.7
10	42.5
infinite	42.9

Conversion of weight per cent to mol/mol:

$$50 \text{ per cent w/w} = 50/18 \div 50/40 = 2.22 \text{ mol } H_2O\text{/mol NaOH}$$

$$5 \text{ per cent w/w} = 95/18 \div 5/40 = 42.2 \text{ mol } H_2O\text{/mol NaOH}$$

From a plot of the integral heats of solution versus concentration,

$$-\Delta H^{\circ}_{\text{soln}}\ 2.22\ \text{mol/mol} = 27.0\ \text{kJ/mol NaOH}$$

$$42.2\ \text{mol/mol} = 42.9\ \text{kJ/mol NaOH}$$

Heat liberated in the dilution per mol NaOH

$$= 42.9 - 27.0 = \underline{\underline{15.9\ \text{kJ}}}$$

Heat released per batch = mol NaOH per batch × 15.9

$$= \frac{2500 \times 10^3 \times 0.05}{40} \times 15.9 = \underline{\underline{49.7 \times 10^3\ \text{kJ}}}$$

Heat transferred to cooling water, neglecting heat losses,

$$\underline{\underline{49.7\ \text{MJ per batch}}}$$

In Example 3.5 the temperature of the feeds and final solution have been taken as the same as the standard temperature for the heat of solution, 25°C, to simplify the calculation. Heats of solution are analogous to heats of reaction, and examples of heat balances on processes where the temperatures are different from the standard temperature are given in the discussion of heats of reaction, Section 3.10.

3.9. ENTHALPY-CONCENTRATION DIAGRAMS

The variation of enthalpy for binary mixtures is conveniently represented on a diagram. An example is shown in Figure 3.3. The diagram shows the enthalpy of mixtures of ammonia and water versus concentration; with pressure and temperature as parameters. It covers the phase changes from solid to liquid to vapour, and the enthalpy values given include the latent heats for the phase transitions.

The enthalpy is per kg of the mixture (ammonia + water)
Reference states: enthalpy ammonia at −77°C = zero
enthalpy water at 0°C = zero

Enthalpy-concentration diagrams greatly facilitate the calculation of energy balances involving concentration and phase changes; this is illustrated in Example 3.6.

Example 3.6

Calculate the maximum temperature when liquid ammonia at 40°C is dissolved in water at 20°C to form a 10 per cent solution.

Solution

The maximum temperature will occur if there are no heat losses (adiabatic process). As no heat or material is removed, the problem can be solved graphically in the enthalpy-concentration diagram (Figure 3.3). The mixing operation is represented on the diagram

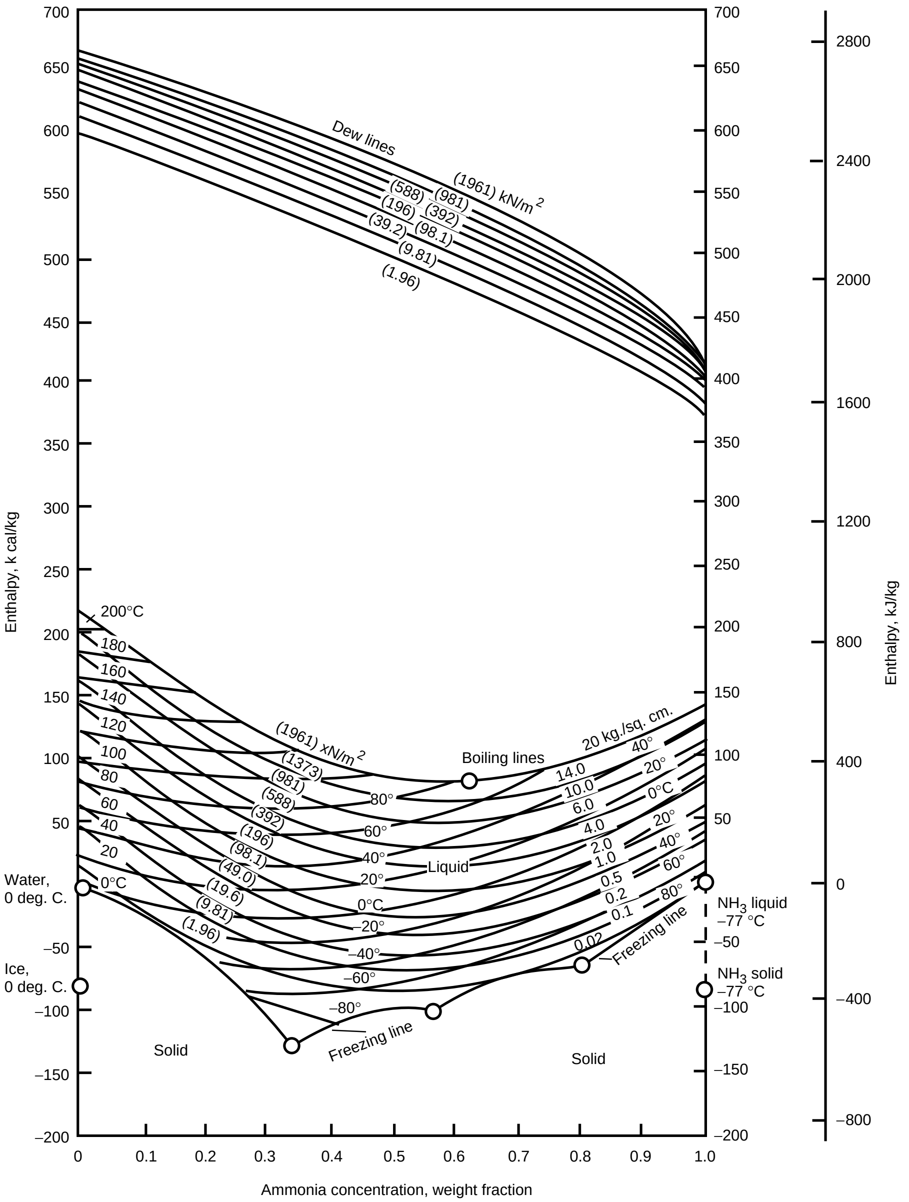
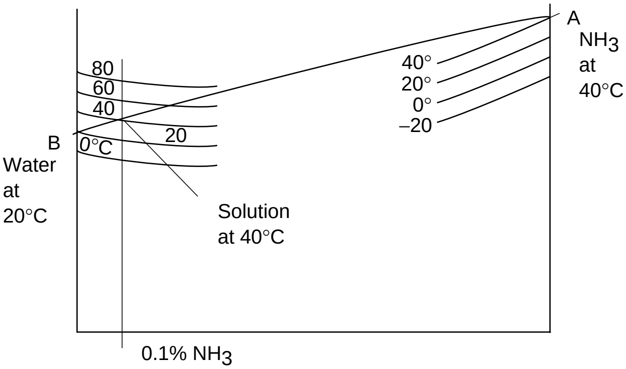


Figure 3.3. Enthalpy-concentration diagram for aqueous ammonia. Reference states: enthalpies of liquid water at 0°C and liquid ammonia at −77°C are zero. (Bosniakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

by joining the point A representing pure ammonia at 40°C with the point B representing pure water at 20°C. The value of the enthalpy of the mixture lies on a vertical line at the required concentration, 0.1. The temperature of the mixture is given by the intersection of this vertical line with the line AB. This method is an application of the "lever rule" for phase diagrams. For a more detailed explanation of the method and further examples see

Himmelbau (1995) or any of the general texts on material and energy balances listed at the end of Chapter 2. The Ponchon-Savarit graphical method used in the design of distillation columns, described in Volume 2, Chapter 11, is a further example of the application of the lever rule, and the use of enthalpy-concentration diagrams.



3.10. HEATS OF REACTION

If a process involves chemical reaction, heat will normally have to be added or removed. The amount of heat given out in a chemical reaction depends on the conditions under which the reaction is carried out. The standard heat of reaction is the heat released when the reaction is carried out under standard conditions: pure components, pressure 1 atm (1.01325 bar), temperature usually, but not necessarily, 25°C.

Values for the standard heats of reactions are given in the literature, or may be calculated by the methods given in Sections 3.11 and 3.12.

When quoting heats of reaction the basis should be clearly stated. Either by giving the chemical equation, for example:

$$\mathrm{NO} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{NO}_2 \qquad \Delta H_r^\circ = -56.68 \text{ kJ}$$

(The equation implies that the quantity of reactants and products are mols)

Or, by stating to which quantity the quoted value applies:

$$\Delta H_r^\circ = -56.68 \text{ kJ per mol NO}_2$$

The reaction is exothermic and the enthalpy change ΔH_r° is therefore *negative*. The heat of reaction $-\Delta H_r^\circ$ is *positive*. The superscript ° denotes a value at *standard* conditions and the subscript r implies that a chemical reaction is involved.

The state of the reactants and products (gas, liquid or solid) should also be given, if the reaction conditions are such that they may exist in more than one state; for example:

$$\mathrm{H}_2(\mathrm{g}) + \tfrac{1}{2}\mathrm{O}_2(\mathrm{g}) \rightarrow \mathrm{H}_2\mathrm{O}(\mathrm{g}),\ \Delta H_r^\circ = -241.6 \text{ kJ}$$

$$\mathrm{H}_2(\mathrm{g}) + \tfrac{1}{2}\mathrm{O}_2(\mathrm{g}) \rightarrow \mathrm{H}_2\mathrm{O}\ (\mathrm{l}),\ \Delta H_r^\circ = -285.6 \text{ kJ}$$

The difference between the two heats of reaction is the latent heat of the water formed.

In process design calculations it is usually more convenient to express the heat of reaction in terms of the mols of product produced, for the conditions under which the reaction is carried out, kJ/mol product.

Standard heats of reaction can be converted to other reaction temperatures by making a heat balance over a hypothetical process, in which the reactants are brought to the standard temperature, the reaction carried out, and the products then brought to the required reaction temperature; as illustrated in Figure 3.4.

$$\Delta H_{r,t} = \Delta H_r^\circ + \Delta H_{\text{prod.}} - \Delta H_{\text{react.}} \tag{3.22}$$

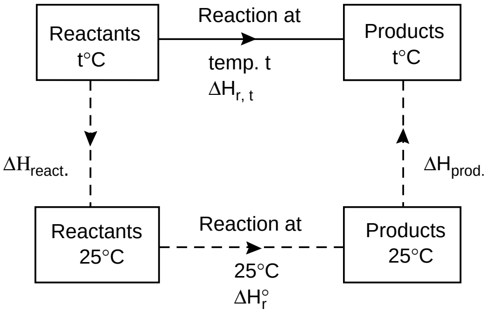


Figure 3.4. ΔH_r at temperature t

where $-\Delta H_{r,t}$ = heat of reaction at temperature t,

$\Delta H_{\text{react.}}$ = enthalpy change to bring reactants to standard temperature,

$\Delta H_{\text{prod.}}$ = enthalpy change to bring products to reaction temperature, t.

For practical reactors, where the reactants and products may well be at temperatures different from the reaction temperature, it is best to carry out the heat balance over the actual reactor using the standard temperature (25°C) as the datum temperature; the standard heat of reaction can then be used without correction.

It must be emphasised that it is unnecessary to correct a heat of reaction to the reaction temperature for use in a reactor heat-balance calculation. To do so is to carry out two heat balances, whereas with a suitable choice of datum only one need be made. For a practical reactor, the heat added (or removed) Q_p to maintain the design reactor temperature will be given by (from equation 3.10):

$$Q_p = H_{\text{products}} - H_{\text{reactants}} - Q_r \tag{3.23}$$

where H_{products} is the *total* enthalpy of the product streams, including unreacted materials and by-products, evaluated from a datum temperature of 25°C;

$H_{\text{reactants}}$ is the total enthalpy of the feed streams, including excess reagent and inerts, evaluated from a datum of 25°C;

Q_r is the total heat generated by the reactions taking place, evaluated from the standard heats of reaction at 25°C (298 K).

$$Q_r = \sum -\Delta H_r^\circ \times \text{(mol of product formed)} \tag{3.24}$$

where $-\Delta H_r^\circ$ is the standard heat of reaction per mol of the particular product.

Note: A negative sign is necessary in equation 3.24 as Q_r is positive when heat is evolved by the reaction, whereas the standard enthalpy change will be negative for exothermic reactions. Q_p will be negative when cooling is required (see Section 3.4).

3.10.1. Effect of pressure on heats of reaction

Equation 3.22 can be written in a more general form:

$$\begin{aligned}\Delta H_{r,P,T} = \Delta H_r^\circ &+ \int_1^P \left[\left(\frac{\partial H_{\text{prod.}}}{\partial P}\right)_T - \left(\frac{\partial H_{\text{react.}}}{\partial P}\right)_T\right] \mathrm{d}P \\ &+ \int_{298}^T \left[\left(\frac{\partial H_{\text{prod.}}}{\partial T}\right)_P - \left(\frac{\partial H_{\text{react.}}}{\partial T}\right)_P\right] \mathrm{d}T \end{aligned} \tag{3.25}$$

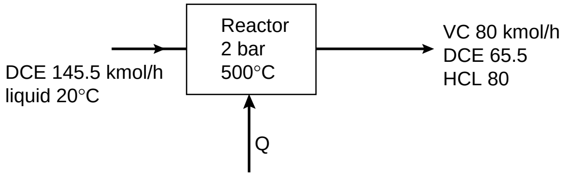
If the effect of pressure is likely to be significant, the change in enthalpy of the products and reactants, from the standard conditions, can be evaluated to include both the effects of temperature and pressure (for example, by using tabulated values of enthalpy) and the correction made in a similar way to that for temperature only.

Example 3.7

Illustrates the manual calculation of a reactor heat balance.

Vinyl chloride (VC) is manufactured by the pyrolysis of 1,2,dichloroethane (DCE). The reaction is endothermic. The flow-rates to produce 5000 kg/h at 55 per cent conversion are shown in the diagram (see Example 2.13).

The reactor is a pipe reactor heated with fuel gas, gross calorific value 33.5 MJ/m^3. Estimate the quantity of fuel gas required.



Solution

Reaction: $C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g) \qquad \Delta H_r^\circ = 70{,}224$ kJ/kmol.

The small quantity of impurities, less than 1 per cent, that would be present in the feed have been neglected for the purposes of this example. Also, the yield of VC has been taken as 100 per cent. It would be in the region of 99 per cent at 55 per cent conversion.

Heat capacity data, for vapour phase

$$C_p^\circ = a + bT + cT^2 + dT^3 \quad \text{kJ/kmolK}$$

	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
VC	5.94	20.16	−15.34	47.65
HCl	30.28	−0.761	1.325	−4.305
DCE	20.45	23.07	−14.36	33.83

for liquid phase: DCE at 20°C, $C_p = 116$ kJ/kmol K,

taken as constant over temperature rise from 20 to 25°C.

Latent heat of vaporisation of DCE at 25°C = 34.3 MJ/kmol.

At 2 bar pressure the change in C_p with pressure will be small and will be neglected. Take base temperature as 25°C (298 K), the standard state for ΔH_r°.

$$\text{Enthalpy of feed} = 145.5 \times 116(293 - 298) = -84{,}390 \text{ kJ/h} = -\underline{\underline{84.4 \text{ MJ/h}}}$$

$$\text{Enthalpy of product stream} = \int_{298}^{773} \sum (n_i C_p)\, \mathrm{d}T$$

Component	n_i (mol/h)	$n_i a$	$n_i b \times 10^2$	$n_i c \times 10^5$	$n_i d \times 10^9$
VC	80	475.2	1612.8	−1227.2	3812.0
HCl	80	2422.4	−60.88	106.0	−344.4
DCE	65.5	1339.5	1511.0	−940.6	2215.9
$\sum n_i C_p$		4237.1	3063.0	−2061.8	5683.5

$$\int_{298}^{773} \sum n_i C_p \,\mathrm{d}T$$

$$= \int_{298}^{773} (4237.1 + 3063.0 \times 10^{-2} T - 2061.8 \times 10^{-5} T^2 + 5683.5 \times 10^{-9} T^3)\, \mathrm{d}T$$

$$= \underline{\underline{7307.3 \text{ MJ/h}}}$$

Heat consumed in system by the endothermic reaction = $\Delta H_r^\circ \times$ mols produced

$$= 70{,}224 \times 80 = 5{,}617{,}920 \text{ kJ/h} = \underline{\underline{5617.9 \text{ MJ/h}}}$$

Heat to vaporise feed (gas phase reaction)

$$= 34.3 \times 145.5 = \underline{\underline{4990.7 \text{ MJ/h}}}$$

Heat balance:

$$\text{Output} = \text{Input} + \text{consumed} + Q$$

$$Q = H_{\text{product}} - H_{\text{feed}} + \text{consumed}$$

$$= 7307.3 - (-84.4) + (5617.9 + 4990.7) = \underline{\underline{18{,}002.3 \text{ MJ/h}}}$$

Taking the overall efficiency of the furnace as 70% the gas rate required

$$= \frac{\text{Heat input}}{(\text{calorific value} \times \text{efficiency})}$$

$$= \frac{18{,}002.3}{33.5 \times 0.7} = \underline{\underline{768\ \text{m}^3/\text{h}}}$$

3.11. STANDARD HEATS OF FORMATION

The standard enthalpy of formation ΔH_f° of a compound is defined as the enthalpy change when one mol of the compound is formed from its constituent elements in the standard state. The enthalpy of formation of the elements is taken as zero. The standard heat of any reaction can be calculated from the heats of formation $-\Delta H_f^\circ$ of the products and reactants; if these are available or can be estimated.

Conversely, the heats of formation of a compound can be calculated from the heats of reaction; for use in calculating the standard heat of reaction for other reactions.

The relationship between standard heats of reaction and formation is given by equation 3.26 and illustrated by Examples 3.8 and 3.9

$$\Delta H_r^\circ = \sum \Delta H_f^\circ, \text{products} - \sum \Delta H_f^\circ, \text{reactants} \tag{3.26}$$

A comprehensive list of enthalpies of formation is given in Appendix D.

As with heats of reaction, the state of the materials must be specified when quoting heats of formation.

Example 3.8

Calculate the standard heat of the following reaction, given the enthalpies of formation:

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(g)}$$

Standard enthalpies of formation kJ/mol

NH_3(g)	−46.2
NO(g)	+90.3
H_2O(g)	−241.6

Solution

Note: the enthalpy of formation of O_2 is zero.

$$\begin{aligned}\Delta H_r^\circ &= \sum \Delta H_f^\circ, \text{products} - \sum \Delta H_f^\circ, \text{reactants}\\ &= (4 \times 90.3 + 6 \times (-241.6)) - (4 \times (-46.2))\\ &= \underline{\underline{-903.6\ \text{kJ/mol}}}\end{aligned}$$

Heat of reaction $-\Delta H_r^\circ = \underline{\underline{904\ \text{kJ/mol}}}$

3.12. HEATS OF COMBUSTION

The heat of combustion of a compound $-\Delta H_c^\circ$ is the standard heat of reaction for complete combustion of the compound with oxygen. Heats of combustion are relatively easy to determine experimentally. The heats of other reactions can be easily calculated from the heats of combustion of the reactants and products.

The general expression for the calculation of heats of reaction from heats of combustion is

$$\Delta H_r^\circ = \sum \Delta H_c^\circ,\ \text{reactants} - \sum \Delta H_c^\circ,\ \text{products} \qquad (3.27)$$

Note: the product and reactant terms are the opposite way round to that in the expression for the calculation from heats of formation (equation 3.26).

For compounds containing nitrogen, the nitrogen will not be oxidised to any significant extent in combustion and is taken to be unchanged in determining the heat of combustion.

Caution. Heats of combustion are large compared with heats of reaction. Do not round off the numbers before subtraction; round off the difference.

Two methods of calculating heats of reaction from heats of combustion are illustrated in Example 3.9.

Example 3.9

Calculate the standard heat of reaction for the following reaction: the hydrogenation of benzene to cyclohexane.

(1) $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

(2) $C_6H_6(g) + 7\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H_c^\circ = -3287.4$ kJ

(3) $C_6H_{12}(g) + 9O_2 \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H_c^\circ = -3949.2$ kJ

(4) $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_c^\circ = -393.12$ kJ

(5) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_c^\circ = -285.58$ kJ

Note: unlike heats of formation, the standard state of water for heats of combustion is liquid. Standard pressure and temperature are the same 25°C, 1 atm.

Solution

Method 1

Using the more general equation 3.26

$$\Delta H_r^\circ = \sum \Delta H_f^\circ,\ \text{products} - \sum \Delta H_f^\circ\ \text{reactants}$$

the enthalpy of formation of C_6H_6 and C_6H_{12} can be calculated, and from these values the heat of reaction (1).

From reaction (2)

$$\Delta H_c^\circ(C_6H_6) = 6 \times \Delta H_c^\circ(CO_2) + 3 \times \Delta H_c^\circ(H_2O) - \Delta H_f^\circ(C_6H_6)$$

$$3287.4 = 6(-393.12) + 3(-285.58) - \Delta H_f^\circ(C_6H_6)$$

$$\Delta H_f^\circ(C_6H_6) = -3287.4 - 3215.52 = \underline{\underline{71.88\ \text{kJ/mol}}}$$

From reaction (3)

$$\Delta H_c^\circ(C_6H_{12}) = -3949.2 = 6(-393.12) + 6(-285.58) - \Delta H_f^\circ(C_6H_{12})$$

$$\Delta H_f^\circ(C_6H_{12}) = 3949.2 - 4072.28 = \underline{\underline{-123.06 \text{ kJ/mol}}}$$

$$\Delta H_r^\circ = \Delta H_f^\circ(C_6H_{12}) - \Delta H_f^\circ(C_6H_6)$$

$$\Delta H_r^\circ = (-123.06) - (71.88) = \underline{\underline{-195 \text{ kJ/mol}}}$$

Note: enthalpy of formation of H_2 is zero.

Method 2

Using equation 3.27

$$\begin{aligned}\Delta H_r^\circ &= (\Delta H_c^\circ(C_6H_6) + 3 \times \Delta H_c^\circ(H_2)) - \Delta H_c^\circ(C_6H_{12})\\ &= (-3287.4 + 3(-285.88)) - (-3949.2) = -\underline{\underline{196 \text{ kJ/mol}}}\end{aligned}$$

Heat of reaction $-\Delta H_r^\circ = \underline{\underline{196 \text{ kJ/mol}}}$

3.13. COMPRESSION AND EXPANSION OF GASES

The work term in an energy balance is unlikely to be significant unless a gas is expanded or compressed as part of the process. To compute the pressure work term:

$$-W = \int_1^2 P\,\mathrm{d}v \qquad \text{(equation 3.5)}$$

a relationship between pressure and volume during the expansion is needed.

If the compression or expansion is isothermal (at constant temperature) then for unit mass of an ideal gas:

$$Pv = \text{constant} \tag{3.28}$$

and the work done,
$$-W = P_1 v_1 \ln \frac{P_2}{P_1} = \frac{\mathbf{R}T_1}{M} \ln \frac{P_2}{P_1} \tag{3.29}$$

where P_1 = initial pressure,
P_2 = final pressure,
v_1 = initial volume.

In industrial compressors or expanders the compression or expansion path will be “polytropic”, approximated by the expression:

$$Pv^n = \text{constant} \tag{3.30}$$

The work produced (or required) is given by the general expression (see Volume 1, Chapter 8):

$$-W = P_1 v_1 \frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] = Z\frac{\mathbf{R}T_1}{M}\frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] \tag{3.31}$$

where Z = compressibility factor (1 for an ideal gas),
$\mathbf{R}$ = universal gas constant, 8.314 $\text{JK}^{-1}\ \text{mol}^{-1}$,
T_1 = inlet temperature, K,
M = molecular mass (weight) of gas,
W = work done, J/kg.

The value of n will depend on the design and operation of the machine.

The energy required to compress a gas, or the energy obtained from expansion, can be estimated by calculating the ideal work and applying a suitable efficiency value. For reciprocating compressors the isentropic work is normally used ($n = \gamma$) (see Figure 3.7); and for centrifugal or axial machines the polytropic work (see Figure 3.6 and Section 3.13.2).

3.13.1. Mollier diagrams

If a Mollier diagram (enthalpy-pressure-temperature-entropy) is available for the working fluid the isentropic work can be easily calculated.

$$W = H_1 - H_2 \tag{3.32}$$

where H_1 is the specific enthalpy at the pressure and temperature corresponding to point 1, the initial gas conditions,
H_2 is the specific enthalpy corresponding to point 2, the final gas condition.

Point 2 is found from point 1 by tracing a path (line) of constant entropy on the diagram.

The method is illustrated in Example 3.10.

Example 3.10

Methane is compressed from 1 bar and 290 K to 10 bar. If the isentropic efficiency is 0.85, calculate the energy required to compress 10,000 kg/h. Estimate the exit gas temperature.

Solution

From the Mollier diagram, shown diagrammatically in Figure 3.5

$$H_1 = 4500 \text{ cal/mol},$$

$$H_2 = 6200 \text{ cal/mol (isentropic path)},$$

$$\text{Isentropic work} = 6200 - 4500 = \underline{\underline{1700 \text{ cal/mol}}}$$

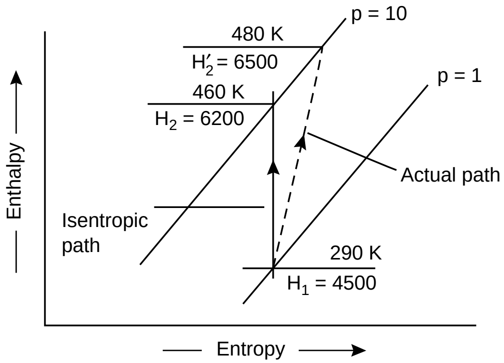


Figure 3.5. Mollier diagram, methane

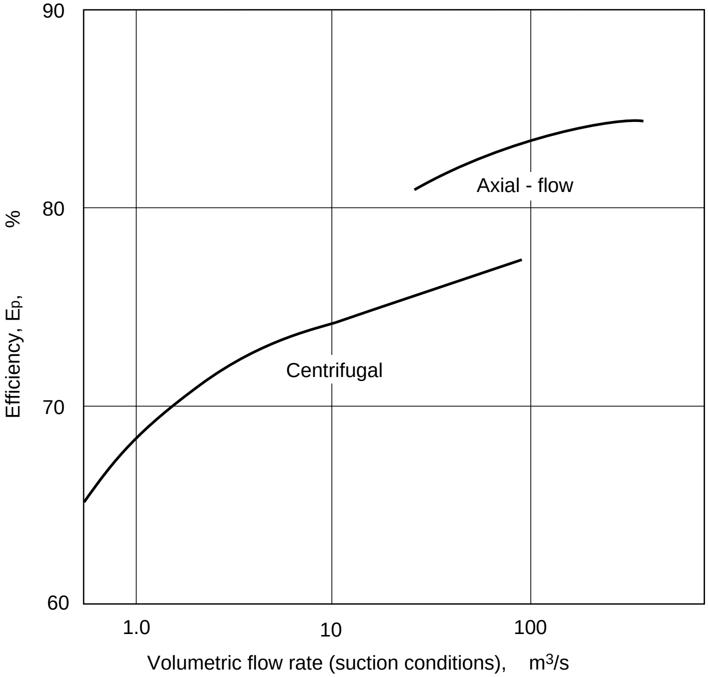


Figure 3.6. Approximate polytropic efficiencies centrifugal and axial-flow compressors

For an isentropic efficiency of 0.85:

$$\text{Actual work done on gas} = \frac{1700}{0.85} = \underline{\underline{2000\ \text{cal/mol}}}$$

So, actual final enthalpy

$$H'_2 = H_1 + 2000 = \underline{\underline{6500\ \text{cal/mol}}}$$

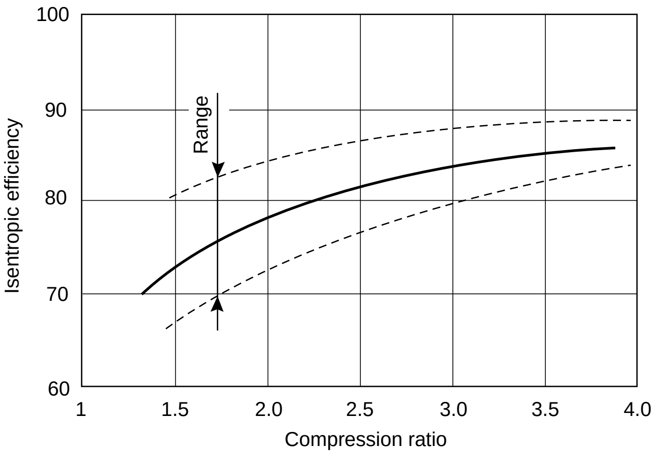


Figure 3.7. Typical efficiencies for reciprocating compressors

From Mollier diagram, if all the extra work is taken as irreversible work done on the gas, the exit gas temperature $= \underline{\underline{480\text{ K}}}$

Molecular weight methane $= 16$

$$
\begin{aligned}
\text{Energy required} &= (\text{mols per hour}) \times (\text{specific enthalpy change}) \\
&= \frac{10{,}000}{16} \times 2000 \times 10^3 \\
&= 1.25 \times 10^9 \text{ cal/h} \\
&= 1.25 \times 10^9 \times 4.187 \\
&= 5.23 \times 10^9 \text{ J/h} \\
\text{Power} &= \frac{5.23 \times 10^9}{3600} = \underline{\underline{1.45\text{ MW}}}
\end{aligned}
$$

3.13.2. Polytropic compression and expansion

If no Mollier diagram is available, it is more difficult to estimate the ideal work in compression or expansion processes. Schultz (1962) gives a method for the calculation of the polytropic work, based on two generalised compressibility functions, X and Y; which supplement the familiar compressibility factor Z.

$$X = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P - 1 \tag{3.33}$$

$$Y = -\frac{P}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{3.34}$$

His charts for X and Y as functions of reduced temperature and pressure are reproduced as Figures 3.9 and 3.10. The functions are used to determine the polytropic exponent n

for use in equation 3.31; and a polytropic temperature exponent m for use in the following equation:

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^m \tag{3.35}$$

where
$$m = \frac{Z\mathbf{R}}{C_p}\left(\frac{1}{E_p} + X\right) \text{ for compression,} \tag{3.36}$$

$$m = \frac{Z\mathbf{R}}{C_p}(E_p + X) \text{ for expansion} \tag{3.37}$$

E_p is the polytropic efficiency, defined by:

$$\text{for compression } E_p = \frac{\text{polytropic work}}{\text{actual work required}}$$

$$\text{for expansion } E_p = \frac{\text{actual work obtained}}{\text{polytropic work}}$$

An estimate of E_p can be obtained from Figure 3.6.

$$n = \frac{1}{Y - m(1 + X)} \tag{3.38}$$

At conditions well removed from the critical conditions equations 3.36, 3.37 and 3.38 reduce to:

$$m = \frac{(\gamma - 1)}{\gamma E_p} \tag{3.36a}$$

$$m = \frac{(\gamma - 1)E_p}{\gamma} \tag{3.37a}$$

$$n = \frac{1}{1 - m} \tag{3.38a}$$

These expressions can be used to calculate the polytropic work and outlet temperature by substitution in equations 3.31 and 3.35. They can also be used to make a first estimate of T_2 in order to estimate the mean reduced temperature for use with Figures 3.9 and 3.10.

The use of Schultz's method is illustrated in Examples 3.11 and 3.16.

Example 3.11

Estimate the power required to compress 5000 kmol/h of HCl at 5 bar, 15°C, to 15 bar.

Solution

For HCl, $P_c = 82$ bar, $T_c = 324.6$ K

$$C_p^\circ = 30.30 - 0.72 \times 10^{-2}T + 12.5 \times 10^{-6}T^2 - 3.9 \times 10^{-9}T^3 \text{ kJ/kmol K}$$

Estimate T_2 from equations 3.35 and 3.36*a*.

For diatomic gases $\gamma \simeq 1.4$.

Note: γ could be estimated from the relationship $\gamma = \dfrac{C_p}{C_v} = \dfrac{C_p}{C_p - \mathbf{R}}$

At the inlet conditions, the flow rate in m^3/s

$$= \frac{5000}{3600} \times 22.4 \times \frac{288}{273} \times \frac{1}{5} = 6.56$$

From Figure 3.6 $E_p = 0.73$

From equations 3.36a and 3.35 $\quad m = \dfrac{1.4 - 1}{1.4 \times 0.73} = 0.39$

$$T_2 = 288\left(\frac{15}{5}\right)^{0.39} = 442 \text{ K}$$

$$T_{r\ (\text{mean})} = \frac{442 + 228}{2 \times 324.6} = 1.03$$

$$P_{r\ (\text{mean})} = \frac{5 + 15}{2 \times 82} = 0.12$$

$$\text{At } T_{(\text{mean})} C_p^{\circ} = 29.14 \text{ kJ/kmol K}$$

Correction for pressure from Figure 3.2, 2 kJ/kmol K

$$C_p = 29.14 + 2 \simeq 31 \text{ kJ/kmol K}$$

From Figures 3.8, 3.9 and 3.10 at mean conditions:

$$X = 0.18, \quad Y = 1.04, \quad Z = 0.97$$

$$Z \text{ at inlet conditions} = 0.98$$

From equations 3.36 and 3.38

$$m = \frac{0.97 \times 8.314}{31}\left(\frac{1}{0.73} + 0.18\right) = \underline{\underline{0.40}}$$

$$n = \frac{1}{1.04 - 0.4(1 + 0.18)} = \underline{\underline{1.76}}$$

From equation 3.31

$$W \text{ polytropic} = 0.98 \times 288 \times 8.314 \times \frac{1.76}{1.76 - 1}\left(\left(\frac{15}{5}\right)^{(1.76-1)/1.76} - 1\right)$$

$$= \underline{\underline{3299 \text{ kJ/kmol}}}$$

$$\text{Actual work required} = \frac{\text{polytropic work}}{E_p}$$

$$= \frac{3299}{0.73} = \underline{\underline{4520 \text{ kJ/kmol}}}$$

$$\text{Power} = \frac{4520}{3600} \times 5000 = 6275 \text{ kW}$$

Say, $\underline{\underline{6.3 \text{ MW}}}$

$$T_2 = 288\left(\frac{15}{5}\right)^{0.4} = \underline{\underline{447 \text{ K}}}$$

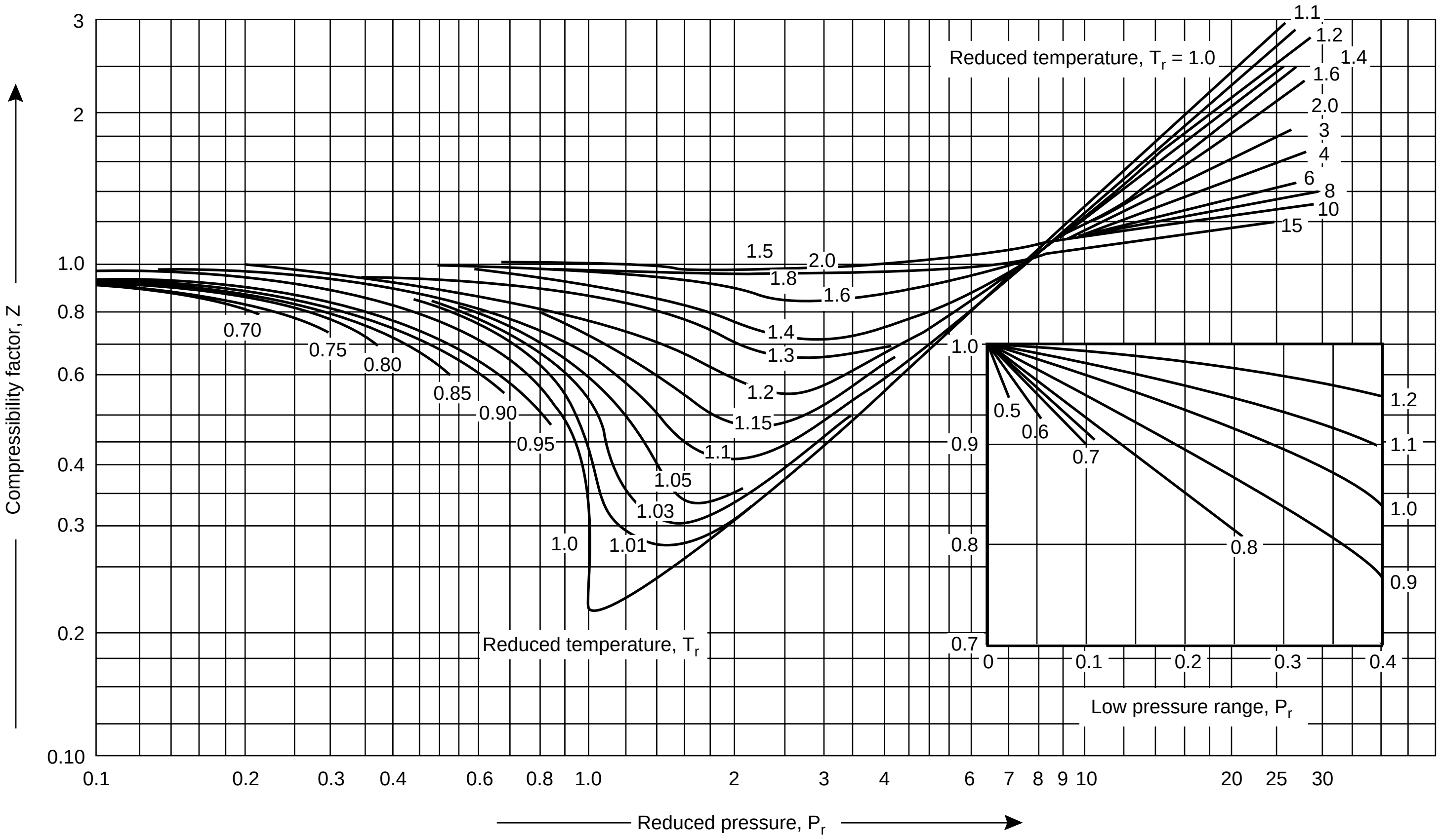


Figure 3.8. Compressibility factors of gases and vapours

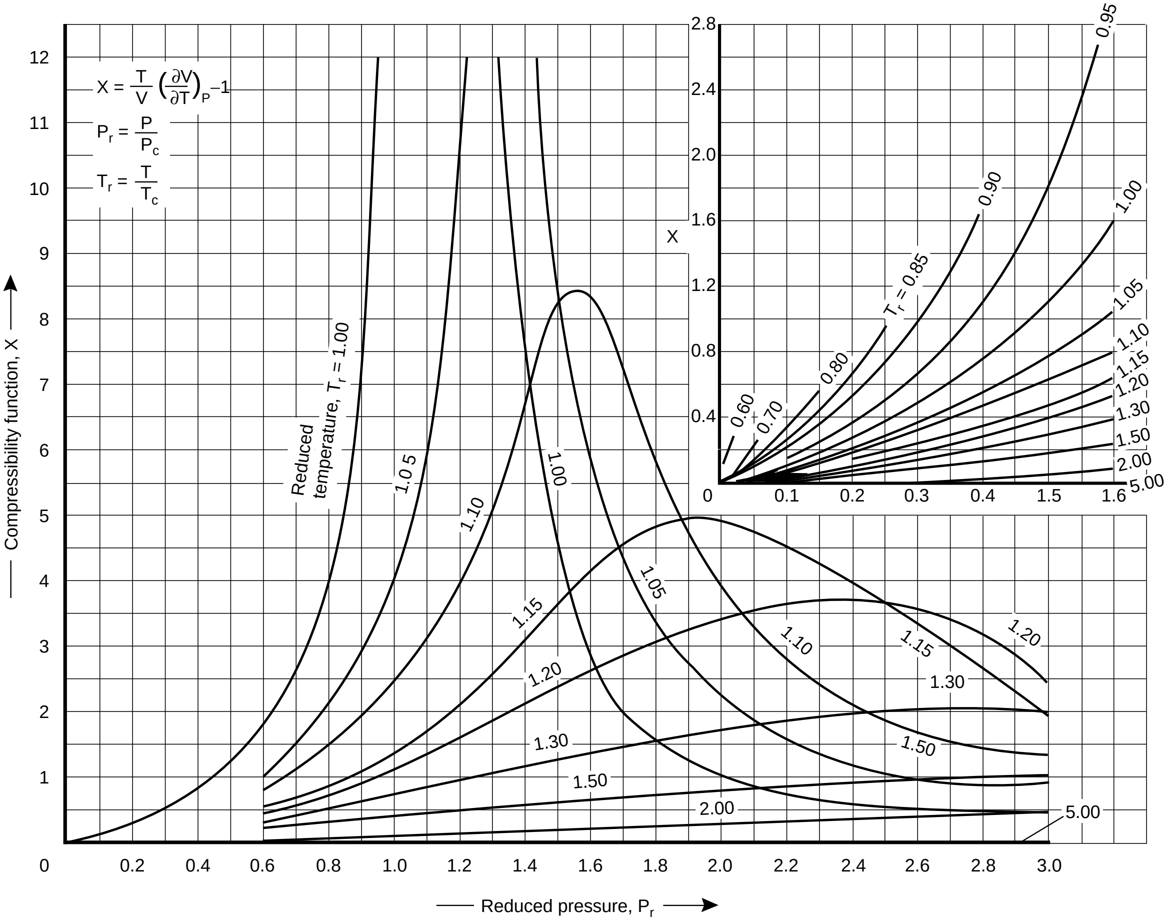


Figure 3.9. Generalised compressibility function *X*

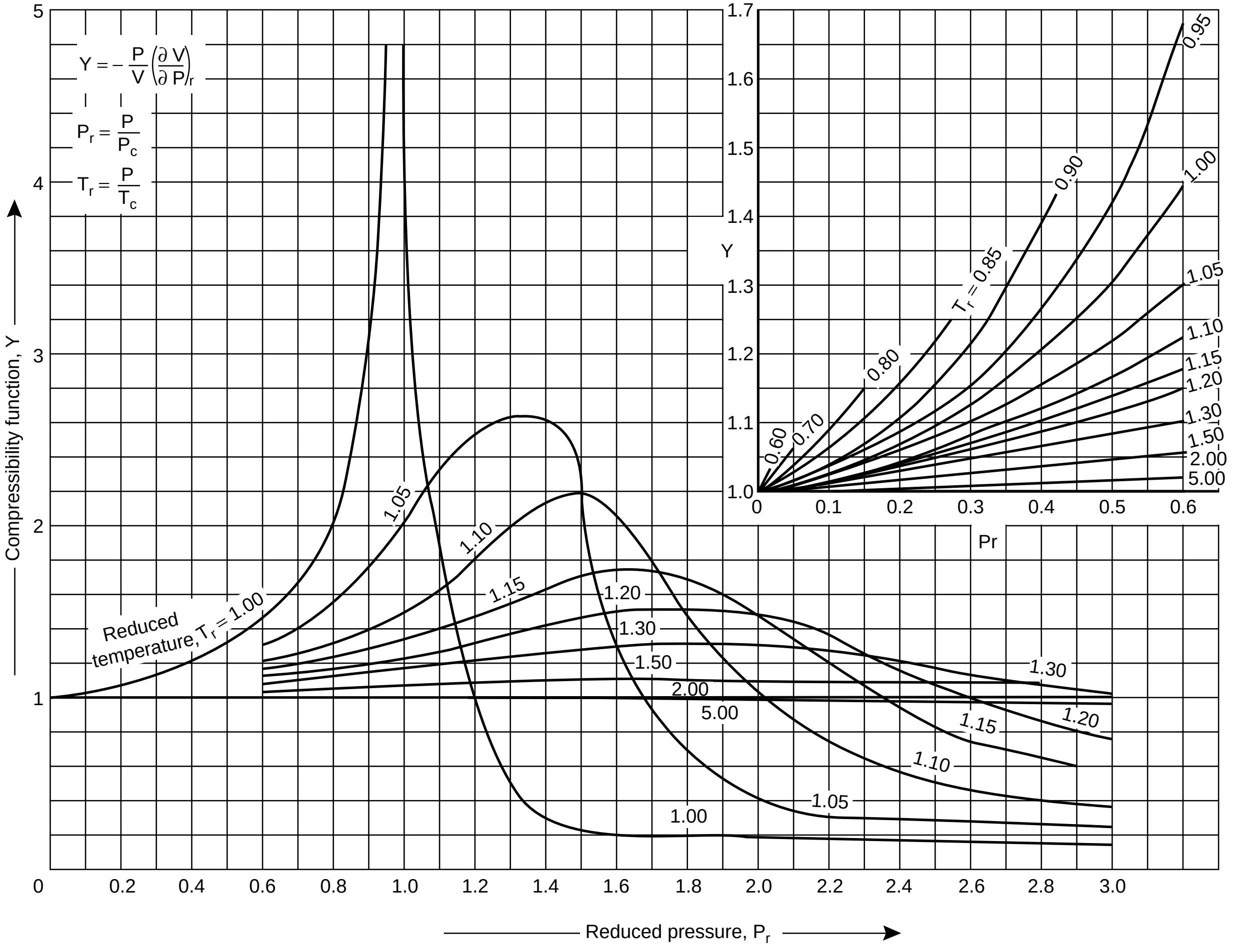


Figure 3.10. Generalised compressibility function *Y*

TABLE 3.2. ENERGY 1, a simple energy balance program

```
10 REM SHORT ENERGY PROGRAM, REWRITTEN IN GWBASIC, MARCH 92
20 PRINT "HEAT BALANCE PROGRAM, BASIS kmol/h, TEMP K, DATUM 298 K"
30 PRINT "INPUT THE NUMBER OF COMPONENTS, MAXIMUM 10"
40 INPUT N1
50 PRINT "INPUT HEAT CAPACITY DATA FOR EQUATION A+BT+CT^2+DT^3"
60 FOR I = 1 TO N1
70 PRINT
80 PRINT "FOR COMPONENT"; I; "INPUT A, B, C, D, INCLUDING ANY ZERO VALUES"
90 INPUT A(I), B(I), C(I), D(I)
100 NEXT I
110 H4=H5=H6=Q1=0
120 PRINT "INPUT THE NUMBER OF FEED STREAMS"
130 INPUT S1
140 FOR I = 1 TO S1
150 PRINT "FOR FEED STREAM"; I; "INPUT STREAM TEMP AND NUMBER OF COMPONENTS"
160 INPUT T1, N2
170 GOSUB 580
180 PRINT "STREAM SENSIBLE HEAT ="; H4; "kJ/h"
190 REM TOTAL SENSIBLE HEAT FEED STREAMS
200 H5 = H5 + H4
210 NEXT I
220 PRINT "INPUT NUMBER OF PRODUCT STREAMS"
230 INPUT S1
240 FOR I = 1 TO S1
250 PRINT "FOR PRODUCT STREAM"; I; "INPUT STREAM TEMP AND NUMBER OF COMPONENTS"
260 INPUT T1, N2
270 GOSUB 580
280 PRINT "STREAM SENSIBLE HEAT ="; H4; "kJ/h"
290 REM TOTAL SENSIBLE HEAT PRODUCT STREAMS
300 H6 = H6 + H4
310 NEXT I
320 PRINT "INPUT THE NUMBER OF REACTIONS AND PHASE CHANGES"
330 INPUT N4
340 IF N4 = 0 THEN 450
350 PRINT "FOR EACH REACTION OR PHASE CHANGE INPUT THE HEAT OF REACTION"
360 PRINT "OR THE LATENT HEAT, kJ/kmol; AND QUANTITY INVOLVED kmol/h"
370 PRINT "REMEMBER: HEAT ENVOLVED:POSITIVE; HEAT ABSORBED:NEGATIVE"
380 FOR I = 1 TO N4
390 PRINT
400 PRINT "NEXT REACTION/PHASE CHANGE: INPUT VALUES"
410 INPUT R, F2
420 H7 = F2*R
430 Q1 = Q1 + H7
440 NEXT I
450 REM HEAT BALANCE
460 Q = H6-H5-Q1
470 IF Q < 0 THEN 500
480 PRINT "HEATING REQUIRED ="; Q; "kJ/h"
490 GOTO 510
500 PRINT "COOLING REQUIRED ="; Q; "kJ/h"
510 PRINT "REPEAT CALCULATION WANTED ? TYPE Y FOR YES, N FOR NO"
520 INPUT P$
530 IF P$ = "N" THEN 560
540 PRINT "REPEAT CALCULATION"
550 GOTO 110
560 PRINT "CALCULATIONS FINISHED"
570 STOP
580 REM SUBROUTINE TO CALCULATE STREAM SENSIBLE HEATS
590 PRINT
600 PRINT "FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE"
610 H4 = 0
620 FOR I1 = 1 TO N2
630 PRINT "NEXT COMPONENT"
640 INPUT J, F
650 REM HEAT CAPACITY EQUATION SPLIT OVER 2 LINES
660 H1 = A(J)*(T1-298) + B(J)*(T1^2-298^2)/2
670 H2 = C(J)*(T1^3-298^3)/3 + D(J)*(T1^4-298^4)/4
680 H3 = F*(H1+H2)
690 H4 = H4+H3
700 NEXT I1
710 RETURN
```

3.13.3. Multistage compressors

Single-stage compressors can only be used for low pressure ratios. At high pressure ratios, the temperature rise will be too high for efficient operation.

To cope with the need for high pressure generation, the compression is split into a number of separate stages, with intercoolers between each stage. The interstage pressures are normally selected to give equal work in each stage.

For a two-stage compressor the interstage pressure is given by:

$$P_i = \sqrt{(P_1 \times P_2)} \tag{3.39}$$

where P_i is the intermediate-stage pressure.

Example 3.12

Estimate the power required to compress 1000 m^3/h air from ambient conditions to 700 kN/m^2 gauge, using a two-stage reciprocating compressor with an intercooler.

Solution

Take the inlet pressure, P_1, as 1 atmosphere = 101.33 kN/m^2, absolute.

Outlet pressure, P_2, = 700 + 101.33 = 801.33 kN/m^2, absolute.

For equal work in each stage the intermediate pressure, P_i,

$$= \sqrt{(1.0133 \times 10^5 \times 8.0133 \times 10^5)} = \underline{\underline{2.8495 \times 10^5}} \text{ N/m}^2$$

For air, take ratio of the specific heats, γ, to be 1.4.

For equal work in each stage the total work will be twice that in the first stage.

Take the inlet temperature to be 20 °C, At that temperature the specific volume is given by

$$v_1 = \frac{29}{22.4} \times \frac{293}{273} = 1.39 \text{ m}^3/\text{kg}$$

Work done, $$-\text{W} = 2 \times 1.0133 \times 10^5 \times 1.39 \times \frac{1.4}{1.4 - 1}\left[\left(\frac{2.8495}{1.0133}\right)^{(1.4-1)/1.4} - 1\right]$$

$$= 338{,}844 \text{ J/kg} = 339 \text{ kJ/kg}$$

From Figure 3.7, for a compression ratio of 2.85 the efficiency is approximately 84%. So work required

$$= 339/0.84 = \underline{\underline{404}} \text{ kJ/kg}$$

Mass flow-rate $$= \frac{1000}{1.39 \times 3600} = 0.2 \text{ kg/s}$$

Power required $$= 404 \times 0.2 = \underline{\underline{80 \text{ kW}}}$$

Example 3.13

In the high-pressure process for the production of polyethylene, ethylene is compressed in a two-step process. In the primary step, the gas is compressed in a two-stage compressor to 25 to 30 MPa. This is followed by compression in a hypercompressor to 150 to 320 MPa.

Estimate the work required to compress ethylene to 25 MPa in a two-stage compressor. A reciprocating compressor will be used. The gas is at an initial temperature of 15°C and is cooled to 25°C after the first-stage compression.

Solution

As the calculations will be repetitive, use a spreadsheet.

Data T_{in} 288 K P_{in} 1 bar P_{out} 250 ba $R = 8.1345$ J/mol K

T_{c} 282.4 K P_c 50.4 bar M 28.05 C_p data from Appendix D

First stage

Intermediate pressure $P_2 = 15.811388$ bar eqn 3.39

Compression ratio $= P_2/P_1 = 15.814$

C_p for ethylene $T_{\text{in}} = 288$ use eqn 3.11a

	A	B	C	D
Coeff.	3.806	0.15359	−8.35E-05	1.755E-08
C_p	3.806	44.23392	−6.924165	0.419256

sum, $C_p =$ 41.535011 kJ/kmol K

gamma $=$ $C_p/(C_p - \text{R}) = 1.2502821$

From Figure 3.7, extrapolated, Ep = 0.86.

$m =$ 0.232768 eqn 3.36a

$T_2 =$ 547.52197 eqn 3.35

Mean temp $= (T_1 + T_2)/2 = 417.76099$

C_p at mean temp of 419.6 K

3.806	0.15359	−8.35E-05	1.755E-08
3.806	64.446364	−14.69784	1.2966068

sum, $C_p = 54.851135$ kJ/kmol K

new gamma $=$ 1.1786657

revised $m =$ 0.1811049

revised $T_2 =$ 474.76117

revised mean temp $= 381.38058$

little change so leave T_{mean} at 419.6 K

$T_{\text{r}} = T_{\text{mean}}/T_{\text{c}} =$ 1.4858357 (1.5)

$P_{\text{mean}} = (P_1 * P_2)/2 = 0.5$

$P_r = P_{\text{mean}}/\text{Pc} = 0.0099206\ (0.17)$

From Figure 3.2 correction to C_p for pressure is negligible.

From Figures 3.8, 3.9, 3.10

$Z = 1.0 \qquad X = 0 \qquad Y = 0$

Essentially ideal at this pressure

$m =$ 0.1762593 eqn 3.36a

$n =$ 1.2139743 eqn 3.38a

$-W =$ 303.47285 kJ/kmol eqn 3.31

Actual work required = polytropic work/efficiency = 352.87541

Say $\underline{\underline{353}}$ kJ/kmol

Second stage work

As the intermediate pressure was selected to give equal work in each stage the second stage work could be taken as equal to the first stage work. This will be checked.

$T_{\text{in}} = 298$ K

compression ratio = $P_3/P_2 =$ 15.822785, i.e. same as first stage

So, take gamma and efficiency as for first stage

$m =$ 0.1811049

$T_3 =$ 491.24593 K

$T_{\text{mean}} = 394.62296$ K

C_p at mean temp

Coeff.	3.806	0.15359	−8.35E-05	1.755E-08
C_p	3.806	60.610141	−13.00011	1.0785715

sum, $C_p = 52.494599$ kJ/kmol K

Little change from first stage, so use same gamma and T_{mean}

Tr = 1.5

$\text{P}_{\text{mean}} =$ 20.4 bar

Pr = 0.4047619 (0.4)

From Figure 3.2 correction to C_p for pressure is approximately 2.5 J/mol.

This is less than 5 per cent, so neglect.

From Figures 3.8, 3.9, 3.10

$Z = 1.0 \qquad X = 0.1$ approx. $\qquad Y = 0$

So, gas can be taken as ideal

$-W = 314.01026$ slightly higher as T_{in} is higher

Actual work = 365.12821 $\underline{\underline{365\ \text{kJ/kmol}}}$

Total work required first step = $\underline{\underline{718}}$ kJ/kmol

The spreadsheet used for this example was Microsoft Works. A copy of the solution using Microsoft Excel can be found on the Butterworth-Heinemann web site: bh.com/companions/0750641428.

3.13.4. Electrical drives

The electrical power required to drive a compressor (or pump) can be calculated from a knowledge of the motor efficiency:

$$\text{Power} = \frac{-W \times \text{mass flow-rate}}{E_e} \tag{3.40}$$

where $-W$ = work of compression per unit mass (equation 3.31),
E_e = electric motor efficiency.

The efficiency of the drive motor will depend on the type, speed and size. The values given in Table 3.1 can be used to make a rough estimate of the power required.

Table 3.1. Approximate efficiencies of electric motors

Size(kW)	Efficiency (%)
5	80
15	85
75	90
200	92
750	95
>4000	97

3.14. ENERGY BALANCE CALCULATIONS

Energy balance calculations are best solved using spreadsheets or by writing a short computer program. A suitable program is listed in Table 3.2 and its use described below. The use of a spreadsheet is illustrated in Example 3.14b.

Energy 1, a simple computer program

This program can be used to calculate the heat input or cooling required for a process unit, where the stream enthalpies relative to the datum temperature can be calculated from the specific heat capacities of the components (equation 3.11).

The datum temperature in the program is 25°C (298 K), which is standard for most heat of reaction data. Specific heats are represented by a cubic equation in temperature:

$$C_p = A + BT + CT^2 + DT^3$$

Any unspecified constants are typed in as zero.

If the process involves a reaction, the heat generated or consumed is computed from the heat of reaction per kmol of product (at 25°C) and the kmols of product produced.

If any component undergoes a phase change in the unit, the heat required is computed from the latent heat (at 25°C) and the quantity involved.

The component specific heat capacity coefficients, A, B, C, D, are stored as a matrix. If an energy balance is to be made on several units, the specific heat coefficients for all the components can be entered at the start, and the program rerun for each unit.

The program listing contains sufficient remark statements for the operation of the program to be easily followed. It is written in GW-BASIC for personal computers. It can easily be adapted for other forms of BASIC and for use on programmable calculators. The use of the program is illustrated in Example 3.14a. It has also been used for other examples in this chapter and in the flow-sheeting, Chapter 4.

Example 3.14a

Use of computer program ENERGY 1

A furnace burns a liquid coal tar fuel derived from coke-ovens. Calculate the heat transferred in the furnace if the combustion gases leave at 1500 K. The burners operate with 20 per cent excess air.

Take the fuel supply temperature as 50°C (323 K) and the air temperature as 15°C (288 K).

The properties of the fuel are:

Carbon	87.5 per cent w/w
Hydrogen	8.0
Oxygen	3.5
Nitrogen	1.0
Sulphur	trace
Ash	balance

Net calorific value	39,540 kJ/kg
Latent heat of vaporisation	350 kJ/kg
Heat capacity	1.6 kJ/kg K

C_p° of gases, kJ/kmol K,

$$C_p = A + BT + CT^2 + DT^3$$

Component		*A*	*B*	*C*	D
1	CO_2	19.763	7.332E-2	−5.518E-5	17.125E-9
2	H_2O	32.190	19.207E-4	10.538E-6	−3.591E-9
3	O_2	28.06	−3.674E-6	17.431E-6	−10.634E-9
4	N_2	31.099	−1.354E-2	26.752E-6	−11.662E-9

Solution

Material balance

Basis: 100 kg (as analysis is by weight).

Assume complete combustion: maximum heat release.

Reactions: $C + O_2 \rightarrow CO_2$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Element	kg	kmol	Stoichiometric O_2 kmol	kmol, products
C	87.5	7.29	7.29	7.29, CO_2
H_2	8.0	4.0	2.0	4.0, H_2O
O_2	3.5	0.11	—	0.11
N_2	1.0	0.04	—	0.04
Total		11.44	9.29	

O_2 required with 20 per cent excess $= 9.29 \times 1.2 = 11.15$ kmol.

Unreacted O_2 from combustion air $= 11.15 - 9.29 = 1.86$ kmol.

N_2 with combustion air $= 11.15 \times \dfrac{79}{21} = 41.94$ kmol.

Composition of combustion gases:

$$\begin{array}{lrl} CO_2 & & = 7.29 \text{ kmol} \\ H_2O & & = 4.0 \\ O_2 & 0.11 + \ \ 1.86 & = 1.97 \\ N_2 & 0.04 + 41.94 & = 41.98 \end{array}$$

Presentation of data to the program:
C_p of fuel (component 5), taken as constant,

$$A = 1.6, \quad B = C = D = 0$$

Heat of reaction and latent heat, taken to be values at datum temperature of 298 K.

There is no need to convert to kJ/kmol, providing quantities are expressed in kg. For the purposes of this example the dissociation of CO_2 and H_2O at 1500 K is ignored.

Computer print-out

Data inputs shown after the symbol (?)

```
RUN
HEAT BALANCE PROGRAM, BASIS kmol/h, TEMP K, DATUM 298 K
INPUT THE NUMBER OF COMPONENTS, MAXIMUM 10
? 5
INPUT HEAT CAPACITY DATA FOR EQUATION A+BT+CT^2+DT^3

FOR COMPONENT 1 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 19.763, 7.332E-2, -5.518E-5, 1.7125E-8

FOR COMPONENT 2 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 32.19, 1.9207E-3, 1.0538E-5, -3.591E-9

FOR COMPONENT 3 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 28.06, -3.67E-6, 1.74E-5, -1.0634E-8

FOR COMPONENT 4 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 31.099, -1.354E-2, 2.6752E-5, -1.1662E-8

FOR COMPONENT 5 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 1.6, 0 0, 0, 0
```

```
INPUT THE NUMBER OF FEED STREAMS
? 2
FOR FEED STREAM 1 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 323, 1

FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 5, 100
STREAM SENSIBLE HEAT = 4000 kJ/h
FOR FEED STREAM 2 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 288, 2

FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 3, 11.15
NEXT COMPONENT
? 4, 41.94
STREAM SENSIBLE HEAT = -15,484.61 kJ/h
INPUT NUMBER OF PRODUCT STREAMS
? 1
FOR PRODUCT STREAM 1 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 1500, 4

FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 1, 7.29
NEXT COMPONENT
? 2, 4.0
NEXT COMPONENT
? 3, 1.97
NEXT COMPONENT
? 4, 41.98
STREAM SENSIBLE HEAT = 2319620 kJ/h
INPUT THE NUMBER OF REACTIONS AND PHASE CHANGES
? 2
FOR EACH REACTION OR PHASE CHANGE INPUT THE HEAT OF REACTION
OR THE LATENT HEAT, kJ/kmol; AND QUANTITY INVOLVED kmol/h
REMEMBER: HEAT ENVOLVED:POSITIVE; HEAT ABSORBED:NEGATIVE

NEXT REACTION/PHASE CHANGE: INPUT VALUES
? +39540, 100

NEXT REACTION/PHASE CHANGE: INPUT VALUES
? -350, 100
COOLING REQUIRED = -1587896 kJ/h
REPEAT CALCULATION WANTED ? TYPE Y FOR YES, N FOR NO
? N
CALCULATIONS FINISHED
```

Heat transferred (cooling required) = 1,590,000 kJ/100 kg
Note: though the program reports kJ/h, any consistent set of units can be used. For the example the basis used was 100 kg.

Use of spreadsheets

A spreadsheet can be used for repetitive calculations as a simpler alternative to writing a program. The procedure is set out below and illustrated in Example 13.14b.

From equation 13.11 the enthalpy of a stream, due to sensible heat, is given by

$$H = m\sum_{m=1}^{m=n}\Big[AT + BT^2/2 + CT^3/3 + DT^4/4\Big]_{T_1}^{T_2} \qquad (13.11a)$$

where H = the stream sensible heat/enthalpy
m = flowrate of the steam component kg/s or kmol/s
n = number of stream components

Procedure

1. Set up the specific heat coefficients as a matrix.
2. Use equation 3.11a to calculate the enthalpy of each component. Tabulate the results. Sum the columns to find the total stream sensible enthalpy.
3. Repeat for all the inlet and exit streams.
4. Calculate and add the enthalpy from any reaction or phase change and add to the stream enthalpies.
5. Subtract the total enthalpy of the outlet streams from the inlet to find the change in enthalpy.

Example 13.14b

Repeat the calculations for the solution of Example 13.4a using a spreadsheet.

Solution

The spreadsheet used for this example is Microsoft Works. A copy of the example using Microsoft Excel can be found on the companion web site: http://books.elsevier.com/companions.

Example 3.14b

Data

Fuel oil	%C =	87.5	%H2 =	8	%N2 =	1
	%oO2 =	3.5				
Cp kJ/kg, K	1.6	CV kJ/kg		39540	lat. heat kJ/kg	350

Specific heats gases

comp.	A	B	C	D
CO2	19.763	0.0733	−5.52E-05	1.713E-08
H2O	32.19	0.0019207	1.054E-05	−3.59E-09
O2	28.06	−3.67E-06	1.743E-05	−1.06E-08
N2	31.099	−0.01354	2.675E-05	−1.17E-08

Tin fuel, K 323 Tin air, K 288 Tout, K 1500

Basis 100 kg, as analysis is by weight.

MATERIAL BALANCE

Reactions C + O2 = CO2 H2 + 1/2 O2 = H2O

element	kg	kmol	stoichiometric O2, kmol	products, kmol	
C	87.5	7.29	7.29	7.29	CO2
H2	8	4.00	2.00	4.00	H2O
O2	3.5	0.11		0.11	
N2	1	0.04		0.04	
Totals	100	11.44	9.29	11.44	

O2 with 20% excess, kmol = 11.15 unreacted O2, kmol = 1.86

N2 with combustion air, kmol = 41.95

Composition of combustion gases

CO2	7.29
H2O	4.00
O2	1.97
N2	41.98

ENERGY BALANCE

Take datum temp, To be 298 K

In

			mols	A	B	C	D		
Air	O2		11.15	28.06	−3.67E-06	1.743E-05	−1.06E-08		
	N2		41.95	31.099	−0.01354	2.675E-05	−1.17E-08		
	mols × Cp	O2		312.869	−4.1E-05	0.0001944	−1.19E-07		
		N2		1304.455	−0.567939	0.0011221	−4.89E-07		
		SUM		1617.324	−0.567979	0.0013165	−6.08E-07		
									total
	Energy kJ	Tin		465789.30	−23555.25	10482.593	−1045.259		451671.39
		To		481962.54	−25219.43	11612.883	−1198.17		467157.83
								Diff	−15486.44

Fuel	sensible heat	mass × Cp × (Tin − To) =	4000
	combustion	mas × cv =	3954000
		total	3958000

Total energy in sensible + combustion: 3942513.6 kJ

Out			mols	A	B	C	D		
	CO2		7.29	19.763	0.0733	−5.52E-05	1.713E-08		
	H2O		4.00	32.19	0.0019207	1.054E-05	−3.59E-09		
	O2		1.97	28.06	−3.67E-06	1.743E-05	−1.06E-08		
	N2		41.98	31.099	−0.01354	2.675E-05	−1.17E-08		
	mols × Cp	CO2		144.07227	0.534357	−0.000402	1.248E-07		
		H2O		128.76	0.0076828	4.215E-05	−1.44E-08		
		O2		55.2782	−7.24E-06	3.434E-05	−2.09E-08		
		N2		1305.536	−0.568409	0.001123	−4.9E-07		
		SUM		1633.6465	−0.026377	0.0008	−4.0E-7		
	Energy	Tout		2.45E+06	−29673.72	896937.56	−506303.8	total	2811429.8
		To		486826.65	−1171.175	7032.9451	−788.6988		491899.72
								Diff	2319530.1

latent heat mass × Lv = 35000

Total out = sensible + latent = 2354530.1

Cooling required = Heat in − heat out = 1587983.5 kJ/100 kg fuel

3.15. UNSTEADY STATE ENERGY BALANCES

All the examples of energy balances considered previously have been for steady-state processes; where the rate of energy generation or consumption did not vary with time and the accumulation term in the general energy balance equation was taken as zero.

If a batch process is being considered, or if the rate of energy generation or removal varies with time, it will be necessary to set up a differential energy balance, similar to the differential material balance considered in Chapter 2. For batch processes the total energy requirements can usually be estimated by taking as the time basis for the calculation 1 batch; but the maximum rate of heat generation will also have to be estimated to size any heat-transfer equipment needed.

The application of a differential energy balance is illustrated in Example 3.13.

Example 3.15

Differential energy balance

In the batch preparation of an aqueous solution the water is first heated to 80°C in a jacketed, agitated vessel; 1000 Imp. gal. (4545 kg) is heated from 15°C. If the jacket area is 300 ft^2 (27.9 m^2) and the overall heat-transfer coefficient can be taken as 50 Btu $\text{ft}^{-2}\ \text{h}^{-1}\ {}^\circ\text{F}^{-1}$ (285 W $\text{m}^{-2}\ \text{K}^{-1}$), estimate the heating time. Steam is supplied at 25 psig (2.7 bar).

Solution

The rate of heat transfer from the jacket to the water will be given by the following expression (see Volume 1, Chapter 9):

$$\frac{\mathrm{d}Q}{\mathrm{d}\mathbf{t}} = UA(t_s - t) \qquad (a)$$

where dQ is the increment of heat transferred in the time interval d$\mathbf{t}$, and

U = the overall-heat transfer coefficient,
t_s = the steam-saturation temperature,
t = the water temperature.

The incremental increase in the water temperature dt is related to the heat transferred dQ by the energy-balance equation:

$$\mathrm{d}Q = WC_p\,\mathrm{d}t \qquad (b)$$

where WC_p is the heat capacity of the system.

Equating equations (*a*) and (*b*)

$$WC_p\frac{\mathrm{d}t}{\mathrm{d}\mathbf{t}} = UA(t_s - t)$$

Integrating

$$\int_0^{\mathbf{t}_B} \mathrm{d}\mathbf{t} = \frac{WC_p}{UA}\int_{t_1}^{t_2}\frac{\mathrm{d}t}{(t_s - t)}$$

Batch heating time

$$\mathbf{t}_B = -\frac{WC_p}{UA}\ln\frac{t_s - t_2}{t_s - t_1}$$

For this example

$$\begin{aligned}
WC_p &= 4.18 \times 4545 \times 10^3\ \text{JK}^{-1}\\
UA &= 285 \times 27\ \text{WK}^{-1}\\
t_1 &= 15^\circ\text{C},\ t_2 = 80^\circ\text{C},\ t_s = 130^\circ\text{C}\\
\mathbf{t}_B &= -\frac{4.18 \times 4545 \times 10^3}{285 \times 27.9}\ln\frac{130 - 80}{130 - 15}\\
&= 1990\text{s} = \underline{\underline{33.2\ \text{min}}}
\end{aligned}$$

In this example the heat capacity of the vessel and the heat losses have been neglected for simplicity. They would increase the heating time by 10 to 20 per cent.

3.16. ENERGY RECOVERY

Process streams at high pressure or temperature, and those containing combustible material, contain energy that can be usefully recovered. Whether it is economic to recover the energy content of a particular stream will depend on the value of the energy that can be usefully extracted and the cost of recovery. The value of the energy will depend on the primary cost of energy at the site. It may be worth while recovering energy from a process stream at a site where energy costs are high but not where the primary energy costs are low. The cost of recovery will be the capital and operating cost of any additional equipment required. If the savings exceed the operating cost, including capital charges, then the energy recovery will usually be worthwhile. Maintenance costs should be included in the operating cost (see Chapter 6).

Some processes, such as air separation, depend on efficient energy recovery for economic operation, and in all processes the efficient utilisation of energy recovery techniques will reduce product cost.

Some of the techniques used for energy recovery in chemical process plants are described briefly in the following sections. The references cited give fuller details of each technique. Miller (1968) gives a comprehensive review of process energy systems; including heat exchange, and power recover from high-pressure fluid streams.

Kenney (1984) reviews the application of thermodynamic principles to energy recovery in the process industries.

3.16.1. Heat exchange

The most common energy-recovery technique is to utilise the heat in a high-temperature process stream to heat a colder stream: saving steam costs; and also cooling water, if the hot stream requires cooling. Conventional shell and tube exchangers are normally used. More total heat-transfer area will be needed, over that for steam heating and water cooling, as the overall driving forces will be smaller.

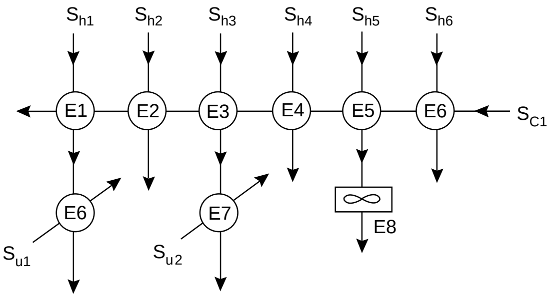
The cost of recovery will be reduced if the streams are located conveniently close.

The amount of energy that can be recovered will depend on the temperature, flow, heat capacity, and temperature change possible, in each stream. A reasonable temperature driving force must be maintained to keep the exchanger area to a practical size. The most efficient exchanger will be the one in which the shell and tube flows are truly countercurrent. Multiple tube pass exchangers are usually used for practical reasons. With multiple tube passes the flow will be part counter-current and part co-current and temperature crosses can occur, which will reduce the efficiency of heat recovery (see Chapter 12).

The hot process streams leaving a reactor or a distillation column are frequently used to preheat the feedstreams.

3.16.2. Heat-exchanger networks

In an industrial process there will be many hot and cold streams and there will be an optimum arrangement of the streams for energy recovery by heat exchange. The problem of synthesising a network of heat exchangers has been studied by many workers,



S_{h1} = residue (360°C)
S_{h2} = reflux stream (260°C)
S_{h3} = heavy gas oil (340°C)
S_{h4} = light gas oil (260°C)
S_{h5} = reflux steam (180°C)
S_{h6} = reflux stream (165°C)
S_{c1} = crude oil (15°C)
S_{u1} and S_{u2} = cooling water (50°C)

Figure 3.11. Typical heat-exchanger network

particularly in respect of optimising heat recovery in crude petroleum distillation. An example of crude preheat train is shown in Figure 3.11. The general problem of the synthesis and optimisation of a network of heat exchangers has been defined by Masso and Rudd (1969).

Consider that there are M hot streams, $S_{hi}(i = 1, 2, 3, \ldots, M)$ to be cooled and N cold streams $S_{cj}(j = 1, 2, 3, \ldots, N)$ to be heated; each stream having an inlet temperature t_f, or an outlet temperature t_0, and a stream heat capacity W_i. There may also be $S_{uk}(k = 1, 2, 3, \ldots, L)$ auxiliary steam heated or water-cooled exchangers.

The problem is to create a minimum cost network of exchangers, that will also meet the design specifications on the required outlet temperature t_0 of each stream. If the strictly mathematical approach is taken of setting up all possible arrangements and searching for the optimum, the problem, even for a small number of exchangers, would require an inordinate amount of computer time. Boland and Linnhoff (1979) point out that for a process with four cold and three hot streams, 2.4×10^{18} arrangements are possible. Most workers have taken a more pragmatic, “heuristic”, approach to the problem, using “rules of thumb” to generate a limited number of feasible networks, which are then evaluated.

Porton and Donaldson (1974) suggest a simple procedure that involves the repeated matching of the hottest stream (highest t_f) against the cold stream with the highest required outlet temperature (highest t_0).

A general survey of computer and manual methods for optimising exchanger networks is given by Nishida *et al*. (1977); see also Siirola (1974).

The design of heat exchanger networks is covered in more detail is Section 3.17.

3.16.3. Waste-heat boilers

If the process streams are at a sufficiently high temperature the heat recovered can be used to generate steam.

Waste-heat boilers are often used to recover heat from furnace flue gases and the process gas streams from high-temperature reactors. The pressure, and superheat temperature, of the stream generated will depend on the temperature of the hot stream and the approach temperature permissible at the boiler exit (see Chapter 12). As with any heat-transfer equipment, the area required will increase as the mean temperature driving force (log mean ΔT) is reduced. The permissible exit temperature may also be limited by process considerations. If the gas stream contains water vapour and soluble corrosive gases, such as HCl or SO_2, the exit gases temperature must be kept above the dew point.

Hinchley (1975) discusses the design and operation of waste heat boilers for chemical plant. Both fire tube and water tube boilers are used. A typical arrangement of a water tube boiler on a reformer furnace is shown in Figure 3.12 and a fire tube boiler in Figure 3.13. The application of a waste-heat boiler to recover energy from the reactor exit streams in a nitric acid plant is shown in Figure 3.14.

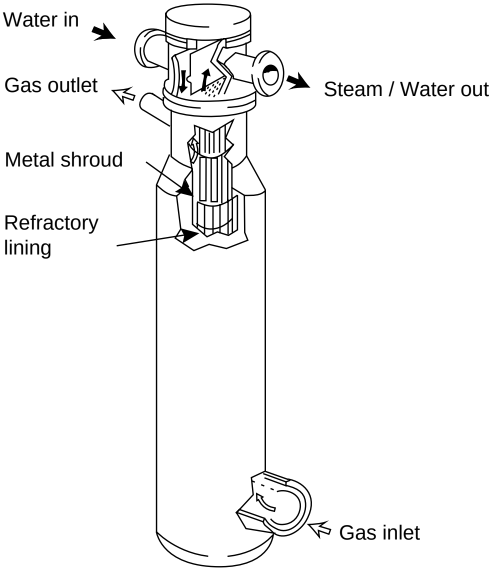


Figure 3.12. Reformed gas waste-heat boiler arrangement of vertical U-tube water-tube boiler (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)

The selection and operation of waste heat boilers for industrial furnaces is discussed in the *Efficient Use of Energy*, Dryden (1975).

3.16.4. High-temperature reactors

If a reaction is highly exothermic, cooling will be needed and, if the reactor temperature is high enough, the heat removed can be used to generate steam. The lowest steam pressure normally used in the process industries is 2.7 bar (25 psig) and steam is normally

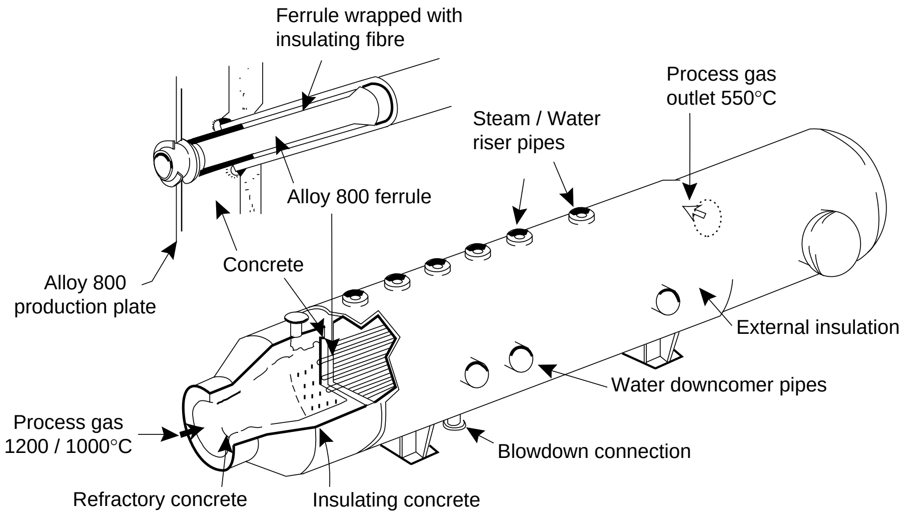
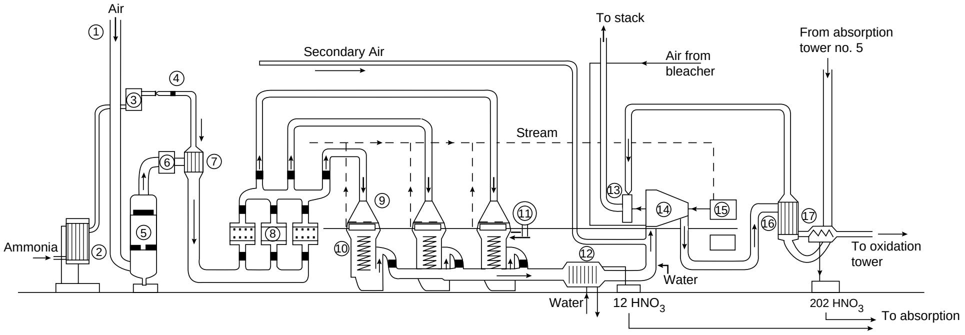


Figure 3.13. Reformed gas waste-heat boiler, principal features of typical natural circulation fire-tube boilers (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)



1. Air entry
2. Ammonia vaporiser
3. Ammonia filter
4. Control valves
5. Air-scrubbing tower
6. Air preheater
7. Gas mixer
8. Gas filters
9. Converters
10. Lamont boilers
11. Steam drum
12. Gas cooler No. 1
13. Exhaust turbine
14. Compressor
15. Steam turbine
16. Heat exchanger
17. Gas cooler No. 2

(From *Nitric Acid Manufacture*, Miles (1961), with permission)

Figure 3.14. Connections of a nitric acid plant, intermediate pressure type

distributed at a header pressure of around 8 bar (100 psig); so any reactor with a temperature above 200°C is a potential steam generator.

Three systems are used:

1. Figure 3.15*a*. An arrangement similar to a conventional water-tube boiler. Steam is generated in cooling pipes within the reactor and separated in a steam drum.

2. Figure 3.15*b*. Similar to the first arrangement but with the water kept at high pressure to prevent vaporisation. The high-pressure water is flashed to steam at lower pressure in a flash drum. This system would give more responsive control of the reactor temperature.
3. Figure 3.15*c*. In this system a heat-transfer fluid, such as Dowtherm (see Perry and Green (1984) and Singh (1985) for details of heat-transfer fluids), is used to avoid the need for high-pressure tubes. The steam is raised in an external boiler.

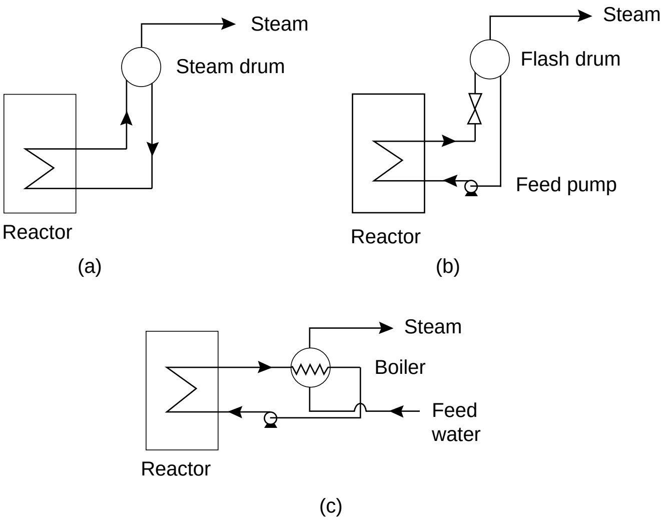


Figure 3.15. Steam generation

3.16.5. Low-grade fuels

The waste products from any process (gases, liquids and solids) which contain significant quantities of combustible material can be used as low-grade fuels; for raising steam or direct process heating. Their use will only be economic if the intrinsic value of the fuel justifies the cost of special burners and other equipment needed to burn the waste. If the combustible content of the waste is too low to support combustion, the waste will have to be supplemented with higher calorific value primary fuels.

Reactor off-gases

The off-gases (vent gas) from reactors, and recycle stream purges are often of high enough calorific value to be used as fuels.

The calorific value of a gas can be calculated from the heats of combustion of its constituents; the method is illustrated in Example 3.14.

Other factors which, together with the calorific value, will determine the economic value of an off-gas as a fuel are the quantity available and the continuity of supply. Waste gases are best used for steam raising, rather than for direct process heating, as this decouples the source from the use and gives greater flexibility.

Example 3.16

Calculation of a waste-gas calorific value

The typical vent-gas analysis from the recycle stream in an oxyhydrochlorination process for the production of dichloroethane (DCE) (British patent BP 1,524,449) is given below, percentages on volume basis.

$$O_2\ 7.96,\quad CO_2 + N_2\ 87.6,\quad CO\ 1.79,\quad C_2H_4\ 1.99,\quad C_2H_6\ 0.1,\quad \text{DCE}\ 0.54$$

Estimate the vent gas calorific value.

Solution

Component calorific values, from Perry and Chilton (1973)

$$\begin{array}{lll} CO & 67.6 \text{ kcal/mol} & = 283 \text{ kJ/mol} \\ C_2H_4 & 372.8 & = 1560.9 \\ C_2H_6 & 337.2 & = 1411.9 \end{array}$$

The value for DCE can be estimated from the heats of formation.

Combustion reaction:

$$C_2H_4Cl_2(g) + 2\tfrac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g) + 2HCl(g)$$

ΔH_f° from Appendix D

$$\begin{aligned} CO_2 &= -393.8 \text{ kJ/mol} \\ H_2O &= -242.0 \\ HCl &= -92.4 \\ \text{DCE} &= -130.0 \\ \Delta H_c^\circ &= \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants} \\ &= [2(-393.8) - 242.0 + 2(-92.4)] - [-130.0] \\ &= \underline{\underline{-1084.4 \text{ kJ}}} \end{aligned}$$

Estimation of vent gas c.v., basis 100 mols.

Component	mols/100 mols		Calorific value (kJ/mol)		Heating value
CO	1.79	×	283.0	=	506.6
C_2H_4	1.99		1560.9		3106.2
C_2H_6	0.1		1411.9		141.2
DCE	0.54		1084.4		585.7
				Total	4339.7

$$\text{Calorific value of vent gas} = \frac{4339.7}{100} = 43.4 \text{ kJ/mol}$$

$$= \frac{43.4}{22.4} \times 10^3 = \underline{\underline{1938 \text{ kJ/m}^3}}(52 \text{ Btu/ft}^3) \text{ at 1 bar, } 0^\circ\text{C}$$

Barely worth recovery, but if the gas has to be burnt to avoid pollution it could be used in an incinerator such as that shown in Figure 3.16, giving a useful steam production to offset the cost of disposal.

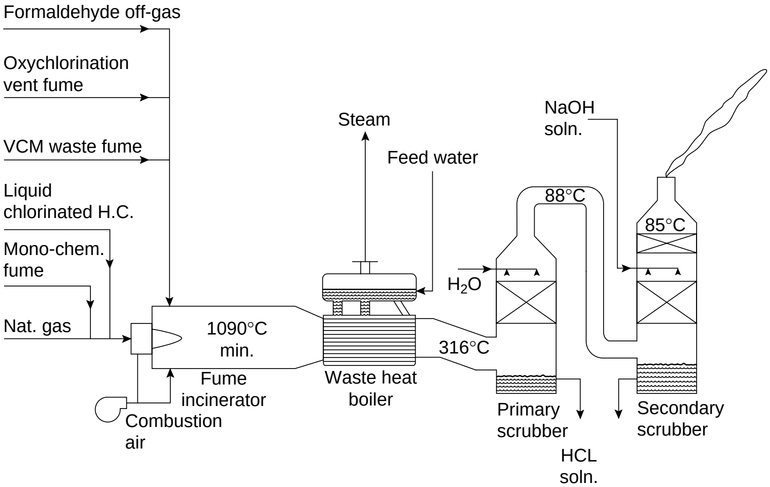


Figure 3.16. Typical incinerator-heat recovery-scrubber system for vinyl-chloride-monomer process waste (Courtesy of John Thurley Ltd.)

Liquid and solid wastes

Combustible liquid and solid waste can be disposed of by burning, which is usually preferred to dumping. Incorporating a steam boiler in the incinerator design will enable an otherwise unproductive, but necessary operation, to save energy. If the combustion products are corrosive, corrosion-resistant materials will be needed, and the flue gases scrubbed to reduce air pollution. An incinerator designed to handle chlorinated and other liquid and solid wastes is shown in Figure 3.16. This incinerator incorporates a steam boiler and a flue-gas scrubber. The disposal of chlorinated wastes is discussed by Santoleri (1973).

Dunn and Tomkins (1975) discuss the design and operation of incinerators for process wastes. They give particular attention to the need to comply with the current clean-air legislation, and the problem of corrosion and erosion of refractories and heat-exchange surfaces.

3.16.6. High-pressure process streams

Where high-pressure gas or liquid process streams are throttled to lower pressures, energy can be recovered by carrying out the expansion in a suitable turbine.

Gas streams

The economic operation of processes which involve the compression and expansion of large quantities of gases, such as ammonia synthesis, nitric acid production and air separation, depends on the efficient recovery of the energy of compression. The energy recovered by expansion is often used to drive the compressors directly; as shown in Figure 3.14. If the gas contains condensible components it may be advisable to consider heating the gas by heat exchange with a higher temperature process stream before expansion. The gas can then be expanded to a lower pressure without condensation and the power generated increased.

An interesting process incorporating an expansion turbine is described by Barlow (1975) who discusses energy recovery in an organic acids plant (acetic and propionic). In this process a thirteen-stage turbo-expander is used to recover energy from the off-gases. The pressure range is deliberately chosen to reduce the off-gases to a low temperature at the expander outlet (-60°C), for use for low-temperature cooling, saving refrigeration.

The energy recoverable from the expansion of a gas can be estimated by assuming polytropic expansion; see Section 3.13.2 and Example 3.17.

The design of turboexpanders for the process industries is discussed by Bloch *et al.* (1982).

Example 3.17

Consider the extraction of energy from the tail gases from a nitric acid adsorption tower, such as that described in Chapter 4, Example 4.4.

Gas composition, kmol/h:

O_2	371.5
N_2	10,014.7
NO	21.9
NO_2	Trace
H_2O	saturated at 250°C

If the gases leave the tower at 6 atm, 25°C, and are expanded to, say, 1.5 atm, calculate the turbine exit gas temperatures without preheat, and if the gases are preheated to 400°C with the reactor off-gas. Also, estimate the power recovered from the preheated gases.

Solution

For the purposes of this calculation it will be sufficient to consider the tail gas as all nitrogen, flow 10,410 kmol/h.

$$P_c = 33.5 \text{ atm}, \quad T_c = 126.2 \text{ K}$$

Figure 3.6 can be used to estimate the turbine efficiency.

$$\text{Exit gas volumetric flow-rate} = \frac{10{,}410}{3600} \times 22.4 \times \frac{1}{1.5}$$
$$\simeq 43 \text{ m}^3/\text{s}$$

from Figure 3.6 $E_P = 0.75$

$$P_r \text{ inlet} = \frac{6}{33.5} = 0.18$$

$$T_r \text{ inlet} = \frac{298}{126.2} = 2.4$$

For these values the simplified equations can be used, equations 3.37*a* and 3.38*a*.

For N_2 $\gamma = 1.4$

$$m = \frac{1.4 - 1}{1.4} \times 0.75 = 0.21$$

$$n = \frac{1}{1 - m} = \frac{1}{1 - 0.21} = 1.27$$

$$\text{without preheat } T_2 = 298 \left(\frac{1.5}{6.0}\right)^{0.21} = 223 \text{ K}$$

$$= \underline{\underline{-50^\circ\text{C}}} \text{ (acidic water would condense out)}$$

$$\text{with preheat } T_2 = 673 \left(\frac{1.5}{6.0}\right)^{0.21} = 503 \text{ K}$$

$$= \underline{\underline{230^\circ\text{C}}}$$

From equation 3.31, work done by gases as a result of polytropic expansion

$$= -1 \times 673 \times 8.314 \times \frac{1.27}{1.27 - 1} \left\{ \left(\frac{1.5}{6.0}\right)^{(1.27-1)/1.27} - 1 \right\}$$

$$= 6718 \text{ kJ/kmol}$$

$$\text{Actual work} = \text{polytropic work} \times E_p$$

$$= 6718 \times 0.75 = \underline{\underline{5039 \text{ kJ/kmol}}}$$

$$\text{Power output} = \text{work/kmol} \times \text{kmol/s} = 5039 \times \frac{10{,}410}{3600}$$

$$= 14{,}571 \text{ kJ/s} = \underline{\underline{14.6 \text{ MW}}}$$

Liquid streams

As liquids are essentially incompressible, less energy is stored in a compressed liquid than a gas. However, it is worth considering power recovery from high-pressure liquid streams ($>$15 bar) as the equipment required is relatively simple and inexpensive. Centrifugal pumps are used as expanders and are often coupled directly to pumps. The design, operation and cost of energy recovery from high-pressure liquid streams is discussed by Jenett (1968), Chada (1984) and Buse (1985).

3.16.7. Heat pumps

A heat pump is a device for raising low grade heat to a temperature at which the heat can be utilised. It pumps the heat from a low temperature source to the higher temperature sink, using a small amount of energy relative to the heat energy recovered.

Heat pumps are increasingly finding applications in the process industries. A typical application is the use of the low grade heat from the condenser of a distillation column to provide heat for the reboiler; see Barnwell and Morris (1982) and Meili (1990). Heat pumps are also used with dryers, heat being abstracted from the exhaust air and used to preheat the incoming air. The use of a heat pump with an evaporator is described in Volume 2, Chapter 14.

Details of the thermodynamic cycles used for heat pumps can be found in most textbooks on Engineering Thermodynamics, and in Reay and MacMichael (1988). In the process industries heat pumps operating on the mechanical vapour compression cycle would normally be used. A vapour compression heat pump applied to a distillation column is shown in Figure 3.17*a*. The working fluid, usually a commercial refrigerant, is fed to the reboiler as a vapour at high pressure and condenses, giving up heat to vaporise the process fluid. The liquid refrigerant from the reboiler is then expanded over a throttle valve and the resulting wet vapour fed to the column condenser. In the condenser the wet refrigerant is dried, taking heat from the condensing process vapour. The refrigerant vapour is then compressed and recycled to the reboiler, completing the working cycle.

If the conditions are suitable the process fluid can be used as the working fluid for the heat pump. This arrangement is shown in Figure 3.17*b*. The hot process liquid at high

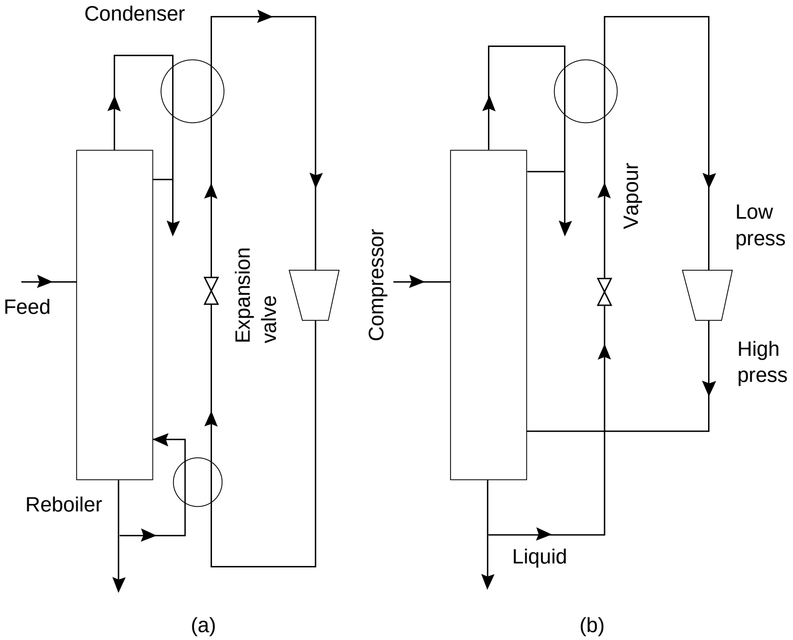


Figure 3.17. Distillation column with heat pump (*a*) Separate refrigerant circuit (*b*) Using column fluid as the refrigerant

pressure is expanded over the throttle value and fed to the condenser, to provide cooling to condense the vapour from the column. The vapour from the condenser is compressed and returned to the base of the column. In an alternative arrangement, the process vapour is taken from the top of the column, compressed and fed to the reboiler to provide heating.

The "efficiency" of a heat pump is measured by the coefficient of performance, *COP*:

$$COP = \frac{\text{energy delivered at higher temperature}}{\text{energy input compressor}}$$

The *COP* will depend principally on the working temperatures.

The economics of the application of heat pumps in the process industries is discussed by Holland and Devotta (1986). Details of the application of heat pumps in a wide range of industries are given by Moser and Schnitzer (1985).

3.17. PROCESS INTEGRATION AND PINCH TECHNOLOGY

Process integration can lead to a substantial reduction in the energy requirements of a process. In recent years much work has been done on developing methods for investigating energy integration and the efficient design of heat exchanger networks; see Gundersen and Naess (1988). One of the most successful and generally useful techniques is that developed by Bodo Linnhoff and other workers: *pinch technology*. The term derives from the fact that in a plot of the system temperatures versus the heat transferred, a *pinch* usually occurs between the hot stream and cold stream curves, see Figure 3.22. It has been shown that the pinch represents a distinct thermodynamic break in the system and that, for minimum energy requirements, heat should not be transferred across the pinch, Linnhoff and Townsend (1982).

In this section the fundamental principles of the pinch technology method for energy integration will be outlined and illustrated with reference to a simple problem. The method and its applications are described fully in a guide published by the Institution of Chemical Engineers, IChemE (1994); see also Douglas (1988).

3.17.1. Pinch technology

The development and application of the method can be illustrated by considering the problem of integrating the utilisation of energy between 4 process streams. Two hot streams which require cooling, and two cold streams that have to be heated. The process data for the streams is set out in Table 3.3. Each stream starts from a source temperature T_s, and is to be heated or cooled to a target temperature T_t. The heat capacity of each stream is shown as CP. For streams where the specific heat capacity can be taken as constant, and there is no phase change, CP will be given by:

$$CP = mCp$$

where m = mass flow-rate, kg/s

Cp = average specific heat capacity between T_s and T_t kJ $\text{kg}^{-1}{}^{\circ}\text{C}^{-1}$

Table 3.3. Data for heat integration problem

Stream number	Type	Heat capacity CP, kW/°C	T_s °C	T_t °C	Heat load kW
1	hot	3.0	180	60	360
2	hot	1.0	150	30	120
3	cold	2.0	20	135	230
4	cold	4.5	80	140	270

The heat load shown in the table is the total heat required to heat, or cool, the stream from the source to target temperature.

The four streams are shown diagrammatically below, Figure 3.18:

There is clearly scope for energy integration between these four streams. Two require heating and two cooling; and the stream temperatures are such that heat can be transferred from the hot to the cold streams. The task is to find the best arrangement of heat exchangers to achieve the target temperatures.

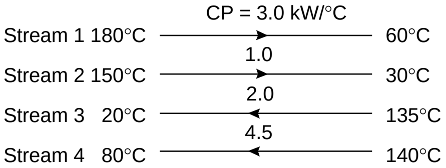


Figure 3.18. Diagrammatic representation of process streams

Simple two-stream problem

Before investigating the energy integration of the four streams shown in Table 3.3, the use of a temperature-enthalpy diagram will be illustrated for a simple problem involving only two streams. The general problem of heating and cooling two streams from source to target temperatures is shown in Figure 3.19. Some heat is exchanged between the streams in the heat exchanger. Additional heat, to raise the cold stream to the target temperature, is provided by the hot utility (usually steam) in the heater; and additional cooling to bring the hot stream to its target temperature, by the cold utility (usually cooling water) in the cooler.

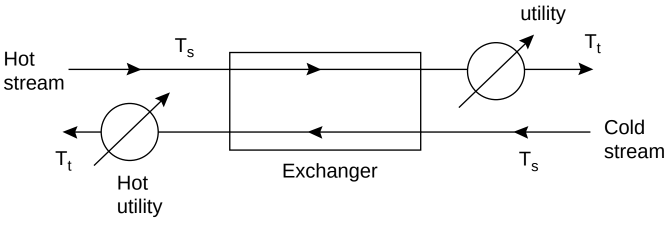


Figure 3.19. Two-stream exchanger problem

In Figure 3.20 the stream temperatures are plotted on the y-axis and the enthalpy change in each stream on the x-axis. For heat to be exchanged a minimum temperature difference must be maintained between the two streams. This is shown as ΔT_{min} on the diagram. The practical minimum temperature difference in a heat exchanger will usually be between 10 and 20°C; see Chapter 12.

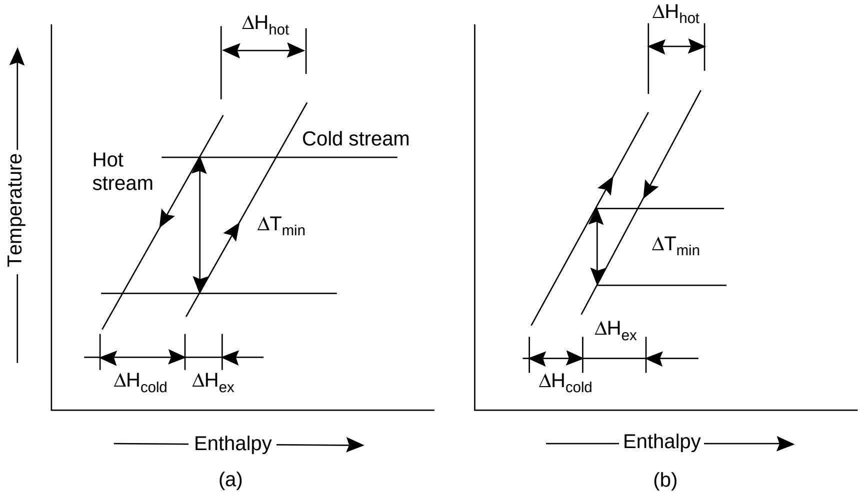


Figure 3.20. Temperature-enthalpy for 2-stream example

The heat transferred between the streams is shown on the diagram as ΔH_{ex}, and the heat transferred from the utilities as ΔH_{cold} and ΔH_{hot}:

$$\Delta H = CP \times (\textit{temperature change})$$

It can be seen by comparing Figure 3.20*a* and *b* that the amount of heating and cooling needed will depend on the minimum temperature difference. Decreasing ΔT_{min} will increase the amount of heat exchanged between the two streams and so decrease the consumption of the hot and cold utilities.

Four stream problem

In Figure 3.21*a* the hot streams given in Table 3.3 are shown plotted on a temperature-enthalpy diagram.

As the diagram shows changes in the enthalpy of the streams, it does not matter where a particular curve is plotted on the enthalpy axis; as long as the curve runs between the correct temperatures. This means that where more than one stream appears in a temperature interval, the stream heat capacities can be added to give the composite curve shown in Figure 3.21*b*.

In Figure 3.22, the composite curve for the hot streams and the composite curve for cold streams are drawn with a minimum temperature difference, the displacement between the curves, of 10°C. This implies that in any of the exchangers to be used in the network the temperature difference between the streams will not be less than 10°C.

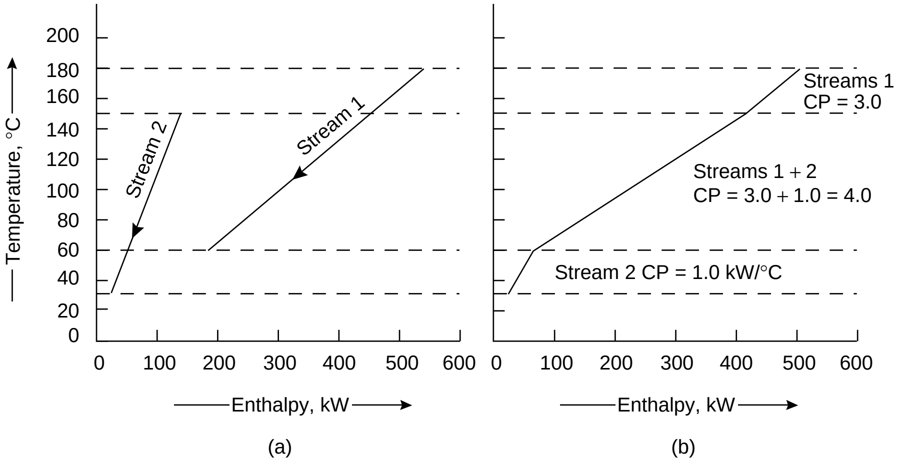


Figure 3.21. Hot stream temperature v. enthalpy (*a*) Separate hot streams (*b*) Composite hot streams

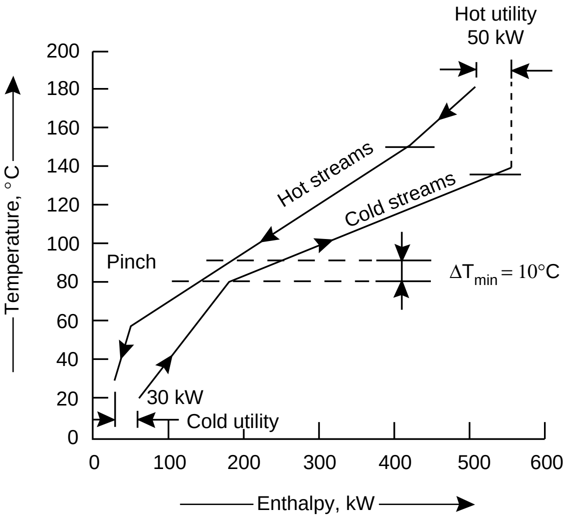


Figure 3.22. Hot and cold stream composite curves

As for the two-stream problem, the displacement of the curves at the top and bottom of the diagram gives the hot and cold utility requirements. These will be the minimum values needed to satisfy the target temperatures. This is valuable information. It gives the designer target values for the utilities to aim for when designing the exchanger network. Any design can be compared with the minimum utility requirements to check if further improvement is possible.

In most exchanger networks the minimum temperature difference will occur at only one point. This is termed the *pinch*. In the problem being considered, the pinch occurs at between 90°C on the hot stream curve and 80°C on the cold stream curve.

Significance of the pinch

The pinch divides the system into two distinct thermodynamic regions. The region above the pinch can be considered a heat sink, with heat flowing into it, from the hot utility, but not out of it. Below the pinch the converse is true. Heat flows out of the region to the cold utility. No heat flows across the pinch.

If a network is designed that requires heat to flow across the pinch, then the consumption of the hot and cold utilities will be greater than the minimum values that could be achieved.

3.17.2. The problem table method

The problem table is the name given by Linnhoff and Flower to a numerical method for determining the pinch temperatures and the minimum utility requirements; Linnhoff and Flower (1978). Once understood, it is the preferred method, avoiding the need to draw the composite curves and manoeuvre the composite cooling curve using, for example, tracing paper or cut-outs, to give the chosen minimum temperature difference on the diagram. The procedure is as follows:

1. Convert the actual stream temperatures T_{act} into interval temperatures T_{int} by subtracting half the minimum temperature difference from the hot stream temperatures, and by adding half to the cold stream temperatures:

$$\text{hot streams } T_{\text{int}} = T_{\text{act}} - \frac{\Delta T_{\text{min}}}{2}$$

$$\text{cold streams } T_{\text{int}} = T_{\text{act}} + \frac{\Delta T_{\text{min}}}{2}$$

The use of the interval temperature rather than the actual temperatures allows the minimum temperature difference to be taken into account. $\Delta T_{\text{min}} = 10^\circ\text{C}$ for the problem being considered; see Table 3.4.

Table 3.4. Interval temperatures for $\Delta T_{\text{min}} = 10^\circ\text{C}$

Stream	Actual temperature		Interval temperature	
1	180	60	175	55
2	150	30	145	25
3	20	135	(25)	140
4	80	140	85	(145)

2. Note any duplicated interval temperatures. These are bracketed in Table 3.4.

3. Rank the interval temperatures in order of magnitude, showing the duplicated temperatures only once in the order; see Table 3.5.

4. Carry out a heat balance for the streams falling within each temperature interval:

For the nth interval:

$$\Delta H_n = (\Sigma CP_c - \Sigma CP_h)(\Delta T_n)$$

where ΔH_n = net heat required in the nth interval
ΣCP_c = sum of the heat capacities of all the cold streams in the interval
ΣCP_h = sum of the heat capacities of all the hot streams in the interval
ΔT_n = interval temperature difference = $(T_{n-1} - T_n)$

See Table 3.6.

Table 3.5. Ranked order of interval temperatures

Rank	Interval ΔT_n °C	Streams in interval
175°C		
145	30	-1
140	5	$4 - (2 + 1)$
85	55	$(3 + 4) - (1 + 2)$
55	30	$3 - (1 + 2)$
25	30	$3 - 2$

Note: Duplicated temperatures are omitted. The interval ΔT and streams in the intervals are included as they are needed for Table 3.6.

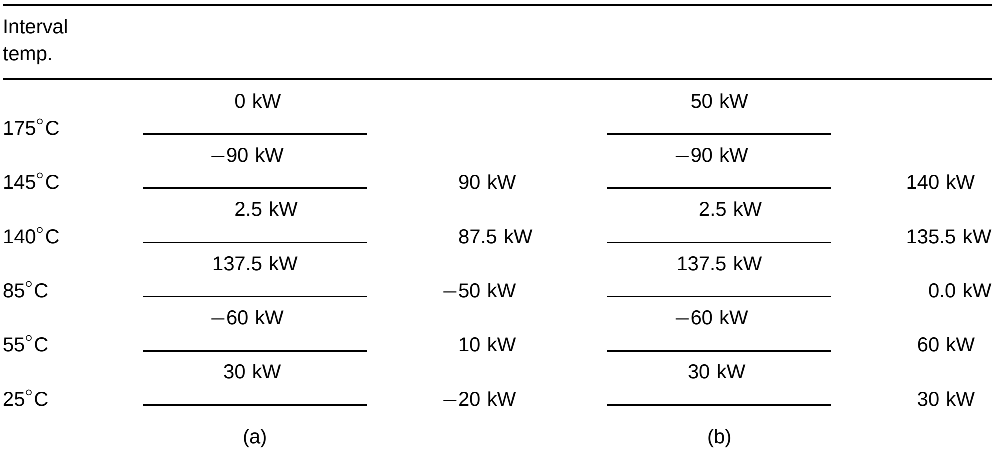
Table 3.6. Problem table

Interval	Interval temp. °C	ΔT_n °C	$\Sigma CP_c - \Sigma CP_h{}^*$ kW/°C	ΔH kW	Surplus or Deficit
	175				
1	145	30	−3.0	−90	s
2	140	5	0.5	2.5	d
3	85	55	2.5	137.5	d
4	55	30	−2.0	−60	s
5	25	30	1.0	30	d

*Note: The streams in each interval are given in Table 3.5.

5. "Cascade" the heat surplus from one interval to the next down the column of interval temperatures; Figure 3.23*a*.

Cascading the heat from one interval to the next implies that the temperature difference is such that the heat can be transferred between the hot and cold streams. The presence



From (b) pinch occurs at interval temperature = 85°C.

Figure 3.23. Heat cascade

of a negative value in the column indicates that the temperature gradient is in the wrong direction and that the exchange is not thermodynamically possible.

This difficulty can be overcome if heat is introduced into the top of the cascade:

6. Introduce just enough heat to the top of the cascade to eliminate all the negative values; see Figure 3.23*b*.

Comparing the composite curve, Figure 3.22, with Figure 3.23*b* shows that the heat introduced to the cascade is the minimum hot utility requirement and the heat removed at the bottom is the minimum cold utility required. The pinch occurs in Figure 3.23*b* where the heat flow in the cascade is zero. This is as would be expected from the rule that for minimum utility requirements no heat flows across the pinch. In Figure 3.23*b* the pinch temperatures are 80 and 90°C, as was found using the composite stream curves.

It is not necessary to draw up a separate cascade diagram. This was done in Figure 3.23 to illustrate the principle. The cascaded values can be added to the problem table as two additional columns; see example 3.16.

Summary

For maximum heat recovery and minimum use of utilities:

1. Do not transfer heat across the pinch
2. Do not use hot utilities below the pinch
3. Do not use cold utilities above the pinch

3.17.3. The heat exchanger network

Grid representation

It is convenient to represent a heat exchanger network as a grid; see Figure 3.24. The process streams are drawn as horizontal lines, with the stream numbers shown in square boxes. Hot streams are drawn at the top of the grid, and flow from left to right. The cold streams are drawn at the bottom, and flow from right to left. The stream heat capacities CP are shown in a column at the end of the stream lines.

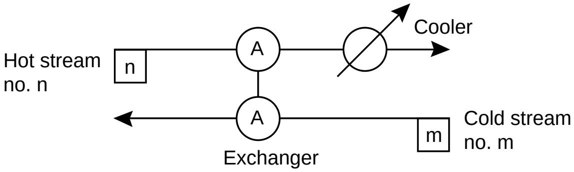


Figure 3.24. Grid representation

Heat exchangers are drawn as two circles connected by a vertical line. The circles connect the two streams between which heat is being exchanged; that is, the streams that would flow through the actual exchanger. Heater and coolers are drawn as a single circle, connected to the appropriate utility.

Network design for maximum energy recovery

The analysis carried out in Figure 3.22, and Figure 3.23, has shown that the minimum utility requirements for the problem set out in Table 3.3 are 50 kW of the hot and 30 kW of the cold utility; and that the pinch occurs where the cold streams are at 80 and the hot 90°C.

The grid representation of the streams is shown in Figure 3.25. The vertical dotted lines represent the pinch and separate the grid into the regions above and below the pinch.

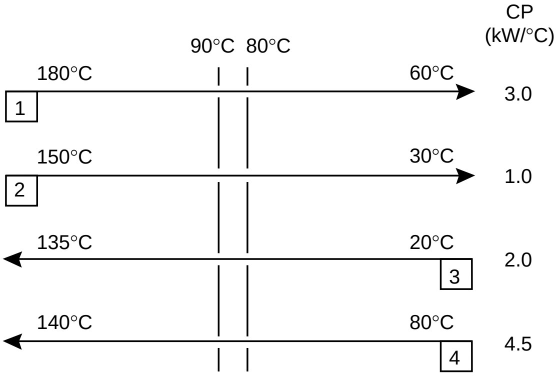


Figure 3.25. Grid for 4 stream problem

For maximum energy recovery (minimum utility consumption) the best performance is obtained if no cooling is used above the pinch. This means that the hot streams above the pinch should be brought to the pinch temperature solely by exchange with the cold streams. The network design is therefore started at the pinch; finding feasible matches between streams to fulfil this aim. In making a match adjacent to the pinch the heat capacity *CP* of the hot stream should be equal to or less than that of the cold stream. This is to ensure that the minimum temperature difference between the curves is maintained. The slope of a line on the temperature-enthalpy diagram is equal to the reciprocal of the heat capacity. So, above the pinch the lines will converge if CP_{hot} exceeds CP_{cold} and as the streams start with a separation at the pinch equal to $\Delta T_{\min}$, the minimum temperature condition would be violated.

Below the pinch the procedure is the same; the aim being to bring the cold streams to the pinch temperature by exchange with the hot streams. For streams adjacent to the pinch the criterion for matching streams is that the heat capacity of the cold stream must be equal to or greater than the hot stream, to avoid breaking the minimum temperature difference condition.

The network design above the pinch

$$CP_{\text{hot}} \leq CP_{\text{cold}}$$

1. Applying this condition at the pinch, stream 1 can be matched with stream 4, but not with 3.

Matching streams 1 and 4 and transferring the full amount of heat required to bring stream 1 to the pinch temperature gives:

$$\Delta H_{\text{ex}} = CP(T_s - T_{\text{pinch}})$$

$$\Delta H_{\text{ex}} = 3.0(180 - 90) = 270 \text{ kW}$$

This will also satisfy the heat load required to bring stream 4 to its target temperature:

$$\Delta H_{\text{ex}} = 4.5(140 - 80) = 270 \text{ kW}$$

2. Stream 2 can be matched with stream 3, whilst satisfying the heat capacity restriction. Transferring the full amount to bring stream 3 to the pinch temperature:

$$\Delta H_{\text{ex}} = 1.0(150 - 90) = 60 \text{ kW}$$

3. The heat required to bring stream 3 to its target temperature, from the pinch temperature, is:

$$\Delta H = 2.0(135 - 80) = 110 \text{ kW}$$

So a heater will have to be included to provide the remaining heat load:

$$\Delta H_{\text{hot}} = 110 - 60 = 50 \text{ kW}$$

This checks with the value given by the problem table, Figure 3.23*b*.

The proposed network design above the pinch is shown in Figure 3.26.

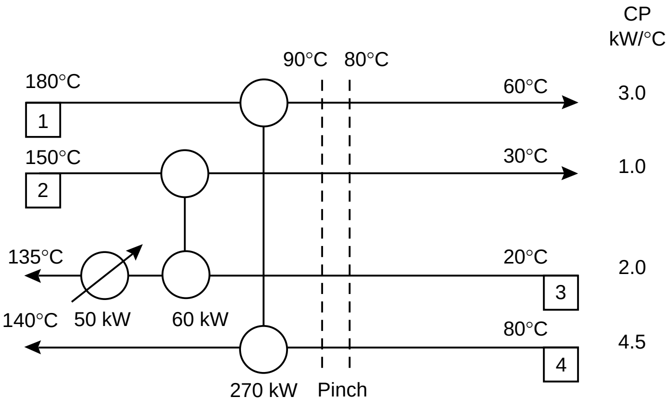


Figure 3.26. Network design above pinch

Network design below the pinch

$$CP_{\text{hot}} \geq CP_{\text{cold}}$$

4. Stream 4 is at the pinch temperature, $T_s = 80^\circ\text{C}$.

5. A match between stream 1 and 3 adjacent to the pinch will satisfy the heat capacity restriction but not one between streams 2 and 3. So 1 is matched with 3 transferring the full amount to bring stream 1 to its target temperature; transferring:

$$\Delta H_{\text{ex}} = 3.0(90 - 60) = 90 \text{ kW}$$

6. Stream 3 requires more heat to bring it to the pinch temperature; amount needed:

$$\Delta H = 2.0(80 - 20) - 90 = 30 \text{ kW}$$

This can be provided from stream 2, as the match will now be away from the pinch. The rise in temperature of stream 3 will be given by:

$$\Delta T = \Delta H / CP$$

So transferring 30 kW will raise the temperature from the source temperature to:

$$20 + 30/2.0 = 35^\circ\text{C}$$

and this gives a stream temperature difference on the outlet side of the exchanger of:

$$90 - 35 = 55^\circ\text{C}$$

So the minimum temperature difference condition, 10°C, will not be violated by this match.

7. Stream 2 will need further cooling to bring it to its target temperature, so a cooler must be included; cooling required.

$$\Delta H_{\text{cold}} = 1.0(90 - 30) - 30 = 30 \text{ kW}$$

Which is the amount of the cold utility predicted by the problem table.

The proposed network for maximum energy recovery is shown in Figure 3.27.

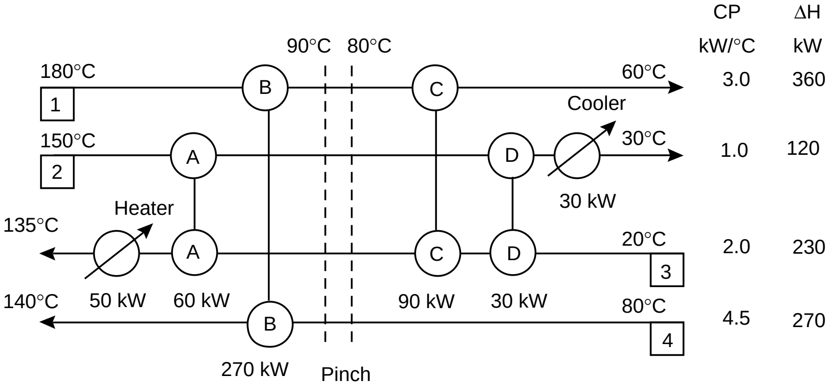


Figure 3.27. Proposed heat exchanger network $\Delta T_{\text{min}} = 10^\circ\text{C}$

Stream splitting

If the heat capacities of streams are such that it is not possible to make a match at the pinch without violating the minimum temperature difference condition, then the heat capacity can be altered by splitting a stream. Dividing the stream will reduce the mass flow-rates in each leg and hence the heat capacities. This is illustrated in Example 3.16.

Guide rules for stream matching and splitting are given in the Institution of Chemical Engineers Guide, IChemE (1994).

Summary

The heuristics (guide rules) for devising a network for maximum heat recovery are given below:

1. Divide the problem at the pinch.
2. Design away from the pinch.
3. Above the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_{\text{hot}} \leq CP_{\text{cold}}$$

4. Below the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_{\text{hot}} \geq CP_{\text{cold}}$$

5. If the stream matching criteria can not be satisfied split a stream.
6. Maximise the exchanger heat loads.
7. Supply external heating only above the pinch, and external cooling only below the pinch.

3.17.4. Minimum number of exchangers

The network shown in Figure 3.27 was designed to give the maximum heat recovery, and will therefore give the minimum consumption, and cost, of the hot and cold utilities.

This will not necessarily be the optimum design for the network. The optimum design will be that which gives the lowest total annual costs: taking into account the capital cost of the system, in addition to the utility and other operating costs. The number of exchangers in the network, and their size, will determine the capital cost.

In Figure 3.27 it is clear that there is scope for reducing the number of exchangers. Exchanger D can be deleted and the heat loads of the cooler and heater increased to bring streams 2 and 3 to their target temperatures. Heat would cross the pinch and the consumption of the utilities would be increased. Whether the revised network would be better, more economic, would depend on the relative cost of capital and utilities. For any network there will be an optimum design that gives the least annual cost: capital charges plus utility and other operating costs. The estimation of capital and operating costs are covered in Chapter 6.

To find the optimum design it will be necessary to cost a number of alternative designs, seeking a compromise between the capital costs, determined by the number and size of the exchangers, and the utility costs, determined by the heat recovery achieved.

For simple networks Holmann (1971) has shown that the minimum number of exchangers is given by:

$$Z_{\min} = N' - 1 \tag{3.41}$$

where $Z_{\min}$ = minimum number of exchangers needed, including heaters and coolers
N' = the number of streams, including the utilities

For complex networks a more general expression is needed to determine the minimum number of exchangers:

$$Z_{\min} = N' + L' - S \tag{3.42}$$

where L' = the number of internal loops present in the network
S = the number of independent branches (subsets) that exist in the network.

A loop exists where a close path can be traced through the network. There is a loop in the network shown in Figure 3.27. The loop is shown in Figure 3.28. The presence of a loop indicates that there is scope for reducing the number of exchangers.

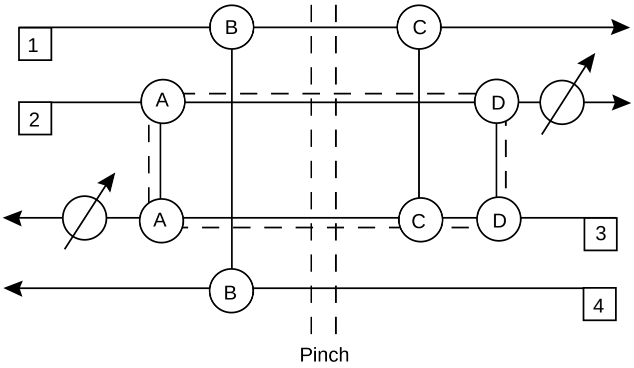


Figure 3.28. Loop in network

For a full discussion of equation 3.42 and its applications see Linnhoff *et al*. (1979), and IChemE (1994).

In summary, to seek the optimum design for a network:

1. Start with the design for maximum heat recovery. The number of exchangers needed will be equal to or less than the number for maximum energy recovery.
2. Identify loops that cross the pinch. The design for maximum heat recovery will usually contain loops.
3. Starting with the loop with the least heat load, break the loops by adding or subtracting heat.
4. Check that the specified minimum temperature difference $\Delta T_{\min}$ has not been violated, and revise the design as necessary to restore the $\Delta T_{\min}$.
5. Estimate the capital and operating costs, and the total annual cost.
6. Repeat the loop breaking and network revision to find the lowest cost design.
7. Consider the safety, operability and maintenance aspects of the proposed design.

Importance of the minimum temperature difference

In a heat exchanger, the heat-transfer area required to transfer a specified heat load is inversely proportional to the temperature difference between the streams; see Chapter 12.

This means that the value chosen for ΔT_{min} will determine the size of the heat exchangers in a network. Reducing ΔT_{min} will increase the heat recovery, decreasing the utility consumption and cost, but at the expense of an increase in the exchanger size and capital cost.

For any network there will be a best value for the minimum temperature difference that will give the lowest total annual costs. The effect of changes in the specified ΔT_{min} need to be investigated when optimising a heat recovery system.

3.17.5. Threshold problems

Problems that show the characteristic of requiring only either a hot utility or a cold utility (but not both) over a range of minimum temperature differences, from zero up to a threshold value, are known as threshold problems. A threshold problem is illustrated in Figure 3.29.

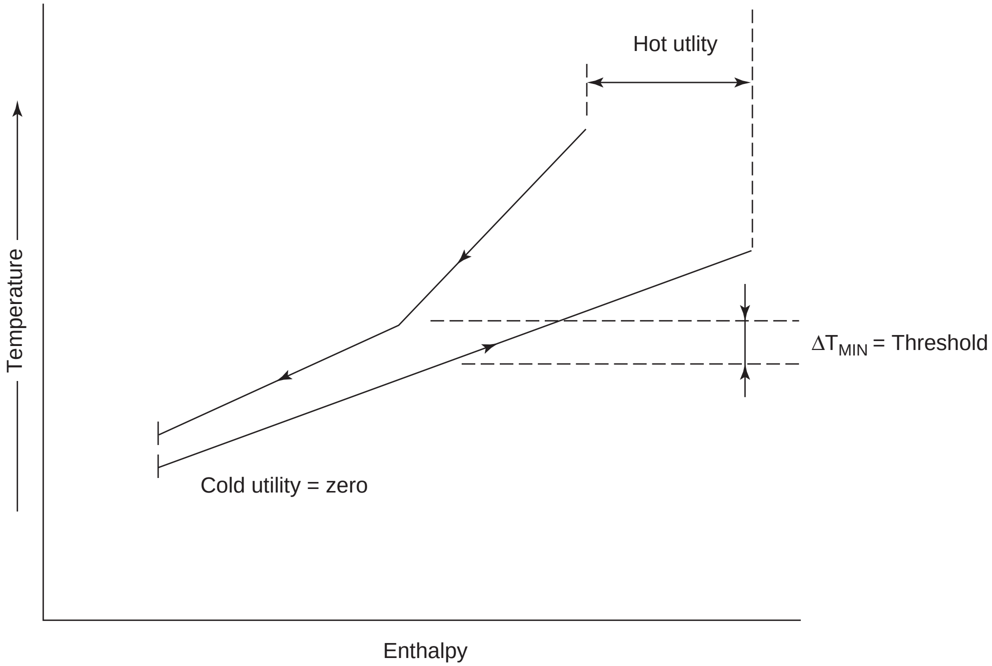


Figure 3.29. Threshold problem

To design the heat exchanger network for a threshold problem, it is normal to start at the most constrained point. The problem can often be treated as one half of a problem exhibiting a pinch.

Threshold problems are encountered in the process industries. A pinch can be introduced in such problems if multiple utilities are used, as in the recovery of heat to generate steam.

The procedures to follow in the design of threshold problems are discussed by Smith (1995) and IChemE (1994).

3.17.6. Multiple pinches and multiple utilities

The use of multiple utilities can lead to more than one pinch in a problem. In introducing multiple utilities the best strategy is to generate at the highest level and use at the lowest level. For a detailed discussion of this type of problem refer to Smith (1995) and IChemE (1994).

3.17.7. Process integration: integration of other process operations

The use of the pinch technology method in the design of heat exchanger networks has been outlined in Sections 3.17.1 to 3.17.6. The method can also be applied to the integration of other process units; such as, separation column, reactors, compressors and expanders, boilers and heat pumps. The wider applications of pinch technology are discussed in the Institution of Chemical Engineers Guide, IChemE (1994) and by Linnhoff *et al*. (1983), and Townsend and Linnhoff (1982), (1983), (1993).

Some guide rules for process integration:

1. Install combined heat and power (co-generation) systems across the pinch; see Chapter 14.
2. Install heat engines either above or below the pinch.
3. Install distillation columns above or below the pinch.
4. Install heat pumps across the pinch; see Section 3.16.7.

The techniques of process integration have been expanded for use in optimising mass transfer operations, and have been applied in waste reduction, water conservation, and pollution control, see Dunn and El-Halwagi (2003).

Example 3.18

Determine the pinch temperatures and the minimum utility requirements for the streams set out in the table below, for a minimum temperature difference between the streams of 20°C. Devise a heat exchanger network to achieve the maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source temp. °C	Target temp. °C	Heat load kW
1	hot	40.0	180	40	5600
2	hot	30.0	150	60	2700
3	cold	60.0	30	180	9000
4	cold	20.0	80	160	1600

Solution

The construction of the problem table to find the minimum utility requirement and the pinch temperature is facilitated by using a spreadsheet. The calculations in each cell are repetitive and the formula can be copied from cell to cell using the cell copy commands.

The spreadsheet AS-EASY-AS (TRIUS Inc) was used to develop the tables for this problem.

First calculate the interval temperatures, for $\Delta T_{\min} = 20°\text{C}$

$$\text{hot streams } T_{\text{int}} = T_{\text{act}} - 10°\text{C}$$

$$\text{cold streams } T_{\text{int}} = T_{\text{act}} + 10°\text{C}$$

	Actual temp. °C		Interval temp. °C	
Stream	Source	Target	Source	Target
1	180	40	170	30
2	150	60	140	50
3	30	180	40	190
4	80	160	90	(170)

Next rank the interval temperatures, ignoring any duplicated values. Show which streams occur in each interval to aid in the calculation of the combined stream heat capacities:

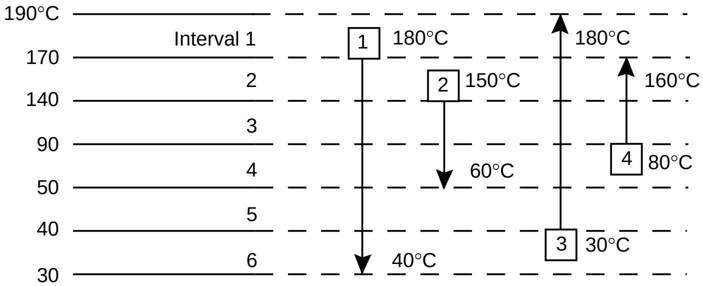


Figure 3.30. Intervals and streams

Now set out the problem table:

Interval	Interval temp. °C	ΔT °C	$\Sigma CP_c \times \Sigma CP_h$ kW/°C	ΔH kW	Cascade	
	190				0	2900
1	170	20	60.0	1200	−1200	1700
2	140	30	40.0	1200	−2400	500
3	90	50	10.0	500	−2900	0
4	50	40	−10.0	−400	−2500	400
5	40	10	20.0	200	−2700	200
6	30	10	−40.0	−400	−2300	600

In the last column 2900 kW of heat have been added to eliminate the negative values in the previous column.

So, the hot utility requirement is 2900 kW and the cold, the bottom value in the column, is 600 kW.

The pinch occurs where the heat transferred is zero, that is at interval number 3, 90°C.

So at the pinch hot streams will be at:

$$90 + 10 = 100^\circ\text{C}$$

and the cold at:

$$90 - 10 = 80^\circ\text{C}$$

To design the network for maximum energy recovery: start at the pinch and match streams following the rules on stream heat capacities for matches adjacent to the pinch. Where a match is made: transfer the maximum amount of heat.

The proposed network is shown in Figure 3.31.

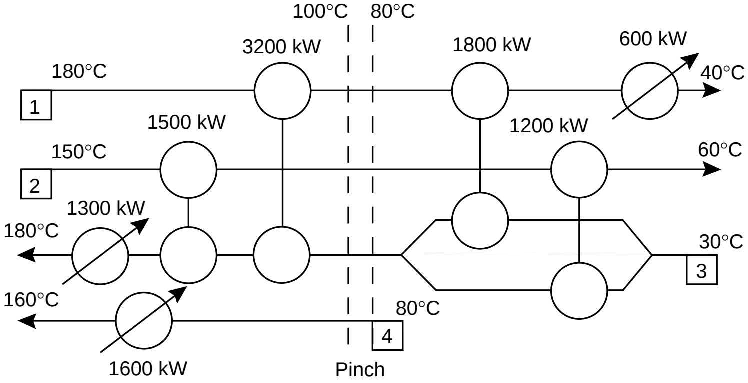


Figure 3.31. Network, example 3.17

The methodology followed in devising this network was:

Above pinch

1. $CP_{\text{hot}} \leq CP_{\text{cold}}$
2. Can match stream 1 and 2 with stream 3 but not with stream 4.
3. Check the heat available in bringing the hot streams to the pinch temperature.
   stream 1 $\Delta H = 40.0(180 - 100) = 3200$ kW
   stream 2 $\Delta H = 30.0(150 - 100) = 1500$ kW
4. Check the heat required to bring the cold streams from the pinch temperature to their target temperatures.
   stream 3 $\Delta H = 60.0(180 - 80) = 6000$ kW
   stream 4 $\Delta H = 20.0(160 - 80) = 1600$ kW
5. Match stream 1 with 3 and transfer 3200 kW, that satisfies (ticks off) stream 1.
6. Match stream 2 with 3 and transfer 1500 kW, that ticks off stream 2.
7. Include a heater on stream 3 to provide the balance of the heat required:

$$\Delta H_{\text{hot}} = 6000 - 4700 = 1300 \text{ kW}$$

8. Include a heater on stream 4 to provide heat load required, 1600 kW.

Below pinch

9. $CP_{\text{hot}} \geq CP_{\text{cold}}$
10. Note that stream 4 starts at the pinch temperature so can not provide any cooling below the pinch.
11. Cannot match stream 1 or 2 with stream 3 at the pinch.
12. So, split stream 3 to reduce *CP*. An even split will allow both streams 1 and 2 to be matched with the split streams adjacent to the pinch, so try this:
13. Check the heat available from bringing the hot streams from the pinch temperature to their target temperatures.
    stream 1 $\Delta H = 40.0(100 - 40) = 2400$ kW
    stream 2 $\Delta H = 30.0(100 - 60) = 1200$ kW
14. Check the heat required to bring the cold streams from their source temperatures to the pinch temperature:
    stream 3 $\Delta H = 60.0(80 - 30) = 3000$ kW
    stream 4 is at the pinch temperature.
15. Note that stream 1 can not be brought to its target temperature of 40°C by full interchange with stream 3 as the source temperature of stream 3 is 30°C, so ΔT_{min} would be violated. So transfer 1800 kW to one leg of the split stream 3.
16. Check temperature at exit of this exchanger:

$$\text{Temp out} = 100 - \frac{1800}{40} = 55^\circ\text{C, satisfactory}$$

17. Provide cooler on stream 1 to bring it to its target temperature, cooling needed:

$$\Delta H_{\text{cold}} = 2400 - 1800 = 600 \text{ kW}$$

18. Transfer the full heat load from stream 2 to second leg of stream 3; this satisfies both streams.

Note that the heating and cooling loads, 2900 kW and 600 kW, respectively, match those predicted from the problem table.

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3.19. NOMENCLATURE

		Dimensions in **MLT**θ
a	Constant in specific heat equation (equation 3.13)	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
b	Constant in specific heat equation (equation 3.13)	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-2}$
CP	Stream heat capacity	$\mathbf{M}\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_p	Specific heat at constant pressure	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_{p_a}	Specific heat component *a*	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_{p_b}	Specific heat component *b*	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_{p_c}	Specific heat component *c*	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_{p_m}	Mean specific heat	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$
C_{p_1}	Specific heat first phase	$\mathbf{L}^2\mathbf{T}^{-2}\theta^{-1}$

C_{p_2}	Specific heat second phase	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
C_v	Specific heat at constant volume	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
C_p^o	Ideal gas state specific heat	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
c	Constant in specific heat equation (equation 3.13)	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-3}$ or $\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1/2}$
ΣCP_c	Sum of heat capacities of cold streams	$\mathbf{ML}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
ΣCP_h	Sum of heat capacities of hot streams	$\mathbf{ML}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
E_e	Efficiency, electric motors	—
E_p	Polytropic efficiency, compressors and turbines	—
F	Force	$\mathbf{MLT}^{-2}$
g	Gravitational acceleration	$\mathbf{LT}^{-2}$
H	Enthalpy	$\mathbf{ML}^2\mathbf{T}^{-2}$
H_a	Specific enthalpy of component *a*	$\mathbf{L}^2\mathbf{T}^{-2}$
H_b	Specific enthalpy of component *b*	$\mathbf{L}^2\mathbf{T}^{-2}$
H_d	Enthalpy top product stream (Example 3.1)	$\mathbf{ML}^2\mathbf{T}^{-3}$
H_f	Enthalpy feed stream (Example 3.1)	$\mathbf{ML}^2\mathbf{T}^{-3}$
H_T	Specific enthalpy at temperature T	$\mathbf{L}^2\mathbf{T}^{-2}$
H_w	Enthalpy bottom product stream (Example 3.1)	$\mathbf{ML}^2\mathbf{T}^{-3}$
ΔH	Change in enthalpy	$\mathbf{ML}^2\mathbf{T}^{-2}$
ΔH_{cold}	Heat transfer from cold utility	$\mathbf{ML}^2\mathbf{T}^{-3}$
ΔH_{ex}	Heat transfer in exchanger	$\mathbf{ML}^2\mathbf{T}^{-3}$
ΔH_{hot}	Heat transfer from hot utility	$\mathbf{ML}^2\mathbf{T}^{-3}$
ΔH_n	Heat available in nth interval	$\mathbf{ML}^2\mathbf{T}^{-3}$
$-\Delta H_{m,t}$	Heat of mixing at temperature t	$\mathbf{L}^2\mathbf{T}^{-2}$
$-\Delta H_{r,t}$	Heat of reaction at temperature t	$\mathbf{L}^2\mathbf{T}^{-2}$
$-\Delta H_c^\circ$	Standard heat of combustion	$\mathbf{L}^2\mathbf{T}^{-2}$
ΔH_f°	Standard enthalpy of formation	$\mathbf{L}^2\mathbf{T}^{-2}$
$-\Delta H_m^\circ$	Standard heat of mixing	$\mathbf{L}^2\mathbf{T}^{-2}$
$-\Delta H_r^\circ$	Standard heat of reaction	$\mathbf{L}^2\mathbf{T}^{-2}$
L	Number of auxiliary streams, heat exchanger networks	—
L'	Number of internal loops in network	—
l	Distance	$\mathbf{L}$
M	Number of hot streams, heat-exchanger networks	—
M	Molecular mass (weight)	—
m	Polytropic temperature exponent	—
m	Mass	$\mathbf{M}$
m	Mass flow-rate	$\mathbf{MT}^{-1}$
N	Number of cold streams, heat-exchanger networks	—
N'	Number of streams	—
n	Expansion or compression index (equation 3.30)	—
P	Pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
P_i	Inter-stage pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
P_r	Reduced pressure	—
P_1	Initial pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
P_2	Final pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
Q	Heat transferred across system boundary	$\mathbf{ML}^2\mathbf{T}^{-2}$ or $\mathbf{ML}^2\mathbf{T}^{-3}$
Q_b	Reboiler heat load (Example 3.1)	$\mathbf{ML}^2\mathbf{T}^{-3}$
Q_c	Condenser heat load (Example 3.1)	$\mathbf{ML}^2\mathbf{T}^{-3}$
Q_p	Heat added (or subtracted) from a system	$\mathbf{ML}^2\mathbf{T}^{-2}$ or $\mathbf{ML}^2\mathbf{T}^{-3}$
Q_r	Heat from reaction	$\mathbf{ML}^2\mathbf{T}^{-2}$ or $\mathbf{ML}^2\mathbf{T}^{-3}$
Q_s	Heat generated in the system	$\mathbf{ML}^2\mathbf{T}^{-2}$ or $\mathbf{ML}^2\mathbf{T}^{-3}$
$\mathbf{R}$	Universal gas constant	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
S	Number of independent branches	—
$\mathbf{S}_{cj}$	Cold streams, heat-exchanger networks	—
S_{hi}	Hot streams, heat-exchanger networks	—
S_{uk}	Auxiliary streams, heat-exchanger networks	—
T	Temperature, absolute	$\boldsymbol{\theta}$
T_{act}	Actual stream temperature	$\boldsymbol{\theta}$

T_d	Datum temperature for enthalpy calculations	$\boldsymbol{\theta}$
T_{int}	Interval temperature	$\boldsymbol{\theta}$
T_n	Temperature in nth interval	$\boldsymbol{\theta}$
T_p	Phase-transition temperature	$\boldsymbol{\theta}$
T_r	Reduced temperature	—
T_s	Source temperature	$\boldsymbol{\theta}$
T_t	Target temperature	$\boldsymbol{\theta}$
ΔT_{min}	Minimum temperature difference in heat exchanger	$\boldsymbol{\theta}$
ΔT_n	Internal temperature difference	$\boldsymbol{\theta}$
t	Temperature, relative scale	$\boldsymbol{\theta}$
t	Time	$\mathbf{T}$
t_r	Reference temperature, mean specific heat	$\boldsymbol{\theta}$
t_f	Inlet-stream temperatures, heat-exchanger networks	$\boldsymbol{\theta}$
t_o	Outlet-stream temperatures, heat-exchanger networks	$\boldsymbol{\theta}$
U	Internal energy per unit mass	$\mathbf{L}^2\mathbf{T}^{-2}$
u	Velocity	$\mathbf{L}\mathbf{T}^{-1}$
V_1	Initial volume	$\mathbf{L}^3$
V_2	Final volume	$\mathbf{L}^3$
v	Volume per unit mass	$\mathbf{M}^{-1}\mathbf{L}^3$
X	Compressibility function defined by equation 3.33	—
x	Distance	$\mathbf{L}$
x_a	Mol fraction component *a* in a mixture	—
x_b	Mol fraction component *b* in a mixture	—
x_c	Mol fraction component *c* in a mixture	—
Y	Compressibility function defined by equation 3.34	—
W	Work per unit mass	$\mathbf{L}^2\mathbf{T}^{-2}$
W_i	Heat capacity of streams in a heat-exchanger network	$\mathbf{M}\mathbf{L}^2\mathbf{T}^{-3}\boldsymbol{\theta}^{-1}$
Z	Compressibility factor	—
z	Height above datum	$\mathbf{L}$
Z_{min}	Minimum number of heat exchangers in network	—

3.20. PROBLEMS

3.1. A liquid stream leaves a reactor at a pressure of 100 bar. If the pressure is reduced to 3 bar in a turbine, estimate the maximum theoretical power that could be obtained from a flow-rate of 1000 kg/h. The density of the liquid is 850 kg/m^3.

3.2. Calculate the specific enthalpy of water at a pressure of 1 bar and temperature of 200 °C. Check your value using steam tables. The specific heat capacity of water can be calculated from the equation:
$C_p = 4.2 - 2 \times 10^{-3} t$; where t is in °C and C_p in kJ/kg.
Take the other data required from Appendix C.

3.3. A gas produced as a by-product from the carbonisation of coal has the following composition, mol per cent: carbon dioxide 4, carbon monoxide 15, hydrogen 50, methane 12, ethane 2, ethylene 4, benzene 2, balance nitrogen. Using the data given in Appendix C, calculate the gross and net calorific values of the gas. Give your answer in MJ/m^3, at standard temperature and pressure.

3.4. In the manufacture of aniline, liquid nitrobenzene at 20 °C is fed to a vaporiser where it is vaporised in a stream of hydrogen. The hydrogen stream is at 30 °C, and the vaporiser operates at 20 bar. For feed-rates of 2500 kg/h nitrobenzene and 366 kg/h hydrogen, estimate the heat input required. The nitrobenzene vapour is not superheated.

3.5. Aniline is produced by the hydrogenation of nitrobenzene. The reaction takes place in a fluidised bed reactor operating at 270 °C and 20 bar. The excess heat of reaction is removed by a heat transfer fluid passing through tubes in the fluidised bed. Nitrobenzene vapour and hydrogen enter the reactor at a temperature of 260 °C. A typical reactor off-gas composition, mol per cent, is: aniline 10.73, cyclo-hexylamine 0.11, water 21.68, nitrobenzene 0.45, hydrogen 63.67, inerts (take as nitrogen) 3.66. Estimate the heat removed by the heat transfer fluid, for a feed-rate of nitrobenzene to the reactor of 2500 kg/h.

The specific heat capacity of nitrobenzene can be estimate using the methods given in Chapter 8. Take the other data required from Appendix C.

3.6. Hydrogen chloride is produced by burning chlorine with an excess of hydrogen. The reaction is highly exothermic and reaches equilibrium very rapidly. The equilibrium mixture contains approximately 4 per cent free chlorine but this is rapidly combined with the excess hydrogen as the mixture is cooled. Below 200°C the conversion of chlorine is essentially complete.

The burner is fitted with a cooling jacket, which cools the exit gases to 200 °C. The gases are further cooled, to 50 °C, in an external heat exchanger.

For a production rate of 10,000 tonnes per year of hydrogen chloride, calculate the heat removed by the burner jacket and the heat removed in the external cooler. Take the excess hydrogen as 1 per cent over stoichiometric. The hydrogen supply contains 5 per cent inerts (take as nitrogen) and is fed to the burner at 25°C. The chlorine is essentially pure and is fed to the burner as a saturated vapour. The burner operates at 1.5 bar.

3.7. A supply of nitrogen is required as an inert gas for blanketing and purging vessels. After generation, the nitrogen is compressed and stored in a bank of cylinders, at a pressure of 5 barg. The inlet pressure to the compressor is 0.5 barg, and temperature 20 °C. Calculate the maximum power required to compress 100 m^3/h. A single-stage reciprocating compressor will be used.

3.8. Hydrogen chloride gas, produced by burning chlorine with hydrogen, is required at a supply pressure of 600 kN/m^2, gauge. The pressure can be achieved by either operating the burner under pressure or by compressing the hydrogen chloride gas. For a production rate of hydrogen chloride of 10,000 kg/h, compare the power requirement of compressing the hydrogen supply to the burner, with that to compress the product hydrogen chloride. The chlorine feed will be supplied at the required pressure from a vaporiser. Both the hydrogen and chlorine feeds are essentially pure. Hydrogen will be supplied to the burner one percent excess of over the stoichiometric requirement.

A two-stage centrifugal compressor will be used for both duties. Take the polytropic efficiency for both compressors as 70 per cent. The hydrogen supply pressure is 120 kN/m^2 and the temperature 25 °C. The hydrogen chloride is cooled to 50 °C after leaving the burner. Assume that the compressor intercooler cools the gas to 50 °C, for both duties.

Which process would you select and why?

3.9. Estimate the work required to compress ethylene from 32 MPa to 250 MPa in a two-stage reciprocating compressor where the gas is initially at 30 °C and leaves the intercooler at 30 °C. See Example 3.13.

3.10. Determine the pinch temperature and the minimum utility requirements for the process set out below. Take the minimum approach temperature as 15 °C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source Temp. °C	Target Temp. °C
1	hot	13.5	180	80
2	hot	27.0	135	45
3	cold	53.5	60	100
4	cold	23.5	35	120

3.11. Determine the pinch temperature and the minimum utility requirements for the process set out below. Take the minimum approach temperature as 15°C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source Temp. °C	Target Temp. °C
1	hot	10.0	200	80
2	hot	20.0	155	50
3	hot	40.0	90	35
4	cold	30.0	60	100
5	cold	8.0	35	90

3.12. To produce a high purity product two distillation columns are operated in series. The overhead stream from the first column is the feed to the second column. The overhead from the second column is the purified product. Both columns are conventional distillation columns fitted with reboilers and total condensers. The bottom products are passed to other processing units, which do not form part of this problem. The feed to the first column passes through a preheater. The condensate from the second column is passed through a product cooler. The duty for each stream is summarised below:

No.	Stream	Type	Source temp. °C.	Target temp. °C	Duty, kW
1	Feed preheater	cold	20	50	900
2	First condenser	hot	70	60	1350
3	Second condenser	hot	65	55	1100
4	First reboiler	cold	85	87	1400
5	Second reboiler	cold	75	77	900
6	Product cooler	hot	55	25	30

Find the minimum utility requirements for this process, for a minimum approach temperature of 10 °C.

Note: the stream heat capacity is given by dividing the exchanger duty by the temperature change.

CHAPTER 11

Separation Columns (Distillation, Absorption and Extraction)

11.1. INTRODUCTION

This chapter covers the design of separating columns. Though the emphasis is on distillation processes, the basic construction features, and many of the design methods, also apply to other multistage processes; such as stripping, absorption and extraction.

Distillation is probably the most widely used separation process in the chemical and allied industries; its applications ranging from the rectification of alcohol, which has been practised since antiquity, to the fractionation of crude oil.

Only a brief review of the fundamental principles that underlie the design procedures will be given; a fuller discussion can be found in Volume 2, and in other text books; King (1980), Hengstebeck (1976), Kister (1992).

A good understanding of methods used for correlating vapour-liquid equilibrium data is essential to the understanding of distillation and other equilibrium-staged processes; this subject was covered in Chapter 8.

In recent years, most of the work done to develop reliable design methods for distillation equipment has been carried out by a commercial organisation, Fractionation Research Inc., an organisation set up with the resources to carry out experimental work on full-size columns. Since their work is of a proprietary nature, it is not published in the open literature and it has not been possible to refer to their methods in this book. Fractionation Research's design manuals will, however, be available to design engineers whose companies are subscribing members of the organisation.

Distillation column design

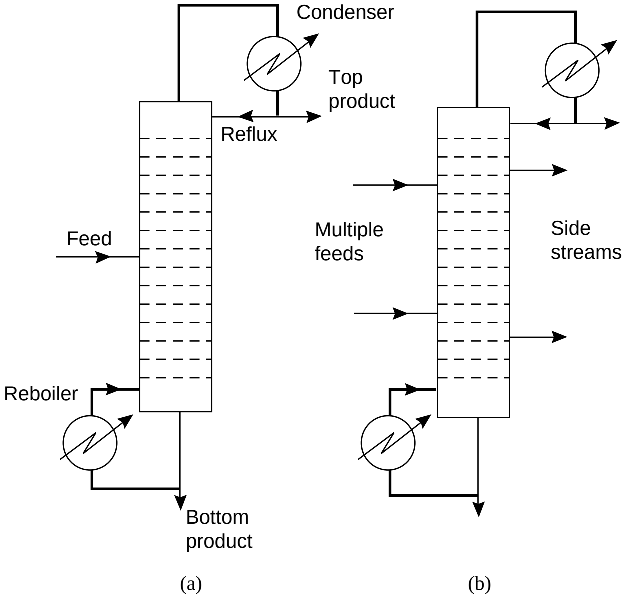
The design of a distillation column can be divided into the following steps:

1. Specify the degree of separation required: set product specifications.
2. Select the operating conditions: batch or continuous; operating pressure.
3. Select the type of contacting device: plates or packing.
4. Determine the stage and reflux requirements: the number of equilibrium stages.
5. Size the column: diameter, number of real stages.
6. Design the column internals: plates, distributors, packing supports.
7. Mechanical design: vessel and internal fittings.

The principal step will be to determine the stage and reflux requirements. This is a relatively simple procedure when the feed is a binary mixture, but a complex and difficult task when the feed contains more than two components (multicomponent systems).

11.2. CONTINUOUS DISTILLATION: PROCESS DESCRIPTION

The separation of liquid mixtures by distillation depends on differences in volatility between the components. The greater the relative volatilities, the easier the separation. The basic equipment required for continuous distillation is shown in Figure 11.1. Vapour flows up the column and liquid counter-currently down the column. The vapour and liquid are brought into contact on plates, or packing. Part of the condensate from the condenser is returned to the top of the column to provide liquid flow above the feed point (reflux), and part of the liquid from the base of the column is vaporised in the reboiler and returned to provide the vapour flow.



(a) (b)

Figure 11.1. Distillation column (*a*) Basic column (*b*) Multiple feeds and side streams

In the section below the feed, the more volatile components are stripped from the liquid and this is known as the *stripping section*. Above the feed, the concentration of the more volatile components is increased and this is called the enrichment, or more commonly, the *rectifying section*. Figure 11.1*a* shows a column producing two product streams, referred to as *tops* and *bottoms*, from a single feed. Columns are occasionally used with more than one feed, and with side streams withdrawn at points up the column, Figure 11.1*b*. This does not alter the basic operation, but complicates the analysis of the process, to some extent.

If the process requirement is to strip a volatile component from a relatively non-volatile solvent, the rectifying section may be omitted, and the column would then be called a *stripping column*.

In some operations, where the top product is required as a vapour, only sufficient liquid is condensed to provide the reflux flow to the column, and the condenser is referred to as a partial condenser. When the liquid is totally condensed, the liquid returned to the column will have the same composition as the top product. In a partial condenser the reflux will be in equilibrium with the vapour leaving the condenser. Virtually pure top and bottom products can be obtained in a single column from a binary feed, but where the feed contains more than two components, only a single "pure" product can be produced, either from the top or bottom of the column. Several columns will be needed to separate a multicomponent feed into its constituent parts.

11.2.1. Reflux considerations

The reflux ratio, R, is normally defined as:

$$R = \frac{\text{flow returned as reflux}}{\text{flow of top product taken off}}$$

The number of stages required for a given separation will be dependent on the reflux ratio used.

In an operating column the effective reflux ratio will be increased by vapour condensed within the column due to heat leakage through the walls. With a well-lagged column the heat loss will be small and no allowance is normally made for this increased flow in design calculations. If a column is poorly insulated, changes in the internal reflux due to sudden changes in the external conditions, such as a sudden rain storm, can have a noticeable effect on the column operation and control.

Total reflux

Total reflux is the condition when all the condensate is returned to the column as reflux: no product is taken off and there is no feed.

At total reflux the number of stages required for a given separation is the minimum at which it is theoretically possible to achieve the separation. Though not a practical operating condition, it is a useful guide to the likely number of stages that will be needed.

Columns are often started up with no product take-off and operated at total reflux till steady conditions are attained. The testing of columns is also conveniently carried out at total reflux.

Minimum reflux

As the reflux ratio is reduced a *pinch point* will occur at which the separation can only be achieved with an infinite number of stages. This sets the minimum possible reflux ratio for the specified separation.

Optimum reflux ratio

Practical reflux ratios will lie somewhere between the minimum for the specified separation and total reflux. The designer must select a value at which the specified separation is achieved at minimum cost. Increasing the reflux reduces the number of stages required, and hence the capital cost, but increases the service requirements (steam and water) and the operating costs. The optimum reflux ratio will be that which gives the lowest annual operating cost. No hard and fast rules can be given for the selection of the design reflux ratio, but for many systems the optimum will lie between 1.2 to 1.5 times the minimum reflux ratio.

For new designs, where the ratio cannot be decided on from past experience, the effect of reflux ratio on the number of stages can be investigated using the short-cut design methods given in this chapter. This will usually indicate the best of value to use in more rigorous design methods.

At low reflux ratios the calculated number of stages will be very dependent on the accuracy of the vapour-liquid equilibrium data available. If the data are suspect a higher than normal ratio should be selected to give more confidence in the design.

11.2.2. Feed-point location

The precise location of the feed point will affect the number of stages required for a specified separation and the subsequent operation of the column. As a general rule, the feed should enter the column at the point that gives the best match between the feed composition (vapour and liquid if two phases) and the vapour and liquid streams in the column. In practice, it is wise to provide two or three feed-point nozzles located round the predicted feed point to allow for uncertainties in the design calculations and data, and possible changes in the feed composition after start-up.

11.2.3. Selection of column pressure

Except when distilling heat-sensitive materials, the main consideration when selecting the column operating-pressure will be to ensure that the dew point of the distillate is above that which can be easily obtained with the plant cooling water. The maximum, summer, temperature of cooling water is usually taken as 30°C. If this means that high pressures will be needed, the provision of refrigerated brine cooling should be considered. Vacuum operation is used to reduce the column temperatures for the distillation of heat-sensitive materials and where very high temperatures would otherwise be needed to distil relatively non-volatile materials.

When calculating the stage and reflux requirements it is usual to take the operating pressure as constant throughout the column. In vacuum columns, the column pressure drop will be a significant fraction of the total pressure and the change in pressure up the column should be allowed for when calculating the stage temperatures. This may require a trial and error calculation, as clearly the pressure drop cannot be estimated before an estimate of the number of stages is made.

11.3. CONTINUOUS DISTILLATION: BASIC PRINCIPLES

11.3.1. Stage equations

Material and energy balance equations can be written for any stage in a multistage process.

Figure 11.2 shows the material flows into and out of a typical stage n in a distillation column. The equations for this stage are set out below, for any component i.

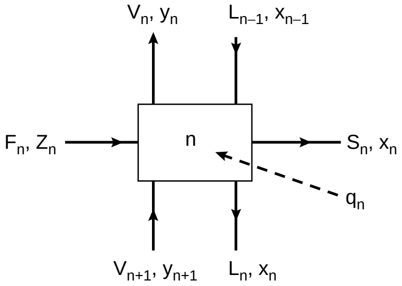


Figure 11.2. Stage flows

material balance

$$V_{n+1}y_{n+1} + L_{n-1}x_{n-1} + F_n z_n = V_n y_n + L_n x_n + S_n x_n \tag{11.1}$$

energy balance

$$V_{n+1}H_{n+1} + L_{n-1}h_{n-1} + Fh_f + q_n = V_n H_n + L_n h_n + S_n h_n \tag{11.2}$$

where V_n = vapour flow from the stage,
V_{n+1} = vapour flow into the stage from the stage below,
L_n = liquid flow from the stage,
L_{n-1} = liquid flow into the stage from the stage above,
F_n = any feed flow into the stage,
S_n = any side stream from the stage,
q_n = heat flow into, or removal from, the stage,
n = any stage, numbered from the top of the column,
z = mol fraction of component i in the feed stream (note, feed may be two-phase),
x = mol fraction of component i in the liquid streams,
y = mol fraction component i in the vapour streams,
H = specific enthalpy vapour phase,
h = specific enthalpy liquid phase,
h_f = specific enthalpy feed (vapour + liquid).

All flows are the total stream flows (mols/unit time) and the specific enthalpies are also for the total stream (J/mol).

It is convenient to carry out the analysis in terms of "equilibrium stages". In an equilibrium stage (theoretical plate) the liquid and vapour streams leaving the stage are taken to be in equilibrium, and their compositions are determined by the vapour-liquid equilibrium relationship for the system (see Chapter 8). In terms of equilibrium constants:

$$y_i = K_i x_i \tag{11.3}$$

The performance of real stages is related to an equilibrium stage by the concept of plate efficiencies for plate contactors, and "height of an equivalent theoretical plate" for packed columns.

In addition to the equations arising from the material and energy balances over a stage, and the equilibrium relationships, there will be a fourth relationship, the summation equation for the liquid and vapour compositions:

$$\Sigma\, x_{i,n} = \Sigma\, y_{i,n} = 1.0 \tag{11.4}$$

These four equations are the so-called MESH equations for the stage: Material balance, Equilibrium, Summation and Heat (energy) balance, equations. MESH equations can be written for each stage, and for the reboiler and condenser. The solution of this set of equations forms the basis of the rigorous methods that have been developed for the analysis for staged separation processes.

11.3.2. Dew points and bubble points

To estimate the stage, and the condenser and reboiler temperatures, procedures are required for calculating dew and bubble points. By definition, a saturated liquid is at its bubble point (any rise in temperature will cause a bubble of vapour to form), and a saturated vapour is at its dew point (any drop in temperature will cause a drop of liquid to form).

Dew points and bubble points can be calculated from a knowledge of the vapour-liquid equilibrium for the system. In terms of equilibrium constants, the bubble point is defined by the equation:

$$\text{bubble point: } \sum y_i = \sum K_i x_i = 1.0 \tag{11.5a}$$

$$\text{and dew point: } \sum x_i = \sum \frac{y_i}{K_i} = 1.0 \tag{11.5b}$$

For multicomponent mixtures the temperature that satisfies these equations, at a given system pressure, must be found by trial and error.

For binary systems the equations can be solved more readily because the component compositions are not independent; fixing one fixes the other.

$$y_a = 1 - y_b \tag{11.6a}$$

$$x_a = 1 - x_b \tag{11.6b}$$

Bubble- and dew-point calculations are illustrated in Example 11.9.

11.3.3. Equilibrium flash calculations

In an equilibrium flash process a feed stream is separated into liquid and vapour streams at equilibrium. The composition of the streams will depend on the quantity of the feed vaporised (flashed). The equations used for equilibrium flash calculations are developed below and a typical calculation is shown in Example 11.1.

Flash calculations are often needed to determine the condition of the feed to a distillation column and, occasionally, to determine the flow of vapour from the reboiler, or condenser if a partial condenser is used.

Single-stage flash distillation processes are used to make a coarse separation of the light components in a feed; often as a preliminary step before a multicomponent distillation column, as in the distillation of crude oil.

Figure 11.3 shows a typical equilibrium flash process. The equations describing this process are:

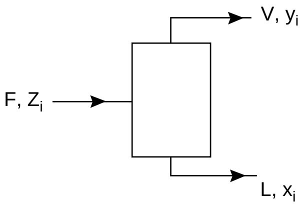


Figure 11.3. Flash distillation

Material balance, for any component, *i*

$$Fz_i = Vy_i + Lx_i \tag{11.7}$$

Energy balance, total stream enthalpies:

$$Fh_f = VH + Lh \tag{11.8}$$

If the vapour-liquid equilibrium relationship is expressed in terms of equilibrium constants, equation 11.7 can be written in a more useful form:

$$\begin{aligned} Fz_i &= VK_ix_i + Lx_i \\ &= Lx_i\left[\frac{V}{L}K_i + 1\right] \end{aligned}$$

from which

$$L = \sum_i \frac{Fz_i}{\left[\dfrac{VK_i}{L} + 1\right]} \tag{11.9}$$

and, similarly,

$$V = \sum_i \frac{Fz_i}{\left[\dfrac{L}{VK_i} + 1\right]} \tag{11.10}$$

The groups incorporating the liquid and vapour flow-rates and the equilibrium constants have a general significance in separation process calculations.

The group L/VK_i is known as the absorption factor A_i, and is the ratio of the mols of any component in the liquid stream to the mols in the vapour stream.

The group VK_i/L is called the stripping factor S_i, and is the reciprocal of the absorption factor.

Efficient techniques for the solution of the trial and error calculations necessary in multicomponent flash calculations are given by several authors; Hengstebeck (1976) and King (1980).

Example 11.1

A feed to a column has the composition given in the table below, and is at a pressure of 14 bar and a temperature of 60°C. Calculate the flow and composition of the liquid and vapour phases. Take the equilibrium data from the Depriester charts given in Chapter 8.

		kmol/h	z_i
Feed	ethane (C_2)	20	0.25
	propane (C_3)	20	0.25
	isobutane (iC_4)	20	0.25
	n-pentane (nC_5)	20	0.25

Solution

For two phases to exist the flash temperature must lie between the bubble point and dew point of the mixture.

From equations 11.5a and 11.5b:

$$\sum K_i z_i > 1.0$$

$$\sum \frac{z_i}{K_i} > 1.0$$

Check feed condition

	K_i	$K_i z_i$	z_i/K_i
C_2	3.8	0.95	0.07
C_3	1.3	0.33	0.19
iC_4	0.43	0.11	0.58
nC_5	0.16	0.04	1.56
		Σ 1.43	Σ 2.40

therefore the feed is a two phase mixture.

Flash calculation

		Try $L/V = 1.5$		Try $L/V = 3.0$	
	K_i	$A_i = L/VK_i$	$V_i = Fz_i/(1 + A_i)$	A_i	V_i
C_2	3.8	0.395	14.34	0.789	11.17
C_3	1.3	1.154	9.29	2.308	6.04
iC_4	0.43	3.488	4.46	6.977	2.51
nC_5	0.16	9.375	1.93	18.750	1.01
		$V_{\text{calc}} = 30.02$		$V_{\text{calc}} = 20.73$	
		$L/V = \dfrac{80 - 30.02}{30.02} = 1.67$		$L/V = 2.80$	

Hengstebeck's method is used to find the third trial value for L/V. The calculated values are plotted against the assumed values and the intercept with a line at 45° (calculated = assumed) gives the new trial value, 2.4.

	Try $L/V = 2.4$			
	A_i	V_i	$y_i = V_i/V$	$x_i = (Fz_i - V_i)/L$
C_2	0.632	12.26	0.52	0.14
C_3	1.846	7.03	0.30	0.23
iC_4	5.581	3.04	0.13	0.30
nC_5	15.00	1.25	0.05	0.33
	$V_{\text{cal}} = 23.58$		1.00	1.00

$L = 80 - 23.58 = 56.42$ kmol/h,
L/V calculated $= 56.42/23.58 = 2.39$ close enough to the assumed value of 2.4.

Adiabatic flash

In many flash processes the feed stream is at a higher pressure than the flash pressure and the heat for vaporisation is provided by the enthalpy of the feed. In this situation the flash temperature will not be known and must be found by trial and error. A temperature must be found at which both the material and energy balances are satisfied.

11.4. DESIGN VARIABLES IN DISTILLATION

It was shown in Chapter 1 that to carry out a design calculation the designer must specify values for a certain number of independent variables to define the problem completely, and that the ease of calculation will often depend on the judicious choice of these design variables.

In manual calculations the designer can use intuition in selecting the design variables and, as he proceeds with the calculation, can define other variables if it becomes clear that the problem is not sufficiently defined. He can also start again with a new set of design variables if the calculations become tortuous. When specifying a problem for a computer method it is essential that the problem is completely and sufficiently defined.

In Chapter 1 it was shown that the number of independent variables for any problem is equal to the difference between the total number of variables and the number of linking equations and other relationships. Examples of the application of this formal procedure for determining the number of independent variables in separation process calculations are given by Gilliand and Reed (1942) and Kwauk (1956). For a multistage, multicomponent, column, there will be a set of material and enthalpy balance equations and equilibrium relationships for each stage (the MESH equations), and for the reboiler and condenser; for each component. If there are more than a few stages the task of counting the variables and equations becomes burdensome and mistakes are very likely to be made. A simpler, more practical, way to determine the number of independent variables is the "description rule" procedure given by Hanson *et al*. (1962). Their description rule states that to determine a separation process completely the number of independent variables which must be set (by the designer) will equal the number that are set in the construction of the column or that can be controlled by external means in its operation. The application of this rule requires the designer to visualise the column in operation and list the number of variables fixed by the column construction; those fixed by the process; and those that have to be controlled for the column to operate steadily and produce product within specification. The method is best illustrated by considering the operation of the simplest type of column: with one feed, no side streams, a total condenser, and a reboiler. The construction will fix the number of stages above and below the feed point (two variables). The feed composition and total enthalpy will be fixed by the processes upstream ($1 + (\mathbf{n} - 1)$ variables, where $\mathbf{n}$ is the number of components). The feed rate, column pressure and condenser and reboiler duties (cooling water and steam flows) will be controlled (four variables).

$$\text{Total number of variables fixed} = 2 + 1 + (\mathbf{n} - 1) + 4 = \underline{\underline{\mathbf{n} + 6}}$$

To design the column this number of variables must be specified completely to define the problem, but the same variables need not be selected.

Typically, in a design situation, the problem will be to determine the number of stages required at a specified reflux ratio and column pressure, for a given feed, and with the product compositions specified in terms of two key components and one product flow-rate. Counting up the number of variables specified it will be seen that the problem is completely defined:

$$\begin{array}{lcl}
\text{Feed flow, composition, enthalpy} & = & 2 + (\mathbf{n} - 1) \\
\text{Reflux (sets } q_c\text{)} & = & 1 \\
\text{Key component compositions, top and bottom} & = & 2 \\
\text{Product flow} & = & 1 \\
\text{Column pressure} & = & 1 \\
 & & \overline{\underline{\mathbf{n} + 6}}
\end{array}$$

Note: *specifying* ($\mathbf{n} - 1$) component compositions completely defines the feed composition as the fractions add up to 1.

In theory any ($\mathbf{n} + 6$) independent variables could have been specified to define the problem, but it is clear that the use of the above variables will lead to a straightforward solution of the problem.

When replacing variables identified by the application of the description rule it is important to ensure that those selected are truly independent, and that the values assigned to them lie within the range of possible, practical, values.

The number of independent variables that have to be specified to define a problem will depend on the type of separation process being considered. Some examples of the application of the description rule to more complex columns are given by Hanson *et al.* (1962).

11.5. DESIGN METHODS FOR BINARY SYSTEMS

A good understanding of the basic equations developed for binary systems is essential to the understanding of distillation processes.

The distillation of binary mixtures is covered thoroughly in Volume 2, Chapter 11, and the discussion in this section is limited to a brief review of the most useful design methods. Though binary systems are usually considered separately, the design methods developed for multicomponent systems (Section 11.6) can obviously also be used for binary systems. With binary mixtures fixing the composition of one component fixes the composition of the other, and iterative procedures are not usually needed to determine the stage and reflux requirements; simple graphical methods are normally used.

11.5.1. Basic equations

Sorel (1899) first derived and applied the basic stage equations to the analysis of binary systems. Figure 11.4*a* shows the flows and compositions in the top part of a column. Taking the system boundary to include the stage *n* and the condenser, gives the following equations:

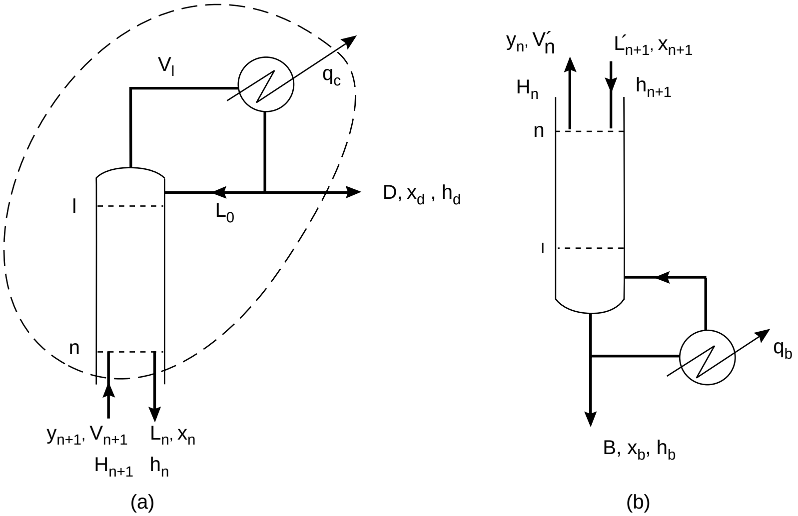


Figure 11.4. Column flows and compositions (*a*) Above feed (*b*) Below feed

Material balance

total flows $$V_{n+1} = L_n + D \tag{11.11}$$

for either component $$V_{n+1}y_{n+1} = L_n x_n + Dx_d \tag{11.12}$$

Energy balance

total stream enthalpies $$V_{n+1}H_{n+1} = L_n h_n + Dh_d + q_c \tag{11.13}$$

where q_c is the heat removed in the condenser.

Combining equations 11.11 and 11.12 gives

$$y_{n+1} = \frac{L_n}{L_n + D}x_n + \frac{D}{L_n + D}x_d \tag{11.14}$$

Combining equations 11.11 and 11.13 gives

$$V_{n+1}H_{n+1} = (L_n + D)H_{n+1} = L_n h_n + Dh_d + q_c \tag{11.15}$$

Analogous equations can be written for the stripping section, Figure 11.6*b*.

$$x_{n+1} = \frac{V'_n}{V'_n + B}y_n + \frac{B}{V'_n + B}x_b \tag{11.16}$$

and

$$L'_{n+1}h_{n+1} = (V'_n + B)h_{n+1} = V'_n H_n + Bh_b - q_b \tag{11.17}$$

At constant pressure, the stage temperatures will be functions of the vapour and liquid compositions only (dew and bubble points) and the specific enthalpies will therefore also be functions of composition

$$H = \mathrm{f}(y) \tag{11.18a}$$

$$h = \mathrm{f}(x) \tag{11.18b}$$

Lewis-Sorel method (equimolar overflow)

For most distillation problems a simplifying assumption, first proposed by Lewis (1909), can be made that eliminates the need to solve the stage energy-balance equations. The molar liquid and vapour flow rates are taken as constant in the stripping and rectifying sections. This condition is referred to as equimolar overflow: the molar vapour and liquid flows from each stage are constant. This will only be true where the component molar latent heats of vaporisation are the same and, together with the specific heats, are constant over the range of temperature in the column; there is no significant heat of mixing; and the heat losses are negligible. These conditions are substantially true for practical systems when the components form near-ideal liquid mixtures.

Even when the latent heats are substantially different the error introduced by assuming equimolar overflow to calculate the number of stages is usually small, and acceptable.

With equimolar overflow equations 11.14 and 11.16 can be written without the subscripts to denote the stage number:

$$y_{n+1} = \frac{L}{L+D}x_n + \frac{D}{L+D}x_d \tag{11.19}$$

$$x_{n+1} = \frac{V'}{V'+B}y_n + \frac{B}{V'+B}x_b \tag{11.20}$$

where $L =$ the constant liquid flow in the rectifying section = the reflux flow, L_0, and V' is the constant vapour flow in the stripping section.

Equations 11.19 and 11.20 can be written in an alternative form:

$$y_{n+1} = \frac{L}{V}x_n + \frac{D}{V}x_d \tag{11.21}$$

$$y_n = \frac{L'}{V'}x_{n+1} - \frac{B}{V'}x_b \tag{11.22}$$

where V is the constant vapour flow in the rectifying section $= (L + D)$; and L' is the constant liquid flow in the stripping section $= V' + B$.

These equations are linear, with slopes L/V and L'/V'. They are referred to as *operating lines*, and give the relationship between the liquid and vapour compositions between stages. For an equilibrium stage, the compositions of the liquid and vapour streams leaving the stage are given by the equilibrium relationship.

11.5.2. McCabe-Thiele method

Equations 11.21 and 11.22 and the equilibrium relationship are conveniently solved by the graphical method developed by McCabe and Thiele (1925). The method is discussed fully in Volume 2. A simple procedure for the construction of the diagram is given below and illustrated in Example 11.2.

Procedure

Refer to Figure 11.5, all compositions are those of the more volatile component.

1. Plot the vapour-liquid equilibrium curve from data available at the column operating pressure. In terms of relative volatility:

   $$y = \frac{\alpha x}{(1 + (\alpha - 1)x)} \tag{11.23}$$

   where α is the geometric average relative volatility of the lighter (more volatile) component with respect to the heavier component (less volatile).
   It is usually more convenient, and less confusing, to use equal scales for the x and y axes.
2. Make a material balance over the column to determine the top and bottom compositions, x_d and x_b, from the data given.
3. The top and bottom operating lines intersect the diagonal at x_d and x_b respectively; mark these points on the diagram.
4. The point of intersection of the two operating lines is dependent on the phase condition of the feed. The line on which the intersection occurs is called the *q line* (see Volume 2). The q line is found as follows:

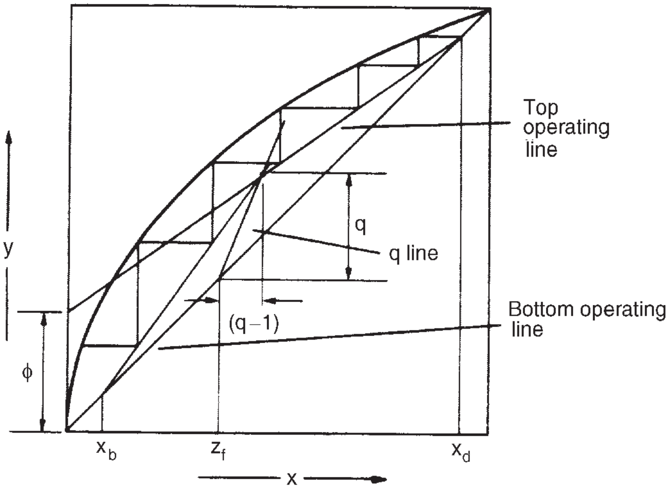


Figure 11.5. McCabe-Thiele diagram

(i) calculate the value of the ratio q given by

$$q = \frac{\text{heat to vaporise 1 mol of feed}}{\text{molar latent heat of feed}}$$

(ii) plot the q line, slope $= q/(q-1)$, intersecting the diagonal at z_f (the feed composition).

5. Select the reflux ratio and determine the point where the top operating line extended cuts the y axis:

$$\phi = \frac{x_d}{1+R} \tag{11.24}$$

6. Draw in the top operating line, from x_d on the diagonal to ϕ.
7. Draw in the bottom operating line; from x_b on the diagonal to the point of intersection of the top operating line and the q line.
8. Starting at x_d or x_b, step off the number of stages.

Note: The feed point should be located on the stage closest to the intersection of the operating lines.

The reboiler, and a partial condenser if used, act as equilibrium stages. However, when designing a column there is little point in reducing the estimated number of stages to account for this; they can be considered additional factors of safety.

The efficiency of real contacting stages can be accounted for by reducing the height of the steps on the McCabe-Thiele diagram, see diagram Figure 11.6. Stage efficiencies are discussed in Section 11.10.

The McCabe-Thiele method can be used for the design of columns with side streams and multiple feeds. The liquid and vapour flows in the sections between the feed and take-off points are calculated and operating lines drawn for each section.

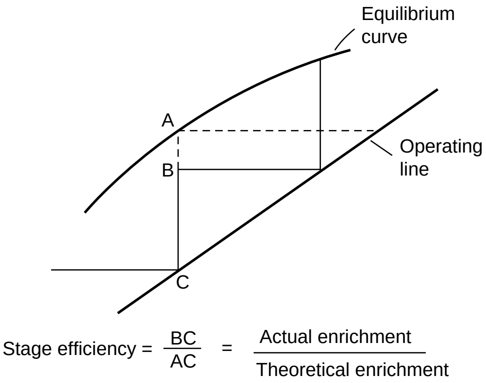


Figure 11.6. Stage efficiency

Stage vapour and liquid flows not constant

The McCabe-Thiele method can be used when the condition of equimolar overflow cannot be assumed, but the operating lines will not then be straight. They can be drawn by making energy balances at a sufficient number of points to determine the approximate slope of the lines; see Hengstebeck (1976). Alternatively the more rigorous graphical method of Ponchon and Savarit derived in Volume 2 can be used. Nowadays, it should rarely be necessary to resort to complex graphical methods when the simple McCabe-Thiele diagram is not sufficiently accurate, as computer programs will normally be available for the rigorous solution of such problems.

11.5.3. Low product concentrations

When concentrations of the more volatile component of either product is very low the steps on the McCabe-Thiele diagram become very small and difficult to plot. This problem can be overcome by replotting the top or bottom sections to a larger scale, or on log-log paper. In a log plot the operating line will not be straight and must be drawn by plotting points calculated using equations 11.21 and 11.22. This technique is described by Alleva (1962) and is illustrated in Example 11.2.

If the operating and equilibrium lines are straight, and they usually can be taken as such when the concentrations are small, the number of stages required can be calculated using the equations given by Robinson and Gilliland (1950).

For the stripping section:

$$N_s^* = \frac{\log\left[\dfrac{\left(\dfrac{K'}{s'}-1\right)\left(\dfrac{x_r'}{x_b}-1\right)}{\dfrac{1}{s'}(K'-1)}+1\right]}{\log\left(\dfrac{K'}{s'}\right)}+1 \tag{11.25}$$

where N_s^* = number of ideal stages required from x_b to some reference point x_r',
x_b = mol fraction of the more volatile component in the bottom product,

x'_r = mol fraction of more volatile component at the reference point,
s' = slope of the bottom operating line,
K' = equilibrium constant for the more volatile component.

For the rectifying section:

$$N_r^* = \frac{\log\left[\dfrac{(1-s)+x_r/x_d(s-K)}{1-K}\right]}{\log\left(\dfrac{s}{K}\right)} - 1 \tag{11.26}$$

where N_r^* = number of stages required from some reference point x_r to the x_d,
x_d = mol fraction of the *least volatile* component in the top product,
x_r = mol fraction of *least volatile* component at reference point,
K = equilibrium constant for the *least volatile* component,
s = slope of top operating line.

Note: at low concentrations $K = \alpha$.

The use of these equations is illustrated in Example 11.3.

Example 11.2

Acetone is to be recovered from an aqueous waste stream by continuous distillation. The feed will contain 10 per cent w/w acetone. Acetone of at least 98 per cent purity is wanted, and the aqueous effluent must not contain more than 50 ppm acetone. The feed will be at 20°C. Estimate the number of ideal stages required.

Solution

There is no point in operating this column at other than atmospheric pressure. The equilibrium data available for the acetone-water system were discussed in Chapter 8, Section 8.4.

The data of Kojima *et al.* will be used.

Mol fraction x, liquid	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95
Acetone y, vapour	0.00	0.6381	0.7301	0.7716	0.7916	0.8034	0.8124	0.8201	0.8269	0.8376	0.8387	0.8455	0.8532	0.8615	0.8712	0.8817	0.8950	0.9118	0.9335	0.9627
bubble point °C	100.0	74.80	68.53	65.26	63.59	62.60	61.87	61.26	60.75	60.35	59.95	59.54	59.12	58.71	58.29	57.90	57.49	57.08	56.68	56.30

The equilibrium curve can be drawn with sufficient accuracy to determine the stages above the feed by plotting the concentrations at increments of 0.1. The diagram would normally be plotted at about twice the size of Figure 11.7.

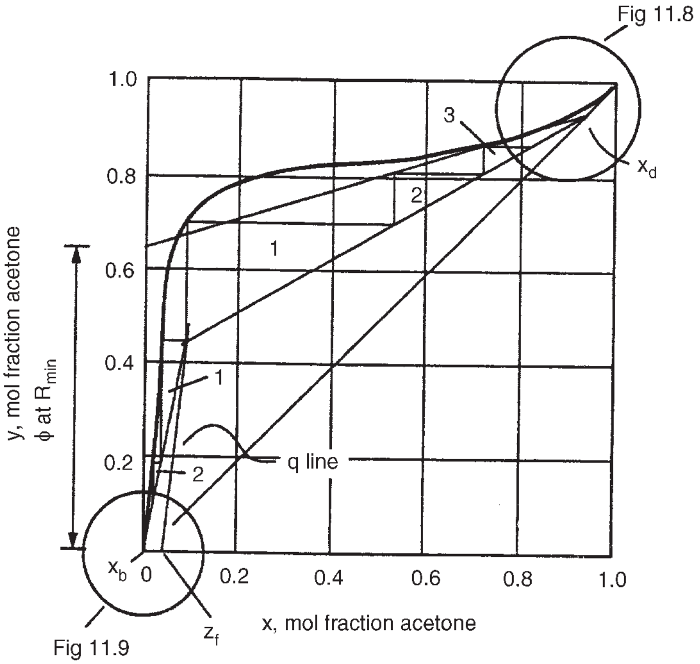


Figure 11.7. McCabe-Thiele plot, Example 11.2

Molecular weights, acetone 58, water 18

$$\text{Mol fractions acetone feed} = \frac{\dfrac{10}{58}}{\dfrac{10}{58} + \dfrac{90}{18}} = 0.033$$

$$\text{top product} = \frac{\dfrac{98}{58}}{\dfrac{98}{58} + \dfrac{2}{18}} = 0.94$$

$$\text{bottom product} = 50 \times 10^{-6} \times \frac{18}{58} = 15.5 \times 10^{-6}$$

Feed condition (q-line)

Bubble point of feed (interpolated) = 83°C
Latent heats, water 41,360, acetone 28,410 J/mol

Mean specific heats, water 75.3, acetone 128 J/mol °C
Latent heat of feed $= 28{,}410 \times 0.033 + (1 - 0.033)\ 41{,}360 = 40{,}933$ J/mol
Specific heat of feed $= (0.033 \times 128) + (1 - 0.033)\ 75.3 = 77.0$ J/mol °C
Heat to vaporise 1 mol of feed $= (83 - 20)\ 77.0 + 40{,}933 = 45{,}784$ J

$$q = \frac{45{,}784}{40{,}933} = 1.12$$

$$\text{Slope of } q \text{ line} = \frac{1.12}{1.12 - 1} = 9.32$$

For this problem the condition of minimum reflux occurs where the top operating line just touches the equilibrium curve at the point where the q line cuts the curve.

From the Figure 11.7,

$$\phi \text{ for the operating line at minimum reflux} = 0.65$$

From equation 11.24, $R_{\text{min}} = 0.94/0.65 - 1 = 0.45$

Take $R = R_{\text{min}} \times 3$

As the flows above the feed point will be small, a high reflux ratio is justified; the condenser duty will be small.

$$\text{At } R = 3 \times 0.45 = 1.35, \quad \phi = \frac{0.94}{1 + 1.35} = 0.4$$

For this problem it is convenient to step the stages off starting at the intersection of the operating lines. This gives three stages above the feed up to $y = 0.8$. The top section is drawn to a larger scale, Figure 11.8, to determine the stages above $y = 0.8$: three to four stages required; total stages above the feed 7.

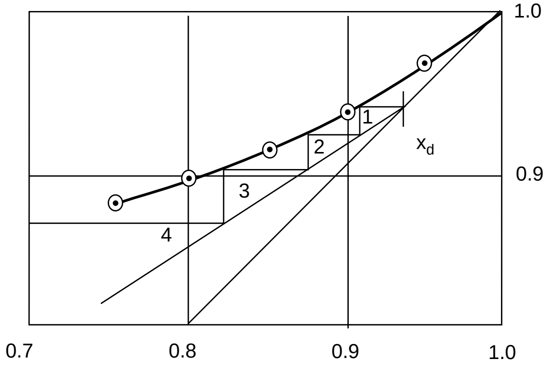


Figure 11.8. Top section enlarged

Below the feed, one stage is required down to $x = 0.04$. A log-log plot is used to determine the stages below this concentration. Data for log-log plot:

operating line slope, from Figure 11.7 $= 0.45/0.09 = 5.0$

operating line equation, $y = 4.63(x - x_b) + x_b$

$$= 5.0x - 62.0 \times 10^{-6}$$

equilibrium line slope, from v–l–e data $= 0.6381/0.05 = 12.8$

	$x =$	4×10^{-2}	10^{-3}	10^{-4}	4×10^{-5}	2×10^{-5}
Equilibrium line	$y =$	0.51	1.3×10^{-2}	1.3×10^{-3}	5.1×10^{-4}	2.6×10^{-4}
Operating line	$y =$	0.20	4.9×10^{-3}	4.4×10^{-4}	1.4×10^{-4}	3.8×10^{-5}

From Figure 11.9, number of stages required for this section = 8

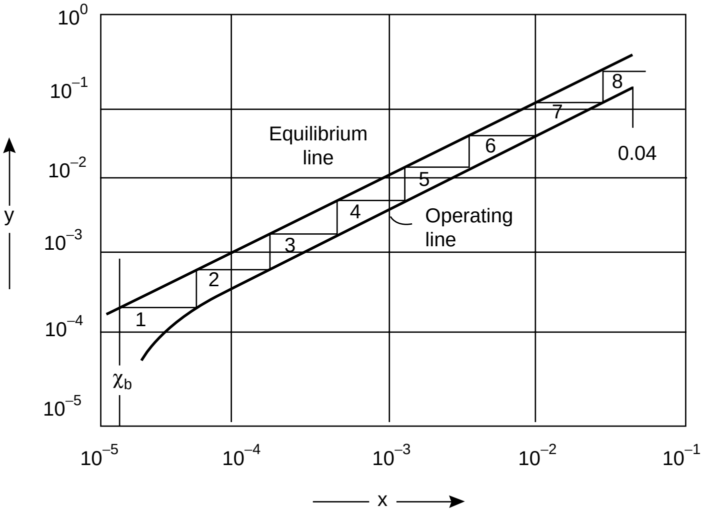


Figure 11.9. Log-log plot of McCabe-Thiele diagram

Total number of stages below feed = 9
Total stages = 7 + 9 = 16

Example 11.3

For the problem specified in Example 11.2, estimate the number of ideal stages required below an acetone concentration of 0.04 (more volatile component), using the Robinson-Gilliland equation.

Solution

From the McCabe-Thiele diagram in Example 11.2:

slope of bottom operating line, $s' = 5.0$
slope of equilibrium line, $K' = 12.8$

$$x_b = 15.5 \times 10^{-6}$$

$$N_s^* = \frac{\log\left[\dfrac{\left(\dfrac{12.8}{5.0} - 1\right)\left(\dfrac{0.04}{15.5 \times 10^{-6}} - 1\right)}{\left(\dfrac{1}{5.0}\right)(12.8 - 1)} + 1\right]}{\log\left(\dfrac{12.8}{5.0}\right)} + 1 = 8.9, \ \underline{\underline{\text{say } 9}} \qquad (11.25)$$

11.5.4. The Smoker equations

Smoker (1938) derived an analytical equation that can be used to determine the number of stages when the relative volatility is constant. Though his method can be used for any problem for which the relative volatilities in the rectifying and stripping sections can be taken as constant, it is particularly useful for problems where the relative volatility is low; for example, in the separation of close boiling isomers. If the relative volatility is close to one, the number of stages required will be very large, and it will be impractical to draw a McCabe-Thiele diagram. The derivation of the equations are outlined below and illustrated in Example 11.4.

Derivation of the equations:

A straight operating line can be represented by the equation:

$$y = sx + c \qquad (11.27)$$

and in terms of relative volatility the equilibrium values of y are given by:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \qquad \text{(equation 11.23)}$$

Eliminating y from these equations gives a quadratic in x:

$$s(\alpha - 1)x^2 + [s + b(\alpha - 1) - \alpha]x + b = 0 \qquad (11.28)$$

For any particular distillation problem equation 11.28 will have only one real root k between 0 and 1

$$s(\alpha - 1)k^2 + [s + b(\alpha - 1) - \alpha]k + b = 0 \qquad (11.29)$$

k is the value of the x ordinate at the point where the extended operating lines intersect the vapour-liquid equilibrium curve. Smoker shows that the number of stages required is given by the equation:

$$N = \log\left[\frac{x_0^*(1 - \beta x_n^*)}{x_n^*(1 - \beta x_0^*)}\right] \Bigg/ \log\left(\frac{\alpha}{sc^2}\right) \qquad (11.30)$$

where

$$\beta = \frac{sc(\alpha - 1)}{\alpha - sc^2} \qquad (11.31)$$

N = number of stages required to effect the separation represented by the concentration change from

$$x_n^* \text{ to } x_0^*; x^* = (x - k) \text{ and } x_0^* > x_n^*$$

$$c = 1 + (\alpha - 1)k \qquad (11.32)$$

s = slope of the operating line between x_n^* and x_0^*,
α = relative volatility, assumed constant over x_n^* to x_0^*.

For a column with a single feed and no side streams:

Rectifying section

$$x_0^* = x_d - k \tag{11.33}$$

$$x_n^* = z_f - k \tag{11.34}$$

$$s = \frac{R}{R+1} \tag{11.35}$$

$$b = \frac{x_d}{R+1} \tag{11.36}$$

Stripping section

$$x_0^* = z_f - k \tag{11.37}$$

$$x_n^* = x_b - k \tag{11.38}$$

$$s = \frac{Rz_f + x_d - (R+1)x_b}{(R+1)(z_f - x_b)} \tag{11.39}$$

$$b = \frac{(z_f - x_d)x_b}{(R+1)(z_f - x_b)} \tag{11.40}$$

If the feed stream is not at its bubble point, z_f is replaced by the value of x at the intersection of operating lines, given by

$$z_f^* = \frac{b + \dfrac{z_f}{q-1}}{\dfrac{q}{q-1} - s} \tag{11.41}$$

All compositions for the more volatile component.

Example 11.4

A column is to be designed to separate a mixture of ethylbenzene and styrene. The feed will contain 0.5 mol fraction styrene, and a styrene purity of 99.5 per cent is required, with a recovery of 85 per cent. Estimate the number of equilibrium stages required at a reflux ratio of 8. Maximum column bottom pressure 0.20 bar.

Solution

Ethylbenzene is the more volatile component.

$$\text{Antoine equations, ethylbenzene, } \ln P^\circ = 9.386 - \frac{3279.47}{T - 59.95}$$

$$\text{styrene } \ln P^\circ = 9.386 - \frac{3328.57}{T - 63.72}$$

$$P \text{ bar, } T \text{ Kelvin}$$

Material balance, basis 100 kmol feed:

at 85 per cent recovery, styrene in bottoms $= 50 \times 0.85 = 42.5$ kmol

at 99.5 per cent purity, ethylbenzene in bottoms $= \dfrac{42.5}{99.5} \times 0.5 = 0.21$ kmol

ethylbenzene in the tops $= 50 - 0.21 = 49.79$ kmol

styrene in tops $= 50 - 42.5 = 7.5$ kmol

mol fraction ethylbenzene in tops $= \dfrac{49.79}{49.79 + 7.5} = 0.87$

$z_f = 0.5,\ x_b = 0.005,\ x_d = 0.87$

Column bottom temperature, from Antoine equation for styrene

$$\ln 0.2 = 9.386 - \frac{3328.57}{T - 63.72}$$

$$T = 366 \text{ K},\ 93.3^\circ\text{C}$$

At 93.3°C, vapour pressure of ethylbenzene

$$\ln P^\circ = 9.386 - \frac{3279.47}{366.4 - 59.95} = 0.27 \text{ bar}$$

$$\text{Relative volatility} = \frac{P^\circ \text{ ethylbenzene}}{P^\circ \text{ styrene}} = \frac{0.27}{0.20} = 1.35$$

The relative volatility will change as the compositions and (particularly for a vacuum column) the pressure changes up the column. The column pressures cannot be estimated until the number of stages is known; so as a first trial the relative volatility will be taken as constant, at the value determined by the bottom pressure.

Rectifying section

$$s = \frac{8}{8+1} = 0.89 \tag{11.35}$$

$$b = \frac{0.87}{8+1} = 0.097 \tag{11.36}$$

$$0.89(1.35 - 1)k^2 + [0.89 + 0.097(1.35 - 1) - 1.35]k + 0.097 = 0 \tag{11.29}$$

$$k = 0.290$$

$$x_0^* = 0.87 - 0.29 = 0.58 \tag{11.33}$$

$$x_n^* = 0.50 - 0.29 = 0.21 \tag{11.34}$$

$$c = 1 + (1.35 - 1)0.29 = 1.10 \tag{11.32}$$

$$\beta = \frac{0.89 \times 1.10(1.35 - 1)}{1.35 - 0.89 \times 1.1^2} = 1.255 \tag{11.31}$$

$$N = \log\left[\frac{0.58(1 - 1.255 \times 0.21)}{0.21(1 - 1.255 \times 0.58)}\right] \Big/ \log\left(\frac{1.35}{0.89 \times 1.1^2}\right) \tag{11.30}$$

$$= \frac{\log 7.473}{\log 1.254} = 8.87, \underline{\underline{\text{say } 9}}$$

Stripping section, feed taken as at its bubble point

$$s = \frac{8 \times 0.5 + 0.87 - (8 + 1)0.005}{(8 + 1)(0.5 - 0.005)} = 1.084 \tag{11.39}$$

$$b = \frac{(0.5 - 0.87)0.005}{(8 + 1)(0.5 - 0.005)} = -4.15 \times 10^{-4} \text{ (essentially zero)} \tag{11.40}$$

$$1.084(1.35 - 1)k^2 + [1.084 - 4.15 \times 10^{-4}(1.35 - 1) - 1.35]k - 4.15 \times 10^{-4}$$

$$k = 0.702 \tag{11.29}$$

$$x_0^* = 0.5 - 0.702 = -0.202 \tag{11.37}$$

$$x_n^* = 0.005 - 0.702 = -0.697 \tag{11.38}$$

$$c = 1 + (1.35 - 1)0.702 = 1.246 \tag{11.32}$$

$$\beta = \frac{1.084 \times 1.246(1.35 - 1)}{1.35 - 1.084 \times 1.246^2} = -1.42 \tag{11.31}$$

$$N = \log\left[\frac{-0.202(1 - 0.697 \times 1.42)}{-0.697(1 - 0.202 \times 1.42)}\right] \Big/ \log\left(\frac{1.35}{1.084 \times 1.246^2}\right) \tag{11.30}$$

$$= \frac{\log[4.17 \times 10^{-3}]}{\log 0.8} = 24.6, \text{ say } \underline{\underline{25}}$$

11.6. MULTICOMPONENT DISTILLATION: GENERAL CONSIDERATIONS

The problem of determining the stage and reflux requirements for multicomponent distillations is much more complex than for binary mixtures. With a multicomponent mixture, fixing one component composition does not uniquely determine the other component compositions and the stage temperature. Also when the feed contains more than two components it is not possible to specify the complete composition of the top and bottom products independently. The separation between the top and bottom products is specified by setting limits on two “key” components, between which it is desired to make the separation.

The complexity of multicomponent distillation calculations can be appreciated by considering a typical problem. The normal procedure is to solve the MESH equations (Section 11.3.1) stage-by-stage, from the top and bottom of the column toward the feed point. For such a calculation to be exact, the compositions obtained from both the bottom-up and top-down calculations must mesh at the feed point and match the feed composition. But the calculated compositions will depend on the compositions assumed for the top and bottom products at the commencement of the calculations. Though it is possible to match the key components, the other components will not match unless the designer was particularly fortunate in choosing the trial top and bottom compositions. For a completely rigorous solution the compositions must be adjusted and the calculations repeated until a satisfactory mesh at the feed point is obtained. Clearly, the greater the number of components, the more difficult the problem. As was shown in Section 11.3.2, trial-and-error calculations will be needed to determine the stage temperatures. For other than ideal mixtures, the calculations will be further complicated by the fact that the component volatilities will be functions of the unknown stage compositions. If more than a few stages are required, stage-by-stage calculations are complex and tedious; as illustrated in Example 11.9.

Before the advent of the modern digital computer, various "short-cut" methods were developed to simplify the task of designing multicomponent columns. A comprehensive summary of the methods used for hydrocarbon systems is given by Edmister (1947 to 1949) in a series of articles in the journal *The Petroleum Engineer*. Though computer programs will normally be available for the rigorous solution of the MESH equations, short-cut methods are still useful in the preliminary design work, and as an aid in defining problems for computer solution. Intelligent use of the short-cut methods can reduce the computer time and costs.

The short-cut methods available can be divided into two classes:

1. Simplification of the rigorous stage-by-stage procedures to enable the calculations to be done by hand, or graphically. Typical examples of this approach are the methods given by Smith and Brinkley (1960) and Hengstebeck (1976). These are described in Section 11.7 and Hengstebeck's method is illustrated by a worked example.
2. Empirical methods, which are based on the performance of operating columns, or the results of rigorous designs. Typical examples of these methods are Gilliland's correlation, which is given in Volume 2, Chapter 11, and the Erbar-Maddox correlation given in Section 11.7.3.

11.6.1. Key components

Before commencing the column design, the designer must select the two "key" components between which it is desired to make the separation. The light key will be the component that it is desired to keep out of the bottom product, and the heavy key the component to be kept out of the top product. Specifications will be set on the maximum concentrations of the keys in the top and bottom products. The keys are known as "adjacent keys" if they are "adjacent" in a listing of the components in order of volatility, and "split keys" if some other component lies between them in the order; they will usually be adjacent.

Which components are the key components will normally be clear, but sometimes, particularly if close boiling isomers are present, judgement must be used in their selection. If any uncertainty exists, trial calculations should be made using different components as the keys to determine the pair that requires the largest number of stages for separation (the worst case). The Fenske equation can be used for these calculations; see Section 11.7.3.

The "non-key" components that appear in both top and bottom products are known as "distributed" components; and those that are not present, to any significant extent, in one or other product, are known as "non-distributed" components.

11.6.2. Number and sequencing of columns

As was mentioned in Section 11.2, in multicomponent distillations it is not possible to obtain more than one pure component, one sharp separation, in a single column. If a multicomponent feed is to be split into two or more virtually pure products, several columns will be needed. Impure products can be taken off as side streams; and the removal of a side stream from a stage where a minor component is concentrated will reduce the concentration of that component in the main product.

For separation of N components, with one essentially pure component taken overhead, or from the bottom of each column, (N − 1) columns will be needed to obtain complete separation of all components. For example, to separate a mixture of benzene, toluene and xylene two columns are needed (3−1). Benzene is taken overhead from the first column and the bottom product, essentially free of benzene, is fed to the second column. This column separates the toluene and xylene.

The order in which the components are separated will determine the capital and operating costs. Where there are several components the number of possible sequences can be very large; for example, with five components the number is 14, whereas with ten components it is near 5000. When designing systems that require the separation of several components, efficient procedures are needed to determine the optimum sequence of separation; see Doherty and Malone (2001), Smith (1995) and Kumar (1982).

Procedures for the sequencing of columns are also available in the commercial process simulator programs; for example, DISTIL in Hyprotech's suite of programs (see Chapter 4, Table 4.1).

In this section, it is only possible to give some general guide rules.

Heuristic rules for optimum sequencing

1. Remove the components one at a time; as in the benzene-toluene-xylene example.
2. Remove any components that are present in large excess early in the sequence.
3. With difficult separations, involving close boiling components, postpone the most difficult separation to late in the sequence.

Difficult separations will require many stages, so to reduce cost, the column diameter should be made a small as possible. Column diameter is dependent on flow-rate; see Section 11.11. The further down the sequence the smaller will be the amount of material that the column has to handle.

Tall columns

Where a large number of stages is required, it may be necessary to split a column into two separate columns to reduce the height of the column, even though the required separation could, theoretically, have been obtained in a single column. This may also be done in vacuum distillations, to reduce the column pressure drop and limit the bottom temperatures.

11.7. MULTICOMPONENT DISTILLATION: SHORT-CUT METHODS FOR STAGE AND REFLUX REQUIREMENTS

Some of the more useful short-cut procedures which can be used to estimate stage and reflux requirements without the aid of computers are given in this section. Most of the short-cut methods were developed for the design of separation columns for hydrocarbon systems in the petroleum and petrochemical systems industries, and caution must be exercised when applying them to other systems. They usually depend on the assumption of constant relative volatility, and should not be used for severely non-ideal systems.

Short-cut methods for non-ideal and azeotropic systems are given by Featherstone (1971) (1973).

11.7.1. Pseudo-binary systems

If the presence of the other components does not significantly affect the volatility of the key components, the keys can be treated as a pseudo-binary pair. The number of stages can then be calculated using a McCabe-Thiele diagram, or the other methods developed for binary systems. This simplification can often be made when the amount of the non-key components is small, or where the components form near-ideal mixtures.

Where the concentration of the non-keys is small, say less than 10 per cent, they can be lumped in with the key components. For higher concentrations the method proposed by Hengstebeck (1946) can be used to reduce the system to an equivalent binary system. Hengstebeck's method is outlined below and illustrated in Example 11.5. Hengstebeck's book (1976) should be consulted for the derivation of the method and further examples of its application.

Hengstebeck's method

For any component i the Lewis-Sorel material balance equations (Section 11.5) and equilibrium relationship can be written in terms of the individual component molar flow rates; in place of the component composition:

$$v_{n+1,i} = l_{n,i} + d_i \tag{11.42}$$

$$v_{n,i} = K_{n,i}\frac{V}{L}l_{n,i} \tag{11.43}$$

for the stripping section:

$$l'_{n+1,i} = v'_{n,i} + b_i \tag{11.44}$$

$$v'_{n,i} = K_{n,i}\frac{V'}{L'}l'_{n,i} \tag{11.45}$$

where $l_{n,i}$ = the liquid flow rate of any component i from stage n,
$v_{n,i}$ = the vapour flow rate of any component i from stage n,
d_i = the flow rate of component i in the tops,
b_i = the flow rate of component i in the bottoms,
$K_{n,i}$ = the equilibrium constant for component i at stage n.

The superscript $'$ denotes the stripping section.

V and L are the total flow-rates, assumed constant.

To reduce a multicomponent system to an equivalent binary it is necessary to estimate the flow-rate of the key components throughout the column. Hengstebeck makes use of the fact that in a typical distillation the flow-rates of each of the light non-key components approaches a constant, limiting, rate in the rectifying section; and the flows of each of the heavy non-key components approach limiting flow-rates in the stripping section. Putting the flow-rates of the non-keys equal to these limiting rates in each section enables the combined flows of the key components to be estimated.

Rectifying section

$$L_e = L - \Sigma \underline{l_i} \tag{11.46}$$

$$V_e = V - \Sigma \underline{v_i} \tag{11.47}$$

Stripping section

$$L'_e = L' - \Sigma \underline{l'_i} \tag{11.48}$$

$$V'_e = V' - \Sigma \underline{v'_i} \tag{11.49}$$

where V_e and L_e are the estimated flow rates of the combined keys,

$\underline{l_i}$ and $\underline{v_i}$ are the limiting liquid and vapour rates of components *lighter* than the keys in the rectifying section,

$\underline{l'_i}$ and $\underline{v'_i}$ are the limiting liquid and vapour rates of components *heavier* than the keys in the stripping section.

The method used to estimate the limiting flow-rates is that proposed by Jenny (1939). The equations are:

$$\underline{l_i} = \frac{d_i}{\alpha_i - 1} \tag{11.50}$$

$$\underline{v_i} = l_i + d_i \tag{11.51}$$

$$\underline{v'_i} = \frac{\alpha_i b_i}{\alpha_{\mathrm{LK}} - \alpha_i} \tag{11.52}$$

$$\underline{l'_i} = v'_i + b_i \tag{11.53}$$

where α_i = relative volatility of component i, relative to the heavy key (HK),

α_{LK} = relative volatility of the light key (LK), relative to the heavy key.

Estimates of the flows of the combined keys enable operating lines to be drawn for the equivalent binary system. The equilibrium line is drawn by assuming a constant relative volatility for the light key:

$$y = \frac{\alpha_{\mathrm{LK}} x}{1 + (\alpha_{\mathrm{LK}} - 1)x} \qquad \text{(equation 11.23)}$$

where y and x refer to the vapour and liquid concentrations of the light key.

Hengstebeck shows how the method can be extended to deal with situations where the relative volatility cannot be taken as constant, and how to allow for variations in the liquid and vapour molar flow rates. He also gives a more rigorous graphical procedure based on the Lewis-Matheson method (see Section 11.8).

Example 11.5

Estimate the number of ideal stages needed in the butane-pentane splitter defined by the compositions given in the table below. The column will operate at a pressure of 8.3 bar, with a reflux ratio of 2.5. The feed is at its boiling point.

Note: a similar problem has been solved by Lyster *et al.* (1959) using a rigorous computer method and it was found that ten stages were needed.

	Feed (f)	Tops (d)	Bottoms (b)
Propane, C_3	5	5	0
i-Butane, iC_4	15	15	0
n-Butane, nC_4	25	24	1
i-Pentane, iC_5	20	1	19
n-Pentane, nC_5	35	0	35
	100	45	55 kmol

Solution

The top and bottom temperatures (dew points and bubble points) were calculated by the methods illustrated in Example 11.9. Relative volatilities are given by equation 8.30:

$$\alpha_i = \frac{K_i}{K_{\mathrm{HK}}}$$

Equilibrium constants were taken from the Depriester charts (Chapter 8).

Relative volatilities

	Top	Bottom	Average
Temp. °C	65	120	
C_3	5.5	4.5	5.0
iC_4	2.7	2.5	2.6
(LK) nC_4	2.1	2.0	2.0
(HK) iC_5	1.0	1.0	1.0
nC_5	0.84	0.85	0.85

Calculations of non-key flows

Equations 11.50, 11.51, 11.52, 11.53

	α_i	d_i	$\underline{l_i} = d_i/(\alpha_i - 1)$	$\underline{v_i} = \underline{l_i} + d_i$
C_3	5	5	1.3	6.3
iC_4	2.6	15	9.4	24.4
		$\Sigma \underline{l_i} = 10.7$	$\Sigma \underline{v_i} = 30.7$	
	α_i	b_i	$\underline{v'_i} = \alpha_i b_i/(\alpha_{\mathrm{LK}} - \alpha_i)$	$\underline{l'_i} = \underline{v'_i} + b_i$
nC_5	0.85	35	25.9	60.9
			$\Sigma \underline{v'_i} = 25.9$	$\Sigma \underline{l'_i} = 60.9$

Flows of combined keys

$$L_e = 2.5 \times 45 - 10.7 = 101.8 \tag{11.46}$$

$$V_e = (2.5 + 1)45 - 30.7 = 126.8 \tag{11.47}$$

$$V'_e = (2.5 + 1)45 - 25.9 = 131.6 \tag{11.49}$$

$$L'_e = (2.5 + 1)45 + 55 - 60.9 = 151.6 \tag{11.48}$$

Slope of top operating line

$$\frac{L_e}{V_e} = \frac{101.8}{126.8} = 0.8$$

Slope of bottom operating line

$$\frac{L'_e}{V'_e} = \frac{151.6}{131.6} = 1.15$$

$$x_b = \frac{\text{flow LK}}{\text{flow (LK + HK)}} = \frac{1}{19 + 1} = 0.05$$

$$x_d = \frac{24}{24 + 1} = 0.96$$

$$x_f = \frac{25}{25 + 20} = 0.56$$

$$y = \frac{2x}{1 + (2 - 1)x} = \frac{2x}{1 + x} \tag{11.23}$$

x	0	0.20	0.40	0.60	0.80	1.0
y	0	0.33	0.57	0.75	0.89	1.0

The McCabe-Thiele diagram is shown in Figure 11.10.
Twelve stages required; feed on seventh from base.

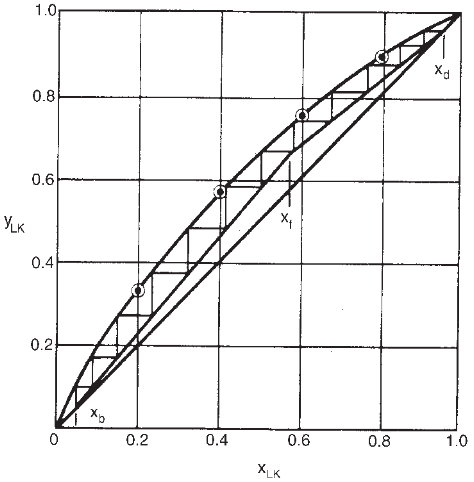


Figure 11.10. McCabe-Thiele diagram for Example 11.5

11.7.2. Smith-Brinkley method

Smith and Brinkley developed a method for determining the distribution of components in multicomponent separation processes. Their method is based on the solution of the finite-difference equations that can be written for multistage separation processes, and can be used for extraction and absorption processes, as well as distillation. Only the equations for distillation will be given here. The derivation of the equations is given by Smith and Brinkley (1960) and Smith (1963). For any component i (suffix i omitted in the equation for clarity)

$$\frac{b}{f} = \frac{(1 - S_r^{N_r - N_s}) + R(1 - S_r)}{(1 - S_r^{N_r - N_s}) + R(1 - S_r) + GS_r^{N_r - N_s}(1 - S_s^{N_s + 1})} \tag{11.54}$$

where b/f is the fractional split of the component between the feed and the bottoms, and:

N_r = number of equilibrium stages above the feed,

N_s = number of equilibrium stages below the feed,

S_r = stripping factor, rectifying section = $K_i V/L$,

S_s = stripping factor, stripping section = $K'_i V'/L'$,

V and L are the total molar vapour and liquid flow rates, and the superscript $'$ denotes the stripping section.

G depends on the condition of the feed.

If the feed is mainly liquid:

$$G_i = \frac{K'_i}{K_i}\frac{L}{L'}\left[\frac{1 - S_r}{1 - S_s}\right]_i \tag{11.55}$$

and the feed stage is added to the stripping section.
If the feed is mainly vapour:

$$G_i = \frac{L}{L'}\left[\frac{1 - S_r}{1 - S_s}\right]_i \tag{11.56}$$

Equation 11.54 is for a column with a total condenser. If a partial condenser is used the number of stages in the rectifying section should be increased by one.

The procedure for using the Smith-Brinkley method is as follows:

1. Estimate the flow-rates L, V and L', V' from the specified component separations and reflux ratio.
2. Estimate the top and bottom temperatures by calculating the dew and bubble points for assumed top and bottom compositions.
3. Estimate the feed point temperature.
4. Estimate the average component K values in the stripping and rectifying sections.
5. Calculate the values of $S_{r,i}$ for the rectifying section and $S_{s,i}$ for the stripping section.

6. Calculate the fractional split of each component, and hence the top and bottom compositions.
7. Compare the calculated with the assumed values and check the overall column material balance.
8. Repeat the calculation until a satisfactory material balance is obtained. The usual procedure is to adjust the feed temperature up and down till a satisfactory balance is obtained.

Examples of the application of the Smith-Brinkley method are given by Smith (1963).

This method is basically a rating method, suitable for determining the performance of an existing column, rather than a design method, as the number of stages must be known.

It can be used for design by estimating the number of stages by some other method and using equation 11.54 to determine the top and bottom compositions. The estimated stages can then be adjusted and the calculations repeated until the required specifications are achieved. However, the Geddes-Hengstebeck method for estimating the component splits, described in Section 11.7.4, is easier to use and satisfactory for preliminary design.

11.7.3. Empirical correlations

The two most frequently used empirical methods for estimating the stage requirements for multicomponent distillations are the correlations published by Gilliland (1940) and by Erbar and Maddox (1961). These relate the number of ideal stages required for a given separation, at a given reflux ratio, to the number at total reflux (minimum possible) and the minimum reflux ratio (infinite number of stages).

Gilliland's correlation is given in Volume 2, Chapter 11.

The Erbar-Maddox correlation is given in this section, as it is now generally considered to give more reliable predictions. Their correlation is shown in Figure 11.11; which gives the ratio of number of stages required to the number at total reflux, as a function of the reflux ratio, with the minimum reflux ratio as a parameter. To use Figure 11.11, estimates of the number of stages at total reflux and the minimum reflux ratio are needed.

Minimum number of stages (Fenske equation)

The Fenske equation (Fenske, 1932) can be used to estimate the minimum stages required at total reflux. The derivation of this equation for a binary system is given in Volume 2, Chapter 11. The equation applies equally to multicomponent systems and can be written as:

$$\left[\frac{x_i}{x_r}\right]_d = \alpha_i^{N_m}\left[\frac{x_i}{x_r}\right]_b \tag{11.57}$$

where $[x_i/x_r]$ = the ratio of the concentration of any component i to the concentration of a reference component r, and the suffixes d and b denote the distillate (tops) (d) and the bottoms (b),

N_m = minimum number of stages at total reflux, including the reboiler,

α_i = average relative volatility of the component i with respect to the reference component.

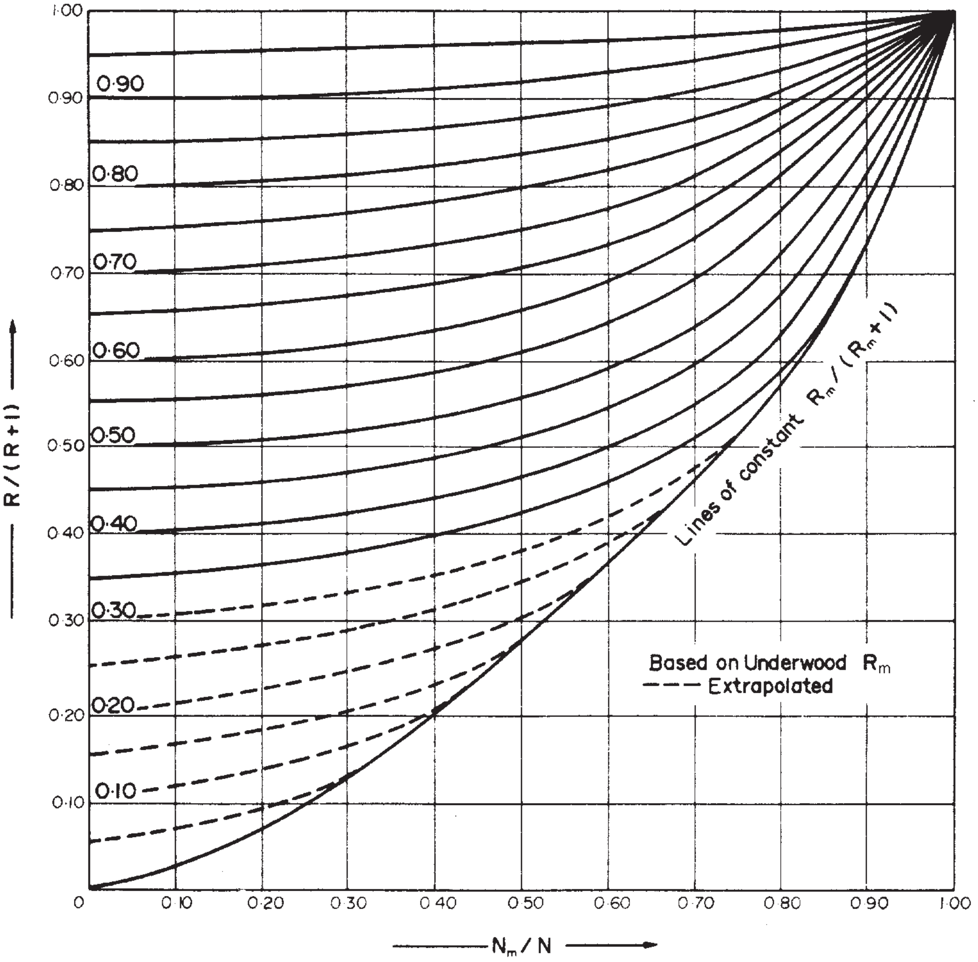


Figure 11.11. Erbar-Maddox correlation (Erbar and Maddox, 1961)

Normally the separation required will be specified in terms of the key components, and equation 11.57 can be rearranged to give an estimate of the number of stages.

$$N_m = \frac{\log\left[\frac{x_{LK}}{x_{HK}}\right]_d \left[\frac{x_{HK}}{x_{LK}}\right]_b}{\log \alpha_{LK}} \tag{11.58}$$

where α_{LK} is the average relative volatility of the light key with respect to the heavy key, and x_{LK} and x_{HK} are the light and heavy key concentrations. The relative volatility is taken as the geometric mean of the values at the column top and bottom temperatures. To calculate these temperatures initial estimates of the compositions must be made, so the calculation of the minimum number of stages by the Fenske equation is a trial-and-error procedure. The procedure is illustrated in Example 11.7. If there is a wide difference between the relative volatilities at the top and bottom of the column the use of the average value in the Fenske equation will underestimate the number of stages. In these circumstances, a better estimate can be made by calculating the number of stages in the rectifying and stripping sections separately; taking the feed concentration as the base concentration for the rectifying section and as the top concentration for the stripping section, and estimating the average relative volatilities separately for each section. This procedure will also give an estimate of the feed point location.

Winn (1958) has derived an equation for estimating the number of stages at total reflux, which is similar to the Fenske equation, but which can be used when the relative volatility cannot be taken as constant.

If the number of stages is known, equation 11.57 can be used to estimate the split of components between the top and bottom of the column at total reflux. It can be written in a more convenient form for calculating the split of components:

$$\frac{d_i}{b_i} = \alpha_i^{N_m} \left[\frac{d_r}{b_r}\right] \tag{11.59}$$

where d_i and b_i are the flow-rates of the component i in the tops and bottoms, d_r and b_r are the flow-rates of the reference component in the tops and bottoms.

Note: from the column material balance:

$$d_i + b_i = f_i$$

where f_i is the flow rate of component i in the feed.

Minimum reflux ratio

Colburn (1941) and Underwood (1948) have derived equations for estimating the minimum reflux ratio for multicomponent distillations. These equations are discussed in Volume 2, Chapter 11. As the Underwood equation is more widely used it is presented in this section. The equation can be stated in the form:

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1 \tag{11.60}$$

where α_i = the relative volatility of component i with respect to some reference component, usually the heavy key,
R_m = the minimum reflux ratio,
$x_{i,d}$ = concentration of component i in the tops at minimum reflux

and θ is the root of the equation:

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q \tag{11.61}$$

where $x_{i,f}$ = the concentration of component i in the feed, and q depends on the condition of the feed and was defined in Section 11.5.2.

The value of θ must lie between the values of the relative volatility of the light and heavy keys, and is found by trial and error.

In the derivation of equations 11.60 and 11.61 the relative volatilities are taken as constant. The geometric average of values estimated at the top and bottom temperatures should be used. This requires an estimate of the top and bottom compositions. Though the compositions should strictly be those at minimum reflux, the values determined at total reflux, from the Fenske equation, can be used. A better estimate can be obtained by replacing the number of stages at total reflux in equation 11.59 by an estimate of the actual number; a value equal to $N_m/0.6$ is often used. The Erbar-Maddox method of estimating the stage and reflux requirements, using the Fenske and Underwood equations, is illustrated in Example 11.7.

Feed-point location

A limitation of the Erbar-Maddox, and similar empirical methods, is that they do not give the feed-point location. An estimate can be made by using the Fenske equation to calculate the number of stages in the rectifying and stripping sections separately, but this requires an estimate of the feed-point temperature. An alternative approach is to use the empirical equation given by Kirkbride (1944):

$$\log\left[\frac{N_r}{N_s}\right] = 0.206\log\left[\left(\frac{B}{D}\right)\left(\frac{x_{f,\mathrm{HK}}}{x_{f,\mathrm{LK}}}\right)\left(\frac{x_{b,\mathrm{LK}}}{x_{d,\mathrm{HK}}}\right)^2\right] \tag{11.62}$$

where N_r = number of stages above the feed, including any partial condenser,
N_s = number of stages below the feed, including the reboiler,
B = molar flow bottom product,
D = molar flow top product,
$x_{f,\mathrm{HK}}$ = concentration of the heavy key in the feed,
$x_{f,\mathrm{LK}}$ = concentration of the light key in the feed,
$x_{d,\mathrm{HK}}$ = concentration of the heavy key in the top product,
$x_{b,\mathrm{LK}}$ = concentration of the light key if in the bottom product.

The use of this equation is illustrated in Example 11.8.

11.7.4. Distribution of non-key components (graphical method)

The graphical procedure proposed by Hengstebeck (1946), which is based on the Fenske equation, is a convenient method for estimating the distribution of components between the top and bottom products.

Hengstebeck and Geddes (1958) have shown that the Fenske equation can be written in the form:

$$\log\left(\frac{d_i}{b_i}\right) = A + C\log\alpha_i \tag{11.63}$$

Specifying the split of the key components determines the constants A and C in the equation.

The distribution of the other components can be readily determined by plotting the distribution of the keys against their relative volatility on log-log paper, and drawing a straight line through these two points. The method is illustrated in Example 11.6.

Yaws *et al*. (1979) have shown that the components distributions calculated by equation 11.63 compare well with those obtained by rigorous plate by plate calculations.

Chang (1980) gives a computer program, based on the Geddes-Hengstebeck equation, for the estimation of component distributions.

Example 11.6

Use the Geddes-Hengstebeck method to check the component distributions for the separation specified in Example 11.5

Summary of problem, flow per 100 kmol feed

Component	α_i	Feed (f_i)	Distillate (d_i)	Bottoms (b_i)
C_3	5	5		
iC_4	2.6	15		
nC_4 (LK)	2.0	25	24	1
iC_5 (HK)	1.0	20	1	19
nC_5	0.85	35		

Solution

The average volatilities will be taken as those estimated in Example 11.5. Normally, the volatilities are estimated at the feed bubble point, which gives a rough indication of the average column temperatures. The dew point of the tops and bubble point of the bottoms can be calculated once the component distributions have been estimated, and the calculations repeated with a new estimate of the average relative volatilities, as necessary.

$$\text{For the light key, } \frac{d_i}{b_i} = \frac{24}{1} = 24$$

$$\text{For the heavy key, } \frac{d_i}{b_i} = \frac{1}{19} = 0.053$$

These values are plotted on Figure 11.12.

The distribution of the non-keys are read from Figure 11.12 at the appropriate relative volatility and the component flows calculated from the following equations:

Overall column material balance

$$f_i = d_i + b_i$$

from which

$$d_i = \frac{f_i}{\left(\dfrac{b_i}{d_i} + 1\right)}$$

$$b_i = \frac{f_i}{\left(\dfrac{d_i}{b_i} + 1\right)}$$

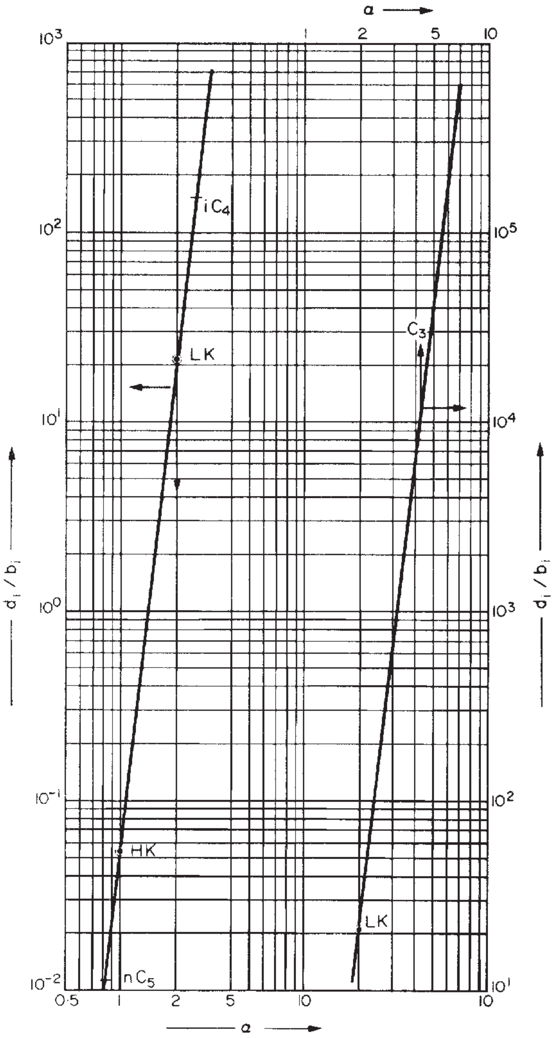


Figure 11.12. Component Distribution (Example 11.6)

	α_i	f_i	d_i/b_i	d_i	b_i
C_3	5	5	40,000	5	0
iC_4	2.6	15	150	14.9	0.1
nC_4	2.0	25	21	24	1
iC_5	1.0	20	0.053	1	19
nC_5	0.85	35	0.011	0.4	34.6

As these values are close to those assumed for the calculation of the dew points and bubble points in Example 11.5, there is no need to repeat with new estimates of the relative volatilities.

Example 11.7

For the separation specified in Example 11.5, evaluate the effect of changes in reflux ratio on the number of stages required. This is an example of the application of the Erbar-Maddox method.

Solution

The relative volatilities estimated in Example 11.5, and the component distributions calculated in Example 11.6 will be used for this example.

Summary of data

	α_i	f_i	d_i	b_i
C_3	5	5	5	0
iC_4	2.6	15	14.9	0.1
nC_4 (LK)	2.0	25	24	1
iC_5 (HK)	1	20	1	19
nC_5	0.85	35	0.4	34.6
		100	$D = 45.3$	$B = 54.7$

Minimum number of stages; Fenske equation, equation 11.58:

$$N_m = \frac{\log\left[\left(\frac{24}{1}\right)\left(\frac{19}{1}\right)\right]}{\log 2} = \underline{\underline{8.8}}$$

Minimum reflux ratio; Underwood equations 11.60 and 11.61.
This calculation is best tabulated.
As the feed is at its boiling point $q = 1$

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 0 \tag{11.61}$$

				Try	
$x_{i,f}$	α_i	$\alpha_i x_{i,f}$	$\theta = 1.5$	$\theta = 1.3$	$\theta = 1.35$
0.05	5	0.25	0.071	0.068	0.068
0.15	2.6	0.39	0.355	0.300	0.312
0.25	2.0	0.50	1.000	0.714	0.769
0.20	1	0.20	−0.400	−0.667	−0.571
0.35	0.85	0.30	−0.462	−0.667	−0.600
			$\Sigma = 0.564$	−0.252	0.022 close enough

$\theta = 1.35$

Equation 11.60

$x_{i,d}$	α_i	$\alpha_i x_{i,d}$	$\alpha_i x_{i,d}/(\alpha_i - \theta)$
0.11	5	0.55	0.15
0.33	2.6	0.86	0.69
0.53	2.0	1.08	1.66
0.02	1	0.02	−0.06
0.01	0.85	0.01	−0.02
			$\Sigma = 2.42$

$$R_m + 1 = 2.42$$

$$R_m = \underline{\underline{1.42}}$$

$$\frac{R_m}{(R_m + 1)} = \frac{1.42}{2.42} = 0.59$$

Specimen calculation, for $R = 2.0$

$$\frac{R}{(R + 1)} = \frac{2}{3} = 0.66$$

from Figure 11.11

$$\frac{N_m}{N} = 0.56$$

$$N = \frac{8.8}{0.56} = \underline{\underline{15.7}}$$

for other reflux ratios

R	2	3	4	5	6
N	15.7	11.9	10.7	10.4	10.1

Note: Above a reflux ratio of 4 there is little change in the number of stages required, and the optimum reflux ratio will be near this value.

Example 11.8

Estimate the position of the feed point for the separation considered in Example 11.7, for a reflux ratio of 3.

Solution

Use the Kirkbride equation, equation 11.62. Product distributions taken from Example 11.6,

$$x_{b,\mathrm{LK}} = \frac{1}{54.7} = 0.018$$

$$x_{d,\mathrm{HK}} = \frac{1}{45.3} = 0.022$$

$$\log\left(\frac{N_r}{N_s}\right) = 0.206\log\left[\frac{54.7}{45.3}\left(\frac{0.20}{0.25}\right)\left(\frac{0.018}{0.022}\right)^2\right]$$

$$\log\left(\frac{N_r}{N_s}\right) = 0.206\log(0.65)$$

$$\frac{N_r}{N_s} = \underline{\underline{0.91}}$$

for $R = 3$, $N = 12$
number of stages, excluding the reboiler $= \underline{\underline{11}}$

$$N_r + N_s = 11$$

$$N_s = 11 - N_r = 11 - 0.91N_s$$

$$N_s = \frac{11}{1.91} = 5.76, \text{ say } \underline{\underline{6}}$$

Checks with the method used in Example 11.5, where the reflux ratio was 2.5.

Example 11.9

This example illustrates the complexity and trial and error nature of stage-by-stage calculation.

The same problem specification has been used in earlier examples to illustrate the shortcut design methods.

A butane-pentane splitter is to operate at 8.3 bar with the following feed composition:

		x_f	f mol/100 mol feed
Propane,	C_3	0.05	5
Isobutane,	iC_4	0.15	15
Normal butane,	nC_4	0.25	25
Isopentane,	iC_5	0.20	20
Normal pentane,	nC_5	0.35	35
Light key	nC_4		
Heavy key	iC_5		

For a specification of not more than 1 mol of the light key in the bottom product and not more than 1 mol of the heavy key in the top product, and a reflux ratio of 2.5, make a stage-by-stage calculation to determine the product composition and number of stages required.

Solution

Only sufficient trial calculations will be made to illustrate the method used. Basis 100 mol feed.

Estimation of dew and bubble points

$$\text{Bubble point} \quad \sum y_i = \sum K_i x_i = 1.0 \tag{11.5a}$$

$$\text{Dew point} \quad \sum x_i = \sum \frac{y_i}{K_i} = 1.0 \tag{11.5b}$$

The K values, taken from the De Priester charts (Chapter 8), are plotted in Figure (*a*) for easy interpolation.

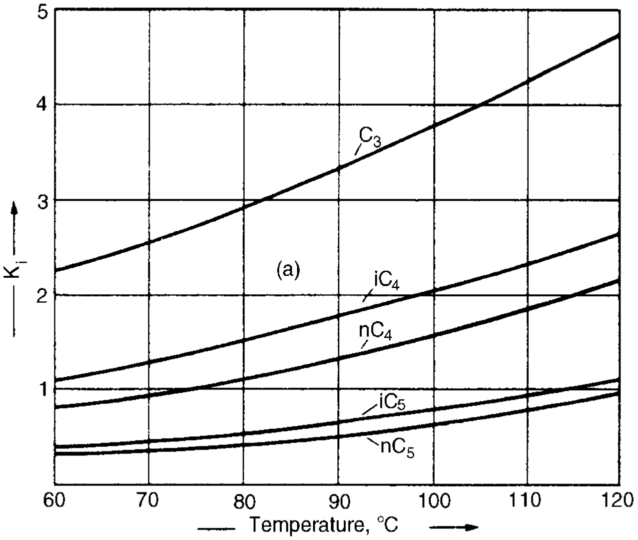


Figure (*a*). K-values at 8.3 bar

To estimate the dew and bubble points, assume that nothing heavier than the heavy key appears in the tops, and nothing lighter than the light key in the bottoms.

	d	x_d	b	x_b
C_3	5	0.11	0	—
C_4	15	0.33	0	—
nC_4	24	0.54	1	0.02
iC_5	1	0.02	19	0.34
nC_5	0	—	35	0.64
	45		55	

Bubble-point calculation, bottoms

		Try 100°C		Try 120°C	
	x_b	K_i	$K_i x_i$	K_i	$K_i x_i$
C_3	—	—	—	—	—
iC_4	—	—	—	—	—
nC_4	0.02	1.85	0.04	2.1	0.04
iC_5	0.34	0.94	0.32	1.1	0.37
nC_5	0.64	0.82	0.52	0.96	0.61
		$\Sigma K_i x_i = 0.88$ temp. too low		1.02 close enough	

Dew-point calculation, tops

		Try 70°C		Try 60°C	
	x_d	K_i	y_i/K_i	K_i	y_i/K_i
C_3	0.11	2.6	0.04	2.20	0.24
iC_4	0.33	1.3	0.25	1.06	0.35
nC_4	0.54	0.9	0.60	0.77	0.42
iC_5	0.02	0.46	0.04	0.36	0.01
nC_5	—	—	—	—	—
		$\Sigma y_i/K_i = 0.94$ temp. too high		1.02 close enough	

Bubble-point calculation, feed (liquid feed)

		Try 80°C		Try 90°C		Try 85°C	
	x_f	K_i	$x_i K_i$	K_i	$x_i K_i$	K_i	$x_i K_i$
C_3	0.05	2.9	0.15	3.4	0.17	3.15	0.16
iC_4	0.15	1.5	0.23	1.8	0.27	1.66	0.25
nC_4	0.25	1.1	0.28	1.3	0.33	1.21	0.30
iC_5	0.20	0.5	0.11	0.66	0.13	0.60	0.12
nC_5	0.35	0.47	0.16	0.56	0.20	0.48	0.17
			0.93 temp. too low		1.10 temp. too high		1.00 satisfactory

Stage-by-stage calculations

Top down calculations, assume total condensation with no subcooling

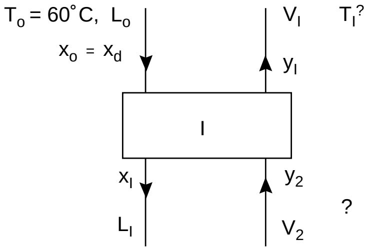
$$y_1 = x_d = x_0$$

It is necessary to estimate the composition of the "non-keys" so that they can be included in the stage calculations. As a first trial the following values will be assumed:

	x_d	d
C_3	0.10	5
iC_4	0.33	15
nC_4	0.54	24
iC_5	0.02	1
nC_5	0.001	0.1
		45.1

In each stage calculation it will necessary to estimate the stage temperatures to determine the K values and liquid and vapour enthalpies. The temperature range from top to bottom of the column will be approximately $120 - 60 = 60°\text{C}$. An approximate calculation (Example 11.7) has shown that around fourteen ideal stages will be needed; so the temperature change from stage to stage can be expected to be around 4 to 5°C.

Stage 1



$$L_0 = R \times D = 2.5 \times 45.1 = 112.8$$
$$V_1 = (R + 1)D = 3.5 \times 45.1 = 157.9$$

Estimation of stage temperature and outlet liquid composition (x_1)

		Try $T_1 = 66°\text{C}$		Try $T_1 = 65°\text{C}$		
	y_1	K_i	y_i/K_i	K_i	y_i/K_i	$x_1 = y_i/K_i$ Normalised
C_3	0.10	2.40	0.042	2.36	0.042	0.042
iC_4	0.33	1.20	0.275	1.19	0.277	0.278
nC_4	0.54	0.88	0.614	0.86	0.628	0.629
iC_5	0.02	0.42	0.048	0.42	0.048	0.048
nC_5	0.001	0.32	0.003	0.32	0.003	0.003
		$\Sigma y_i/K_i = 0.982$ too low			0.998 close enough	

Summary of stage equations

$$L_0 + V_2 = L_1 + V_1 \tag{i}$$

$$L_0x_0 + V_2y_2 = L_1x_1 + V_1y_1 \tag{ii}$$

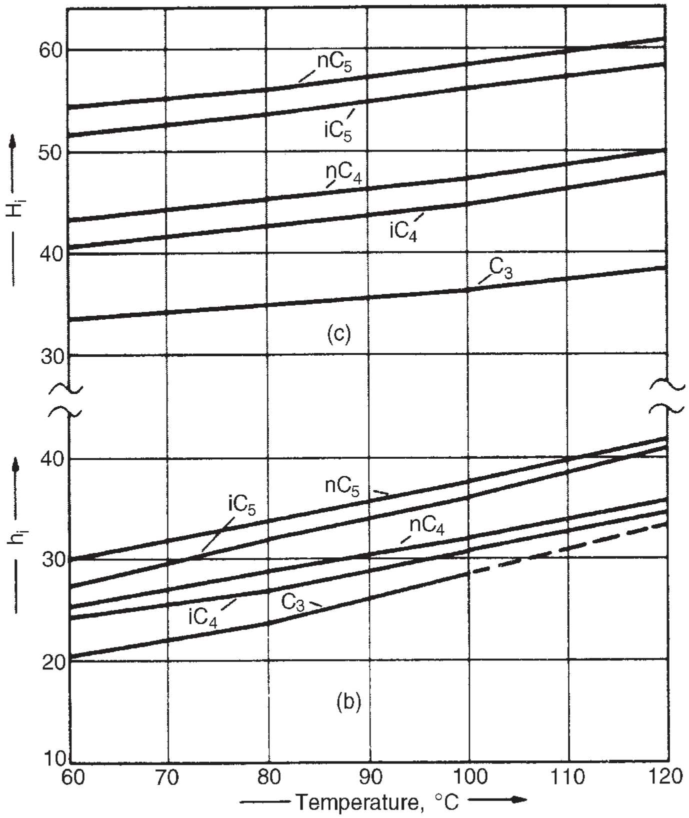
$$h_0L_0 + H_2V_2 = h_1L_1 + H_1V_1 \tag{iii}$$

$$h = f(x, T) \tag{iv}$$

$$H = f(x, T) \tag{v}$$

The enthalpy relationship is plotted in Figures (*b*) and (*c*).

$$y_i = K_ix_i \tag{vi}$$



Figures (*b*) and (*c*). Enthalpy kJ/mol (adapted from J. B. Maxwell, *Data Book of Hydrocarbons* (Van Nostrand, 1962))

Before a heat balance can be made to estimate L_1 and V_2, an estimate of y_2 and T_2 is needed. y_2 is dependent on the liquid and vapour flows, so as a first trial assume that these are constant and equal to L_0 and V_1; then, from equations (i) and (ii),

$$y_2 = \left(\frac{L_0}{V_1}\right)(x_1 - x_0) + y_1$$

$$\frac{L_0}{V_1} = \frac{112.8}{157.9} = 0.71$$

	x_1	x_0	$y_2 = 0.71(x_1 - x_0) + y_1$	y_2 Normalised
C_3	0.042	0.10	0.057	0.057
iC_4	0.278	0.33	0.294	0.292
nC_4	0.629	0.54	0.604	0.600
iC_5	0.048	0.02	0.041	0.041
nC_5	0.003	0.001	0.013	0.013
			1.009 close enough	

Enthalpy data from Figures (*b*) and (*c*) J/mol

	$h_0(T_0 = 60°C)$			$h_1(T_1 = 65°C)$		
	x_0	h_i	$h_i x_i$	x_1	h_i	$h_i x_i$
C_3	0.10	20,400	2040	0.042	21,000	882
iC_4	0.33	23,400	7722	0.278	24,900	6897
nC_4	0.54	25,200	13,608	0.629	26,000	16,328
iC_5	0.02	27,500	550	0.048	28,400	1363
nC_5	0.001	30,000	30	0.003	30,700	92
		$h_0 = 23{,}950$			$h_1 = 25{,}562$	

	$H_1(T_1 = 65°C)$			$H_2(T_2 = 70°C \text{ assumed})$		
	v_1	H_i	$H_i y_i$	y_2	H_i	$H_i y_i$
C_3	0.10	34,000	3400	0.057	34,800	1984
iC_4	0.33	41,000	13,530	0.292	41,300	12,142
nC_4	0.54	43,700	23,498	0.600	44,200	26,697
iC_5	0.02	52,000	1040	0.041	52,500	2153
nC_5	0.001	54,800	55	0.013	55,000	715
		$H_1 = 41{,}623$			$H_2 = 43{,}691$	

Energy balance (equation iii)

$$23{,}950 \times 112.8 + 43{,}691 V_2 = 25{,}562 L_1 + 41{,}623 \times 157.9$$

$$43{,}691 V_2 = 255{,}626 L_1 + 3{,}870{,}712$$

Material balance (equation i)

$$112.8 + V_2 = L_1 + 157.9$$

substituting

$$43{,}691(L_1 + 45.1) = 25{,}562L_1 + 3{,}870{,}712$$

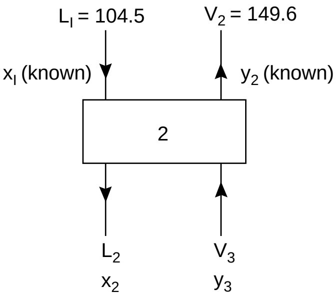
$$L_1 = 104.8$$

$$V_2 = 104.8 + 45.1 = 149.9$$

$$\frac{L_1}{V_2} = 0.70$$

Could revise calculated values for y_2 but L_1/V_2 is close enough to assumed value of 0.71, so there would be no significant difference from first estimate.

Stage 2



Estimation of stage temperature and outlet liquid composition (x_2).

		$T_2 = 70°\text{C}$ (use assumed value as first trial)		
	y_2	K_i	$x_2 = y_2/K_i$	x_2 Normalised
C_3	0.057	2.55	0.022	0.022
iC_4	0.292	1.30	0.226	0.222
nC_4	0.600	0.94	0.643	0.630
iC_5	0.041	0.43	0.095	0.093
nC_5	0.013	0.38	0.034	0.033
			1.020 close enough to 1.0	

$$y_3 = \frac{L}{V}(x_2 - x_1) + y_2$$

As a first trial take L/V as $L_1/V_1 = 0.70$

	x_2	x_1	$y_3 = 0.70(x_2 - x_1) + y_2$	y_3 Normalised
C_3	0.022	0.042	0.044	0.043
iC_4	0.222	0.277	0.256	0.251
nC_4	0.630	0.628	0.613	0.601
iC_5	0.093	0.048	0.072	0.072
nC_5	0.033	0.003	0.035	0.034
			1.020	

Enthalpy data from Figures (*b*) and (*c*)

	$h_2(T_2 = 70°\text{C})$			$H_3(T_3 = 75°\text{C assumed})$		
	x_2	h_i	$h_i x_2$	y_3	H_i	$H_i y_3$
C_3	0.022	21,900	482	0.043	34,600	1488
iC_4	0.222	25,300	5617	0.251	41,800	10,492
nC_4	0.630	27,000	17,010	0.601	44,700	26,865
iC_5	0.093	29,500	2744	0.072	53,000	3816
nC_5	0.033	31,600	1043	0.035	55,400	1939
	$h_2 = 26,896$			$H_3 = 44,600$		

Energy balance

$$25{,}562 \times 104.8 + 44{,}600 V_3 = 4369 \times 149.9 + 26{,}896 L_2$$

Material balance

$$104.8 + V_3 = 149.9 + L_2$$

$$L_2 = 105.0$$

$$V_3 = 150.1$$

$$\frac{L_2}{V_3} = 0.70 \text{ checks with assumed value.}$$

Stage 3

As the calculated liquid and vapour flows are not changing much from stage to stage the calculation will be continued with the value of L/V taken as constant at 0.7.

	Try $T_3 = 75$°C (assumed value)			
	K_i	$x_3 = y_3/K_i$	Normalised	$y_4 = 0.7(x_3 - x_2) + y_3$
C_3	2.71	0.016	0.015	0.38
iC_4	1.40	0.183	0.177	0.217
nC_4	1.02	0.601	0.580	0.570
iC_5	0.50	0.144	0.139	0.104
nC_5	0.38	0.092	0.089	0.074
		1.036		1.003
		Close enough		

Stage 4

	Try $T_4 = 81$°C			
	K_i	$x_4 = y_4/K_i$	Normalised	$y_5 = 0.7(x_4 - x_3) + y_4$
C_3	2.95	0.013	0.013	0.039
iC_4	1.55	0.140	0.139	0.199
nC_4	1.13	0.504	0.501	0.515
iC_5	0.55	0.189	0.188	0.137
nC_5	0.46	0.161	0.166	0.118
		1.007		1.008
			Close enough	

Stage 5

	Try $T_5 = 85$°C			
	K_i	x_5	Normalised	$y_6 = 0.7(x_5 - x_4) + y_5$
C_3	3.12	0.013	0.012	0.038
iC_4	1.66	0.120	0.115	0.179
nC_4	1.20	0.430	0.410	0.450
iC_5	0.60	0.228	0.218	0.159
nC_5	0.46	0.257	0.245	0.192
		1.048		1.018
			Close enough	

Stage 6

	Try $T_6 = 90°\text{C}$		Try $T_6 = 92°\text{C}$			
	K_i	x_6	K_i	x_6	Normalised	y_7
C_3	3.35	0.011	3.45	0.011	0.011	0.037
iC_4	1.80	0.099	1.85	0.097	0.095	0.166
nC_4	1.32	0.341	1.38	0.376	0.318	0.386
iC_5	0.65	0.245	0.69	0.230	0.224	0.163
nC_5	0.51	0.376	0.53	0.362	0.350	0.268
		1.072 too low		1.026 close enough		1.020

$$\text{Note: ratio of LK to HK in liquid from this stage} = \frac{0.386}{0.163} = 2.37$$

Stage 7

	Try $T_6 = 97°\text{C}$		
	K_i	x_7	Normalised
C_3	3.65	0.010	0.010
iC_4	1.98	0.084	0.083
nC_4	1.52	0.254	0.251
iC_5	0.75	0.217	0.214
nC_5	0.60	0.447	0.442
		1.012	

$$\text{ratio } \frac{\text{LK}}{\text{HK}} = \frac{0.251}{0.214} = 1.17$$

This is just below the ratio in the feed

$$= \frac{25}{20} = 1.25$$

So, the feed would be introduced at this stage.

But the composition of the non-key components on the plate does not match the feed composition.

	x_f	x_7
C_3	0.05	0.10
iC_4	0.15	0.084
nC_4	0.25	0.254
iC_5	0.20	0.217
nC_5	0.35	0.447

So it would be necessary to adjust the assumed top composition and repeat the calculation.

Bottom-up calculation

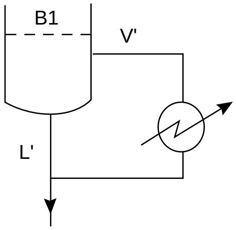
To illustrate the procedure the calculation will be shown for the reboiler and bottom stage, assuming constant molar overflow.

With the feed at its boiling point and constant molar overflow the base flows can be calculated as follows:

$$V' = V_0 = 157.9$$

$$L' = L_0 + \text{FEED} = 112.8 + 100 = 212.8$$

$$\frac{V'}{L'} = \frac{157.9}{212.8} = 0.74$$



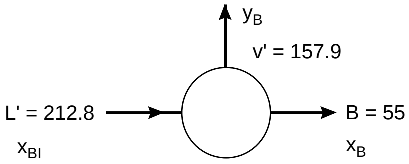
It will be necessary to estimate the concentration of the non-key components in the bottom product; as a first trial take:

C_3	iC_4	nC_4	iC_5	nC_5
0.001	0.001	0.02	0.34	0.64

Reboiler

Check bubble-point estimate of 120°C

	Try 120°C			Try 118°C	
	x_B	K_i	$y_B = K_i x_B$	K_i	y_B
C_3	0.001	4.73	0.005	4.60	0.005
iC_4	0.001	2.65	0.003	2.58	0.003
nC_4	0.02	2.10	0.042	2.03	0.041
iC_5	0.34	1.10	0.374	1.06	0.360
nC_5	0.64	0.96	0.614	0.92	0.589
			1.038 too high		0.998 close enough



Material balance:

$$
\begin{aligned}
x_{B1}L' &= y_B V' + x_B B \\
x_{B1} &= \frac{V'}{L'} y_B + \frac{B}{L'} x_B \\
x_{B1} &= \frac{157.9}{212.8} y_B + \frac{55}{212.8} x_B \\
&= 0.74 y_B + 0.26 x_B
\end{aligned}
$$

Stage 1 from base (B1)

	x_B	y_B	x_{B1}	$x_{B2} = 0.74(y_{1B} - y_B) + x_{1B}$
C_3	0.001	0.005	0.004	0.014
iC_4	0.001	0.003	0.002	0.036
nC_4	0.02	0.041	0.020	0.019
iC_5	0.34	0.361	0.356	0.357
nC_5	0.64	0.590	0.603	0.559
				0.985

The calculation is continued stage-by-stage up the column to the feed point (stage 7 from the top). If the vapour composition at the feed point does not mesh with the top-down calculation, the assumed concentration of the non-keys in the bottom product is adjusted and the calculations repeated.

11.8. MULTICOMPONENT SYSTEMS: RIGOROUS SOLUTION PROCEDURES (COMPUTER METHODS)

The application of digital computers has made the rigorous solution of the MESH equations (Section 11.3.1) a practical proposition, and computer methods for the design of multicomponent separation columns will be available in most design organisations. Programs, and computer time, can also be rented from commercial computing bureaux. A considerable amount of work has been done over the past twenty or so years to develop efficient and reliable computer-aided design procedures for distillation and other staged processes. A detailed discussion of this work is beyond the scope of this book and the reader is referred to the specialist books that have been published on the subject, Smith (1963), Holland (1997) and Kister (1992), and to the numerous papers that have appeared in the chemical engineering literature. A good summary of the present state of the art is given by Haas (1992).

Several different approaches have been taken to develop programs that are efficient in the use of computer time, and suitable for the full range of multicomponent separation processes that are used in the process industries. A design group will use those methods that are best suited to the processes that it normally handles.

In this section only a brief outline of the methods that have been developed will be given.

The basic steps in any rigorous solution procedure will be:

1. Specification of the problem; complete specification is essential for computer methods.
2. Selection of values for the iteration variables; for example, estimated stage temperatures, and liquid and vapour flows (the column temperature and flow profiles).
3. A calculation procedure for the solution of the stage equations.
4. A procedure for the selection of new values for the iteration variables for each set of trial calculations.
5. A procedure to test for convergence; to check if a satisfactory solution has been achieved.

It is convenient to consider the methods available under the following four headings:

1. Lewis-Matheson method.
2. Thiele-Geddes method.
3. Relaxation methods.
4. Linear algebra methods.

Rating and design methods

With the exception of the Lewis-Matheson method, all the methods listed above require the specification of the number of stages below and above the feed point. They are therefore not directly applicable to design: where the designer wants to determine the number of stages required for a specified separation. They are strictly what are referred to as "rating methods"; used to determine the performance of existing, or specified, columns. Given the number of stages they can be used to determine product compositions. Iterative procedures are necessary to apply rating methods to the design of new columns. An initial estimate of the number of stages can be made using short-cut methods and the programs used to calculate the product compositions; repeating the calculations with revised estimates till a satisfactory design is obtained.

11.8.1. Lewis-Matheson method

The method proposed by Lewis and Matheson (1932) is essentially the application of the Lewis-Sorel method (Section 11.5.1) to the solution of multicomponent problems. Constant molar overflow is assumed and the material balance and equilibrium relationship equations are solved stage by stage starting at the top or bottom of the column, in the manner illustrated in Example 11.9. To define a problem for the Lewis-Matheson method the following variables must be specified, or determined from other specified variables:

Feed composition, flow rate and condition.
Distribution of the key components.
One product flow.
Reflux ratio.
Column pressure.
Assumed values for the distribution of the non-key components.

The usual procedure is to start the calculation at the top and bottom of the column and proceed toward the feed point. The initial estimates of the component distributions in the products are then revised and the calculations repeated until the compositions calculated from the top and bottom starts mesh, and match the feed at the feed point.

Efficient procedures for adjusting the compositions to achieve a satisfactory mesh at the feed point are given by Hengstebeck (1976).

In some computer applications of the method, where the assumption of constant molar overflow is not made, it is convenient to start the calculations by assuming flow and temperature profiles. The stage component compositions can then be readily determined and used to revise the profiles for the next iteration. With this modification the procedure is similar to the Thiele-Geddes method discussed in the next section.

In general, the Lewis-Matheson method has not been found to be an efficient procedure for computer solutions, other than for relatively straightforward problems. It is not suitable for problems involving multiple feeds, and side-streams, or where more than one column is needed.

The method is suitable for interactive programs run on programmable calculators and Personal Computers. Such programs can be "semi-manual" in operation: the computer solving the stage equations, while control of the iteration variables, and convergence is kept by the designer. As the calculations are carried out one stage at a time, only a relatively small computer memory is needed.

11.8.2. Thiele-Geddes method

Like the Lewis-Matheson method, the original method of Thiele and Geddes (1933) was developed for manual calculation. It has subsequently been adapted by many workers for computer applications. The variables specified in the basic method, or that must be derived from other specified variables, are:

Reflux temperature.
Reflux flow rate.
Distillate rate.
Feed flows and condition.
Column pressure.
Number of equilibrium stages above and below the feed point.

The basic procedure used in the Thiele-Geddes method, with examples, is described in books by Smith (1963) and Deshpande (1985). The application of the method to computers is covered in a series of articles by Lyster *et al*. (1959) and Holland (1963).

The method starts with an assumption of the column temperature and flow profiles. The stage equations are then solved to determine the stage component compositions and the results used to revise the temperature profiles for subsequent trial calculations. Efficient convergence procedures have been developed for the Thiele-Geddes method. The so-called "theta method", described by Lyster *et al*. (1959) and Holland (1963), is recommended. The Thiele-Geddes method can be used for the solution of complex distillation problems, and for other multi-component separation processes. A series of programs for the solution of problems in distillation, extraction, stripping and absorption, which use an iterative procedure similar to the Thiele-Geddes method, are given by Hanson *et al.* (1962).

11.8.3. Relaxation methods

With the exception of this method, all the methods described solve the stage equations for the steady-state design conditions. In an operating column other conditions will exist at start-up, and the column will approach the "design" steady-state conditions after a period of time. The stage material balance equations can be written in a finite difference form, and procedures for the solution of these equations will model the unsteady-state behaviour of the column.

Rose *et al.* (1958) and Hanson and Sommerville (1963) have applied "relaxation methods" to the solution of the unsteady-state equations to obtain the steady-state values. The application of this method to the design of multistage columns is described by Hanson and Sommerville (1963). They give a program listing and worked examples for a distillation column with side-streams, and for a reboiled absorber.

Relaxation methods are not competitive with the "steady-state" methods in the use of computer time, because of slow convergence. However, because they model the actual operation of the column, convergence should be achieved for all practical problems. The method has the potential of development for the study of the transient behaviour of column designs, and for the analysis and design of batch distillation columns.

11.8.4. Linear algebra methods

The Lewis-Matheson and Thiele-Geddes methods use a stage-by-stage procedure to solve the equations relating the component compositions to the column temperature and flow profiles. However, the development of high-speed digital computers with large memories makes possible the simultaneous solution of the complete set of MESH equations that describe the stage compositions throughout the column.

If the equilibrium relationships and flow-rates are known (or assumed) the set of material balance equations for each component is linear in the component compositions. Amundson and Pontinen (1958) developed a method in which these equations are solved simultaneously and the results used to provide improved estimates of the temperature and flow profiles. The set of equations can be expressed in matrix form and solved using the standard inversion routines available in modern computer systems. Convergence can usually be achieved after a few iterations.

This approach has been further developed by other workers; notably Wang and Henke (1966) and Naphtali and Sandholm (1971).

The linearisation method of Naphtali and Sandholm has been used by Fredenslund *et al.* (1977) for the multicomponent distillation program given in their book. Included in their book, and coupled to the distillation program, are methods for estimation of the liquid-vapour relationships (activity coefficients) using the UNIFAC method (see Chapter 8, Section 16.3). This makes the program particularly useful for the design of columns for new processes, where experimental data for the equilibrium relationships are unlikely to be available. The program is recommended to those who do not have access to their own "in house" programs.

11.9. OTHER DISTILLATION SYSTEMS

11.9.1. Batch distillation

In batch distillation the mixture to be distilled is charged as a batch to the still and the distillation carried out till a satisfactory top or bottom product is achieved. The still usually consists of a vessel surmounted by a packed or plate column. The heater may be incorporated in the vessel or a separate reboiler used. Batch distillation should be considered under the following circumstances:

1. Where the quantity to be distilled is small.
2. Where a range of products has to be produced.
3. Where the feed is produced at irregular intervals.
4. Where the feed composition varies over a wide range.

Where the choice between batch and continuous is uncertain an economic evaluation of both systems should be made.

Batch distillation is an unsteady state process, the composition in the still (bottoms) varying as the batch is distilled.

Two modes of operation are used.

1. Fixed reflux, where the reflux rate is kept constant. The compositions will vary as the more volatile component is distilled off, and the distillation stopped when the average composition of the distillate collected, or the bottoms left, meet the specification required.
2. Variable reflux, where the reflux rate is varied throughout the distillation to produce a fixed overhead composition. The reflux ratio will need to be progressively increased as the fraction of the more volatile component in the base of the still decreases.

The basic theory of batch distillation is given in Volume 2, Chapter 11 and in several other texts: Hart (1997), Perry *et al.* (1997) and Walas (1990). In the simple theoretical analysis of batch distillation columns the liquid hold-up in the column is usually ignored. This hold-up can have a significant effect on the separating efficiency and should be taken into account when designing batch distillation columns. The practical design of batch distillation columns is covered by Hengstebeck (1976), Ellerbe (1997) and Hart (1997).

11.9.2. Steam distillation

In steam distillation, steam is introduced into the column to lower the partial pressure of the volatile components. It is used for the distillation of heat sensitive products and for compounds with a high boiling point. It is an alternative to vacuum distillation. The products must be immiscible with water. Some steam will normally be allowed to condense to provide the heat required for the distillation. Live steam can be injected directly into the column base, or the steam generated by a heater in the still or in an external boiler.

The design procedures for columns employing steam distillation is essentially the same as that for conventional columns, making allowance for the presence of steam in the vapour; see Volume 2, Chapter 11.

Steam distillation is used extensively in the extraction of essential oils from plant materials.

11.9.3. Reactive distillation

Reactive distillation is the name given to the process where the chemical reaction and product separation are carried out simultaneously in one unit. Carrying out the reaction, with separation and purification of the product by distillation, gives the following advantages:

1. Chemical equilibrium restrictions are overcome, as the product is removed as it is formed.
2. Energy savings can be obtained, as the heat of reaction can be utilised for the distillation.
3. Capital costs are reduced, as only one vessel is required.

The design of reactive distillation columns is complicated by the complex interactions between the reaction and separation processes. A comprehensive discussion of the process is given by Sundmacher and Kiene (2003).

Reactive distillation is used in the production of MTBE (methyl tertiary butyl ether) and methyl acetate.

11.10. PLATE EFFICIENCY

The designer is concerned with real contacting stages; not the theoretical equilibrium stage assumed for convenience in the mathematical analysis of multistage processes. Equilibrium will rarely be attained in a real stage. The concept of a stage efficiency is used to link the performance of practical contacting stages to the theoretical equilibrium stage.

Three principal definitions of efficiency are used:

1. Murphree plate efficiency (Murphree, 1925), defined in terms of the vapour compositions by:

$$E_{mV} = \frac{y_n - y_{n-1}}{y_e - y_{n-1}} \tag{11.64}$$

   where y_e is the composition of the vapour that would be in equilibrium with the liquid leaving the plate. The Murphree plate efficiency is the ratio of the actual separation achieved to that which would be achieved in an equilibrium stage (see Figure 11.6). In this definition of efficiency the liquid and the vapour stream are taken to be perfectly mixed; the compositions in equation 11.64 are the average composition values for the streams.
2. Point efficiency (Murphree point efficiency). If the vapour and liquid compositions are taken at a point on the plate, equation 11.64 gives the local or point efficiency, E_{mv}.

3. Overall column efficiency. This is sometimes confusingly referred to as the overall plate efficiency.

$$E_o = \frac{\text{number of ideal stages}}{\text{number of real stages}} \tag{11.65}$$

An estimate of the overall column efficiency will be needed when the design method used gives an estimate of the number of ideal stages required for the separation.

In some methods, the Murphree plate efficiencies can be incorporated into the procedure for calculating the number of stages and the number of real stages determined directly.

For the idealised situation where the operating and equilibrium lines are straight, the overall column efficiency and the Murphree plate efficiency are related by an equation derived by Lewis (1936):

$$E_0 = \frac{\log\left[1 + E_{mV}\left(\frac{mV}{L} - 1\right)\right]}{\log\left(\frac{mV}{L}\right)} \tag{11.66}$$

where m = slope of the equilibrium line,
V = molar flow rate of the vapour,
L = molar flow rate of the liquid.

Equation 11.66 is not of much practical use in distillation, as the slopes of the operating and equilibrium lines will vary throughout the column. It can be used by dividing the column into sections and calculating the slopes over each section. For most practical purposes, providing the plate efficiency does not vary too much, a simple average of the plate efficiency calculated at the column top, bottom and feed points will be sufficiently accurate.

11.10.1. Prediction of plate efficiency

Whenever possible the plate efficiencies used in design should be based on experimental values for similar systems, obtained on full-sized columns. There is no entirely satisfactory method for predicting plate efficiencies from the system physical properties and plate design parameters. However, the methods given in this section can be used to make a rough estimate where no reliable experimental values are available. They can also be used to extrapolate data obtained from small-scale experimental columns. If the system properties are at all unusual, experimental confirmation of the predicted values should always be obtained. The small, laboratory scale, glass sieve plate column developed by Oldershaw (1941) has been shown to give reliable values for scale-up. The use of Oldershaw columns is described in papers by Swanson and Gester (1962), Veatch *et al.* (1960) and Fair *et al.* (1983).

Some typical values of plate efficiency for a range of systems are given in Table 11.1. More extensive compilations of experimental data are given by Vital *et al.* (1984) and Kister (1992).

Plate, and overall column, efficiencies will normally be between 30 per cent and 70 per cent, and as a rough guide a figure of 50 per cent can be assumed for preliminary designs.

Table 11.1. Representative efficiencies, sieve plates

System	Column dia., m	Pressure kPa, abs	Efficiency % E_{mV}	E_o
Water-methanol	1.0	—	80	
Water-ethanol	0.2	101	90	
Water-isopropanol	—	—		70
Water-acetone	0.15	90	80	
Water-acetic acid	0.46	101	75	
Water-ammonia	0.3	101	90	
Water-carbon dioxide	0.08	—	80	
Toluene-propanol	0.46	—	65	
Toluene-ethylene dichloride	0.05	101		75
Toluene-methylethylketone	0.15	—		85
Toluene-cyclohexane	2.4	—		70
Toluene-methylcyclohexane	—	27		90
Toluene-octane	0.15	101		40
Heptane-cyclohexane	1.2	165	95	85
	2.4	165		75
Propane-butane	—	—		100
Isobutane-n-butane	—	2070		110
Benzene-toluene	0.13	—	75	
Benzene-methanol	0.18	690	94	
Benzene-propanol	0.46	—	55	
Ethylbenzene-styrene	—	—	75	

E_{mV} = Murphree plate efficiency,
E_o = Overall column efficiency.

Efficiencies will be lower for vacuum distillations, as low weir heights are used to keep the pressure drop small (see Section 11.10.4).

Multicomponent systems

The prediction methods given in the following sections, and those available in the open literature, are invariably restricted to binary systems. It is clear that in a binary system the efficiency obtained for each component must be the same. This is not so for a multicomponent system; the heavier components will usually exhibit lower efficiencies than the lighter components.

The following guide rules, adapted from a paper by Toor and Burchard (1960), can be used to estimate the efficiencies for a multicomponent system from binary data:

1. If the components are similar, the multicomponent efficiencies will be similar to the binary efficiency.
2. If the predicted efficiencies for the binary pairs are high, the multicomponent efficiency will be high.
3. If the resistance to mass transfer is mainly in the liquid phase, the difference between the binary and multicomponent efficiencies will be small.
4. If the resistance is mainly in the vapour phase, as it normally will be, the difference between the binary and multicomponent efficiencies can be substantial.

The prediction of efficiencies for multicomponent systems is also discussed by Chan and Fair (1984b). For mixtures of dissimilar compounds the efficiency can be very different from that predicted for each binary pair, and laboratory or pilot-plant studies should be made to confirm any predictions.

11.10.2. O'Connell's correlation

A quick estimate of the overall column efficiency can be obtained from the correlation given by O'Connell (1946), which is shown in Figure 11.13. The overall column efficiency is correlated with the product of the relative volatility of the light key component (relative to the heavy key) and the molar average viscosity of the feed, estimated at the average column temperature. The correlation was based mainly on data obtained with hydrocarbon systems, but includes some values for chlorinated solvents and water-alcohol mixtures. It has been found to give reliable estimates of the overall column efficiency for hydrocarbon systems; and can be used to make an approximate estimate of the efficiency for other systems. The method takes no account of the plate design parameters; and includes only two physical property variables.

Eduljee (1958) has expressed the O'Connell correlation in the form of an equation:

$$E_o = 51 - 32.5 \log(\mu_a \alpha_a) \tag{11.67}$$

where μ_a = the molar average liquid viscosity, mNs/m^2,
α_a = average relative volatility of the light key.

Absorbers

O'Connell gave a similar correlation for the *plate efficiency* of absorbers; Figure 11.14. Appreciably lower plate efficiencies are obtained in absorption than in distillation.

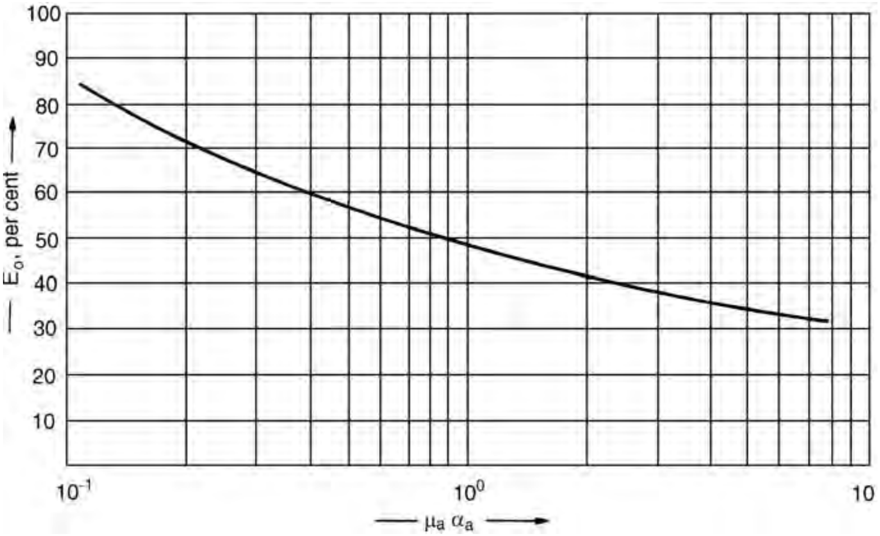


Figure 11.13. Distillation column efficiencies (bubble-caps) (after O'Connell, 1946)

CHAPTER 13

Mechanical Design of Process Equipment

13.1. INTRODUCTION

This chapter covers those aspects of the mechanical design of chemical plant that are of particular interest to chemical engineers. The main topic considered is the design of pressure vessels. The design of storage tanks, centrifuges and heat-exchanger tube sheets are also discussed briefly.

The chemical engineer will not usually be called on to undertake the detailed mechanical design of a pressure vessel. Vessel design is a specialised subject, and will be carried out by mechanical engineers who are conversant with the current design codes and practices, and methods of stress analysis. However, the chemical engineer will be responsible for developing and specifying the basic design information for a particular vessel, and needs to have a general appreciation of pressure vessel design to work effectively with the specialist designer.

The basic data needed by the specialist designer will be:

1. Vessel function.
2. Process materials and services.
3. Operating and design temperature and pressure.
4. Materials of construction.
5. Vessel dimensions and orientation.
6. Type of vessel heads to be used.
7. Openings and connections required.
8. Specification of heating and cooling jackets or coils.
9. Type of agitator.
10. Specification of internal fittings.

A data sheet for pressure vessel design is given in Appendix G.

There is no strict definition of what constitutes a pressure vessel, but it is generally accepted that any closed vessel over 150 mm diameter subject to a pressure difference of more than 0.5 bar should be designed as a pressure vessel.

It is not possible to give a completely comprehensive account of vessel design in one chapter. The design methods and data given should be sufficient for the preliminary design of conventional vessels. Sufficient for the chemical engineer to check the feasibility of a proposed equipment design; to estimate the vessel cost for an economic analysis; and to determine the vessel's general proportions and weight for plant layout purposes. For a more detailed account of pressure vessel design the reader should refer to the books by Singh and Soler (1992), Escoe (1994) and Moss (1987). Other useful books on the mechanical design of process equipment are listed in the bibliography at the end of this chapter.

An elementary understanding of the principles of the "Strength of Materials" (Mechanics of Solids) will be needed to follow this chapter. Readers who are not familiar with the subject should consult one of the many textbooks available; such as those by Case *et al.* (1999), Mott, R. L. (2001), Seed (2001) and Gere and Timoshenko (2000).

13.1.1. Classification of pressure vessels

For the purposes of design and analysis, pressure vessels are sub-divided into two classes depending on the ratio of the wall thickness to vessel diameter: thin-walled vessels, with a thickness ratio of less than 1 : 10; and thick-walled above this ratio.

The principal stresses (see Section 13.3.1) acting at a point in the wall of a vessel, due to a pressure load, are shown in Figure 13.1. If the wall is thin, the radial stress σ_3 will be small and can be neglected in comparison with the other stresses, and the longitudinal and circumferential stresses σ_1 and σ_2 can be taken as constant over the wall thickness. In a thick wall, the magnitude of the radial stress will be significant, and the circumferential stress will vary across the wall. The majority of the vessels used in the chemical and allied industries are classified as thin-walled vessels. Thick-walled vessels are used for high pressures, and are discussed in Section 13.15.

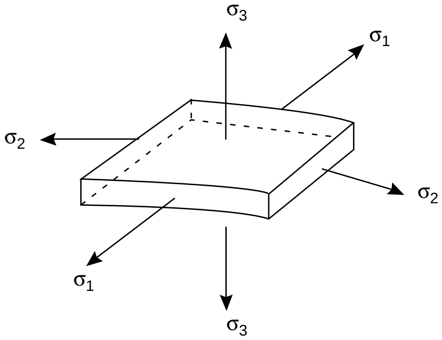


Figure 13.1. Principal stresses in pressure-vessel wall

13.2. PRESSURE VESSEL CODES AND STANDARDS

In all the major industrialised countries the design and fabrication of thin-walled pressure vessels is covered by national standards and codes of practice. In most countries the standards and codes are legally enforceable.

In the United Kingdom all conventional pressure vessels for use in the chemical and allied industries will invariably be designed and fabricated according to the British Standard PD 5500 or the European Standard EN 13445; or an equivalent code such as the American Society of Mechanical Engineers code Section VIII (the ASME code). The codes and standards cover design, materials of construction, fabrication (manufacture and workmanship), and inspection and testing. They form a basis of agreement between the manufacturer and customer, and the customer's insurance company.

In the European Union the design, manufacture and use of pressure systems is also covered by the Pressure Equipment Directive (Council Directive 97/23/EC) whose use became mandatory in May 2002.

The current (2003) edition of PD 5500 covers vessels fabricated in carbon and alloy steels, and aluminium. The design of vessels constructed from reinforced plastics is covered by BS 4994. The ASME code covers steels, non-ferrous metals, and fibre-reinforced plastics.

Where national codes are not available, the British, European or American codes would be used.

Information and guidance on the pressure vessel codes can be found on the Internet; www.bsi-global.com.

A comprehensive review of the ASME code is given by Chuse and Carson (1992) and Yokell (1986); see also Perry *et al.* (1997).

The national codes and standards dictate the minimum requirements, and give general guidance for design and construction; any extension beyond the minimum code requirement will be determined by agreement between the manufacturer and customer.

The codes and standards are drawn up by committees of engineers experienced in vessel design and manufacturing techniques, and are a blend of theory, experiment and experience. They are periodically reviewed, and revisions issued to keep abreast of developments in design, stress analysis, fabrication and testing. The latest version of the appropriate national code or standard should always be consulted before undertaking the design of any pressure vessel.

Computer programs to aid in the design of vessels to PD 5500 and the ASME code are available from several commercial organisations and can be found by making a search of the World Wide Web.

13.3. FUNDAMENTAL PRINCIPLES AND EQUATIONS

This section has been included to provide a basic understanding of the fundamental principles that underlie the design equations given in the sections that follow. The derivation of the equations is given in outline only. A full discussion of the topics covered can be found in any text on the "Strength of Materials" (Mechanics of Solids).

13.3.1. Principal stresses

The state of stress at a point in a structural member under a complex system of loading is described by the magnitude and direction of the principal stresses. The principal stresses are the maximum values of the normal stresses at the point; which act on planes on which the shear stress is zero. In a two-dimensional stress system, Figure 13.2, the principal stresses at any point are related to the normal stresses in the x and y directions σ_x and σ_y and the shear stress τ_{xy} at the point by the following equation:

$$\text{Principal stresses, } \sigma_1, \sigma_2 = \frac{1}{2}(\sigma_y + \sigma_x) \pm \frac{1}{2}\sqrt{[(\sigma_y - \sigma_x)^2 + 4\tau_{xy}^2]} \tag{13.1}$$

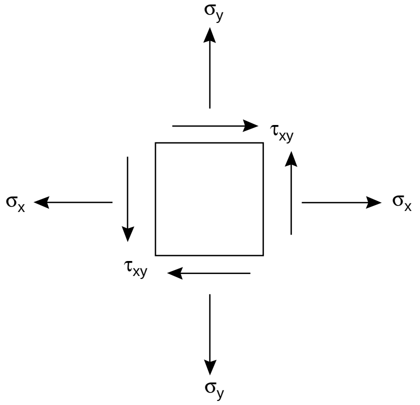


Figure 13.2. Two-dimensional stress system

The maximum shear stress at the point is equal to half the algebraic difference between the principal stresses:

$$\text{Maximum shear stress } = \tfrac{1}{2}(\sigma_1 - \sigma_2) \tag{13.2}$$

Compressive stresses are conventionally taken as negative; tensile as positive.

13.3.2. Theories of failure

The failure of a simple structural element under unidirectional stress (tensile or compressive) is easy to relate to the tensile strength of the material, as determined in a standard tensile test, but for components subjected to combined stresses (normal and shear stress) the position is not so simple, and several theories of failure have been proposed. The three theories most commonly used are described below:

Maximum principal stress theory: which postulates that a member will fail when one of the principal stresses reaches the failure value in simple tension, σ'_e. The failure point in a simple tension is taken as the yield-point stress, or the tensile strength of the material, divided by a suitable factor of safety.

Maximum shear stress theory: which postulates that failure will occur in a complex stress system when the maximum shear stress reaches the value of the shear stress at failure in simple tension.

For a system of combined stresses there are three shear stresses maxima:

$$\tau_1 = \frac{\sigma_1 - \sigma_2}{2} \tag{13.3a}$$

$$\tau_2 = \frac{\sigma_2 - \sigma_3}{2} \tag{13.3b}$$

$$\tau_3 = \frac{\sigma_3 - \sigma_1}{2} \tag{13.3c}$$

In the tensile test,

$$\tau_e = \frac{\sigma'_e}{2} \tag{13.4}$$

The maximum shear stress will depend on the sign of the principal stresses as well as their magnitude, and in a two-dimensional stress system, such as that in the wall of a thin-walled pressure vessel, the maximum value of the shear stress may be that given by putting $\sigma_3 = 0$ in equations 13.3*b* and *c*.

The maximum shear stress theory is often called Tresca's, or Guest's, theory.

Maximum strain energy theory: which postulates that failure will occur in a complex stress system when the total strain energy per unit volume reaches the value at which failure occurs in simple tension.

The maximum shear-stress theory has been found to be suitable for predicting the failure of ductile materials under complex loading and is the criterion normally used in the pressure-vessel design.

13.3.3. Elastic stability

Under certain loading conditions failure of a structure can occur not through gross yielding or plastic failure, but by buckling, or wrinkling. Buckling results in a gross and sudden change of shape of the structure; unlike failure by plastic yielding, where the structure retains the same basic shape. This mode of failure will occur when the structure is not elastically stable: when it lacks sufficient stiffness, or rigidity, to withstand the load. The stiffness of a structural member is dependent not on the basic strength of the material but on its elastic properties (E and v) and the cross-sectional shape of the member.

The classic example of failure due to elastic instability is the buckling of tall thin columns (struts), which is described in any elementary text on the "Strength of Materials".

For a structure that is likely to fail by buckling there will be a certain critical value of load below which the structure is stable; if this value is exceeded catastrophic failure through buckling can occur.

The walls of pressure vessels are usually relatively thin compared with the other dimensions and can fail by buckling under compressive loads.

Elastic buckling is the decisive criterion in the design of thin-walled vessels under external pressure.

13.3.4. Membrane stresses in shells of revolution

A shell of revolution is the form swept out by a line or curve rotated about an axis. (A solid of revolution is formed by rotating an area about an axis.) Most process vessels are made up from shells of revolution: cylindrical and conical sections; and hemispherical, ellipsoidal and torispherical heads; Figure 13.3.

The walls of thin vessels can be considered to be "membranes"; supporting loads without significant bending or shear stresses; similar to the walls of a balloon.

The analysis of the membrane stresses induced in shells of revolution by internal pressure gives a basis for determining the minimum wall thickness required for vessel shells. The actual thickness required will also depend on the stresses arising from the other loads to which the vessel is subjected.

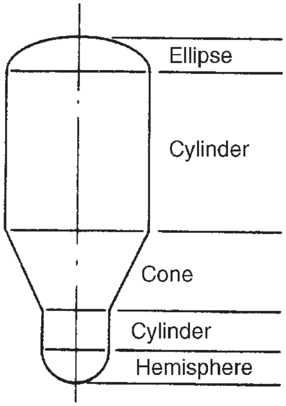


Figure 13.3. Typical vessel shapes

Consider the shell of revolution of general shape shown in Figure 13.4, under a loading that is rotationally symmetric; that is, the load per unit area (pressure) on the shell is constant round the circumference, but not necessarily the same from top to bottom.

Let P = pressure,
t = thickness of shell,
σ_1 = the meridional (longitudinal) stress, the stress acting along a meridian,
σ_2 = the circumferential or tangential stress, the stress acting along parallel circles (often called the hoop stress),
r_1 = the meridional radius of curvature,
r_2 = circumferential radius of curvature.

Note: the vessel has a double curvature; the values of r_1 and r_2 are determined by the shape.

Consider the forces acting on the element defined by the points a, b, c, d. Then the normal component (component acting at right angles to the surface) of the pressure force on the element

$$= P\left[2r_1 \sin\left(\frac{d\theta_1}{2}\right)\right]\left[2r_2 \sin\left(\frac{d\theta_2}{2}\right)\right]$$

This force is resisted by the normal component of the forces associated with the membrane stresses in the walls of the vessel (given by, force = stress × area)

$$= 2\sigma_2 t \mathrm{d}S_1 \sin\left(\frac{\mathrm{d}\theta_2}{2}\right) + 2\sigma_1 t\,\mathrm{d}S_2 \sin\left(\frac{\mathrm{d}\theta_1}{2}\right)$$

Equating these forces and simplifying, and noting that in the limit $\mathrm{d}\theta/2 \rightarrow \mathrm{d}S/2r$, and $\sin \mathrm{d}\theta \rightarrow \mathrm{d}\theta$, gives:

$$\frac{\sigma_1}{r_1} + \frac{\sigma_2}{r_2} = \frac{P}{t} \tag{13.5}$$

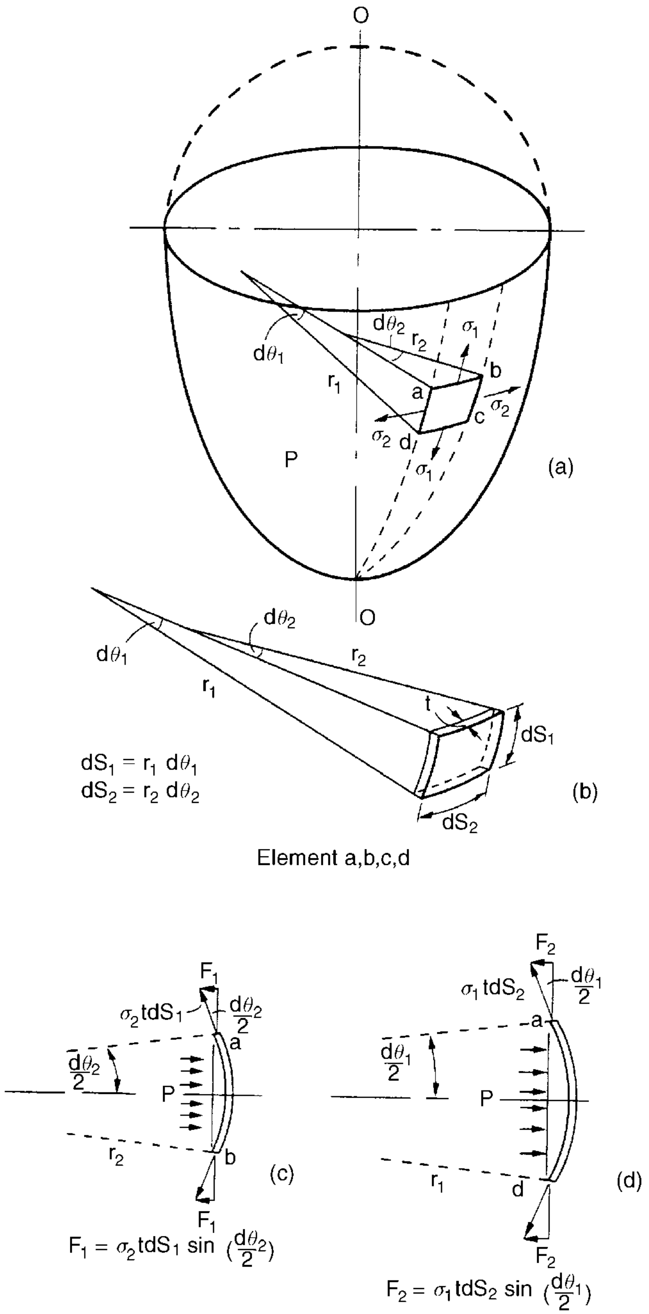


Figure 13.4(*a*)(*b*). Stress in a shell of revolution (*c*)(*d*). Forces acting on sides of element *abcd*

An expression for the meridional stress σ_1 can be obtained by considering the equilibrium of the forces acting about any circumferential line, Figure 13.5. The vertical component of the pressure force

$$= P\pi(r_2 \sin\theta)^2$$

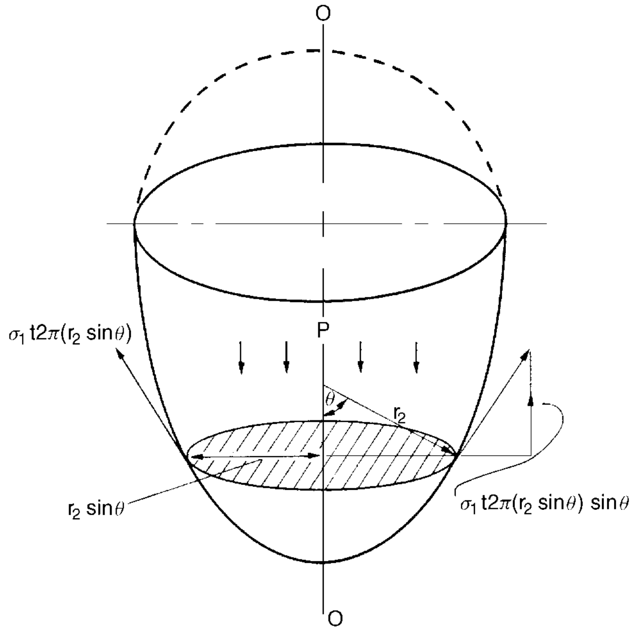


Figure 13.5. Meridional stress, force acting at a horizontal plane

This is balanced by the vertical component of the force due to the meridional stress acting in the ring of the wall of the vessel

$$= 2\sigma_1 t\pi(r_2 \sin\theta)\sin\theta$$

Equating these forces gives:

$$\sigma_1 = \frac{Pr_2}{2t} \tag{13.6}$$

Equations 13.5 and 13.6 are completely general for any shell of revolution.

Cylinder (Figure 13.6a)

A cylinder is swept out by the rotation of a line parallel to the axis of revolution, so:

$$r_1 = \infty$$

$$r_2 = \frac{D}{2}$$

where *D* is the cylinder diameter.

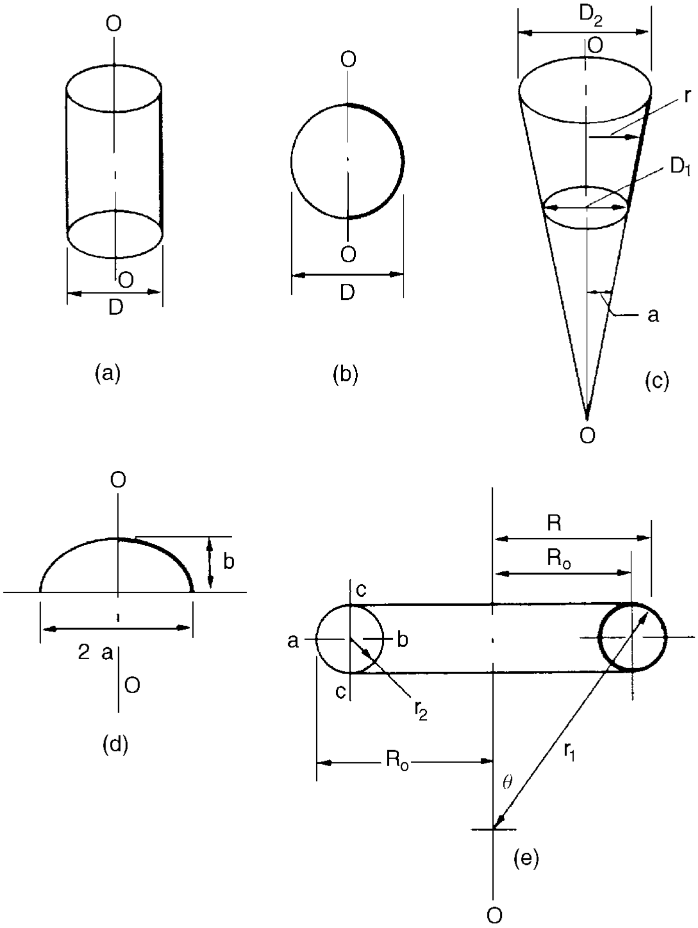


Figure 13.6. Shells of revolution

Substitution in equations 13.5 and 13.6 gives:

$$\sigma_2 = \frac{PD}{2t} \tag{13.7}$$

$$\sigma_1 = \frac{PD}{4t} \tag{13.8}$$

Sphere (Figure 13.6b)

$$r_1 = r_2 = \frac{D}{2}$$

hence:

$$\sigma_1 = \sigma_2 = \frac{PD}{4t} \tag{13.9}$$

Cone (Figure 13.6c)

A cone is swept out by a straight line inclined at an angle α to the axis.

$$r_1 = \infty$$

$$r_2 = \frac{r}{\cos\alpha}$$

substitution in equations 13.5 and 13.6 gives:

$$\sigma_2 = \frac{Pr}{t\cos\alpha} \tag{13.10}$$

$$\sigma_1 = \frac{Pr}{2t\cos\alpha} \tag{13.11}$$

The maximum values will occur at $r = D_2/2$.

Ellipsoid (Figure 13.6d)

For an ellipse with major axis $2a$ and minor axis $2b$, it can be shown that (see any standard geometry text):

$$r_1 = \frac{r_2^3 b^2}{a^4}$$

From equations 13.5 and 13.6

$$\sigma_1 = \frac{Pr_2}{2t} \qquad \text{(equation 13.6)}$$

$$\sigma_2 = \frac{P}{t}\left[r_2 - \frac{r_2^2}{2r_1}\right] \tag{13.12}$$

At the crown (top)

$$r_1 = r_2 = \frac{a^2}{b}$$

$$\sigma_1 = \sigma_2 = \frac{Pa^2}{2tb} \tag{13.13}$$

At the equator (bottom) $r_2 = a$, so $r_1 = b^2/a$

so
$$\sigma_1 = \frac{Pa}{2t} \tag{13.13}$$

$$\sigma_2 = \frac{P}{t}\left[a - \frac{a^2}{2b^2/a}\right] = \frac{Pa}{t}\left[1 - \frac{1}{2}\frac{a^2}{b^2}\right] \tag{13.14}$$

It should be noted that if $\frac{1}{2}(a/b)^2 > 1$, σ_2 will be negative (compressive) and the shell could fail by buckling. This consideration places a limit on the practical proportions of ellipsoidal heads.

Torus (Figure 13.6e)

A torus is formed by rotating a circle, radius r_2, about an axis.

$$\sigma_1 = \frac{Pr_2}{2t} \qquad \text{(equation 13.6)}$$

$$r_1 = \frac{R}{\sin\theta} = \frac{R_0 + r_2 \sin\theta}{\sin\theta}$$

and

$$\sigma_2 = \frac{Pr_2}{t}\left[1 - \frac{r_2 \sin\theta}{2(R_0 + r_2 \sin\theta)}\right] \tag{13.15}$$

On the centre line of the torus, point c, $\theta = 0$ and

$$\sigma_2 = \frac{Pr_2}{t} \tag{13.16}$$

At the outer edge, point a, $\theta = \pi/2$, $\sin\theta = 1$ and

$$\sigma_2 = \frac{Pr_2}{2t}\left[\frac{2R_0 + r_2}{R_0 + r_2}\right] \tag{13.17}$$

the minimum value.

At the inner edge, point b, $\theta = 3\pi/2$, $\sin\theta = -1$ and

$$\sigma_2 = \frac{Pr_2}{2t}\left[\frac{2R_0 - r_2}{R_0 - r_2}\right] \tag{13.18}$$

the maximum value.

So σ_2 varies from a maximum at the inner edge to a minimum at the outer edge.

Torispherical heads

A torispherical shape, which is often used as the end closure of cylindrical vessels, is formed from part of a torus and part of a sphere, Figure 13.7. The shape is close to that of an ellipse but is easier and cheaper to fabricate.

In Figure 13.7 R_k is the knuckle radius (the radius of the torus) and R_c the crown radius (the radius of the sphere). For the spherical portion:

$$\sigma_1 = \sigma_2 = \frac{PR_c}{2t} \tag{13.19}$$

For the torus:

$$\sigma_1 = \frac{PR_k}{2t} \tag{13.20}$$

σ_2 depends on the location, and is a function of R_c and R_k; it can be calculated from equations 13.15 and 13.9.

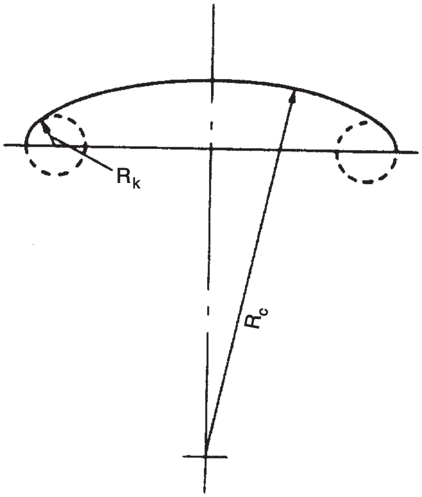


Figure 13.7. Torisphere

The ratio of the knuckle radius to crown radius should be made not less than 6/100 to avoid buckling. The stress will be higher in the torus section than the spherical section.

13.3.5. Flat plates

Flat plates are used as covers for manholes, as blind flanges, and for the ends of small diameter and low pressure vessels.

For a uniformly loaded circular plate supported at its edges, the slope ϕ at any radius x is given by:

$$\phi = -\frac{\mathrm{d}w}{\mathrm{d}x} = -\frac{1}{\mathbf{D}}\frac{Px^3}{16} + \frac{C_1 x}{2} + \frac{C_2}{x} \tag{13.21}$$

(The derivation of this equation can be found in any text on the strength of materials.)

Integration gives the deflection w:

$$w = \frac{Px^4}{64\mathbf{D}} - C_1\frac{x^2}{4} - C_2 \ln x + C_3 \tag{13.22}$$

where P = intensity of loading (pressure),
x = radial distance to point of interest,
$\mathbf{D}$ = flexual rigidity of plate $= (Et^3)/(12(1 - \nu^2))$,
t = plate thickness,
ν = Poisson's ratio for the material,
E = modulus of elasticity of the material (Young's modulus).

C_1, C_2, C_3 are constants of integration which can be obtained from the boundary conditions at the edge of the plate.

Two limiting situations are possible:

1. When the edge of the plate is rigidly clamped, not free to rotate; which corresponds to a heavy flange, or a strong joint.
2. When the edge is free to rotate (simply supported); corresponding to a weak joint, or light flange.

1. Clamped edges (Figure 13.8a)

The edge (boundary) conditions are:

$$\phi = 0 \text{ at } x = 0$$

$$\phi = 0 \text{ at } x = a$$

$$w = 0 \text{ at } x = a$$

where a is the radius of the plate.
Which gives:

$$C_2 = 0, \quad C_1 = \frac{Pa^2}{8\mathbf{D}}, \quad \text{and} \quad C_3 = \frac{Pa^4}{64\mathbf{D}}$$

hence

$$\phi = \frac{Px}{16\mathbf{D}}(a^2 - x^2) \tag{13.23}$$

and

$$w = \frac{P}{64\mathbf{D}}(x^2 - a^2)^2 \tag{13.24}$$

The maximum deflection will occur at the centre of the plate at $x = 0$

$$\hat{w} = \frac{Pa^4}{64\mathbf{D}} \tag{13.25}$$

The bending moments per unit length due to the pressure load are related to the slope and deflection by:

$$M_1 = \mathbf{D}\left[\frac{\mathrm{d}\phi}{\mathrm{d}x} + \nu\frac{\phi}{x}\right] \tag{13.26}$$

$$M_2 = \mathbf{D}\left[\frac{\phi}{x} + \nu\frac{\mathrm{d}\phi}{\mathrm{d}x}\right] \tag{13.27}$$

Where M_1 is the moment acting along cylindrical sections, and M_2 that acting along diametrical sections.

Substituting for ϕ and $\mathrm{d}\phi/\mathrm{dx}$ in equations 13.26 and 13.27 gives:

$$M_1 = \frac{P}{16}[a^2(1+\nu) - x^2(3+\nu)] \tag{13.28}$$

$$M_2 = \frac{P}{16}[a^2(1+\nu) - x^2(1+3\nu)] \tag{13.29}$$

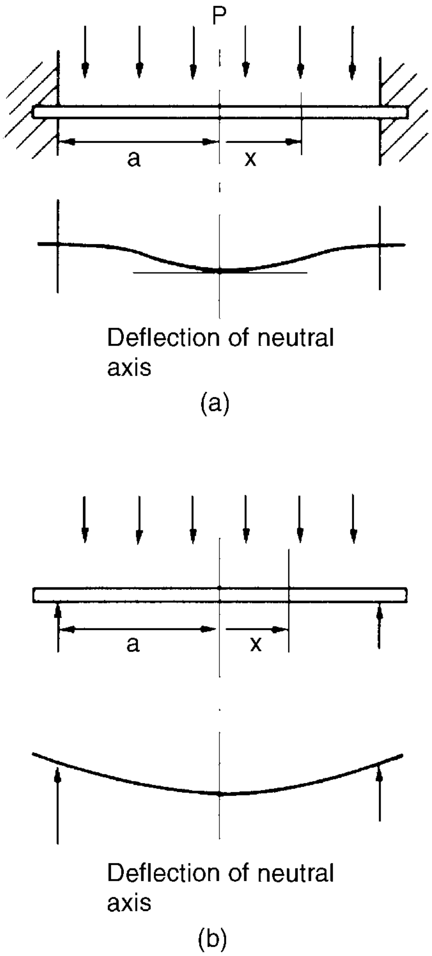


Figure 13.8. Flat circular plates (*a*) Clamped edges (*b*) Simply supported

The maximum values will occur at the edge of the plate, $x = a$.

$$\hat{M}_1 = -\frac{Pa^2}{8}, \quad \hat{M}_2 = -\nu\frac{Pa^2}{8}$$

The bending stress is given by:

$$\sigma_b = \frac{M_1}{I'} \times \frac{t}{2}$$

where I' = second moment of area per unit length $= t^3/12$, hence

$$\hat{\sigma}_b = \frac{6\hat{M}_1}{t^2} = \tfrac{3}{4}\frac{Pa^2}{t^2} \qquad (13.30)$$

2. Simply supported plate (Figure 13.8b)

The edge (boundary) conditions are:

$$\phi = 0 \text{ at } x = 0$$

$$w = 0 \text{ at } x = a$$

$$M_1 = 0 \text{ at } x = a \text{ (free to rotate)}$$

which gives C_2 and $C_3 = 0$.
Hence

$$\phi = -\frac{1}{\mathbf{D}}\frac{Px^3}{16} + \frac{C_1 x}{2}$$

and

$$\frac{d\phi}{dx} = -\frac{1}{\mathbf{D}}\left[\frac{3Px^2}{16}\right] + \frac{C_1}{2}$$

Substituting these values in equation 13.26, and equating to zero at $x = a$, gives:

$$C_1 = \frac{Pa^2}{8\mathbf{D}}\frac{(3+\nu)}{(1+\nu)}$$

and hence

$$M_1 = \frac{P}{16}(3+\nu)(a^2 - x^2) \tag{13.31}$$

The maximum bending moment will occur at the centre, where $M_1 = M_2$

so

$$\hat{M}_1 = \hat{M}_2 = \frac{P(3+\nu)a^2}{16} \tag{13.32}$$

and

$$\hat{\sigma}_b = \frac{6\hat{M}_1}{t^2} = \tfrac{3}{8}(3+\nu)\frac{Pa^2}{t^2} \tag{13.33}$$

General equation for flat plates

A general equation for the thickness of a flat plate required to resist a given pressure load can be written in the form:

$$t = CD\sqrt{\frac{P}{f}} \tag{13.34}$$

where f = the maximum allowable stress (the design stress),
D = the effective plate diameter,
C = a constant, which depends on the edge support.

The limiting value of C can be obtained from equations 13.30 and 13.33. Taking Poisson's ratio as 0.3, a typical value for steels, then if the edge can be taken as completely rigid $C = 0.43$, and if it is essentially free to rotate $C = 0.56$.

13.3.6. Dilation of vessels

Under internal pressure a vessel will expand slightly. The radial growth can be calculated from the elastic strain in the radial direction. The principal strains in a two-dimensional system are related to the principal stresses by:

$$\varepsilon_1 = \frac{1}{E}(\sigma_1 - \nu\sigma_2) \tag{13.35}$$

$$\varepsilon_2 = \frac{1}{E}(\sigma_2 - \nu\sigma_1) \tag{13.36}$$

The radial (diametrical strain) will be the same as the circumferential strain ε_2. For any shell of revolution the dilation can be found by substituting the appropriate expressions for the circumferential and meridional stresses in equation 13.36.

The diametrical dilation $\Delta = D\varepsilon_1$.

For a cylinder

$$\sigma_1 = \frac{PD}{4t}$$

$$\sigma_2 = \frac{PD}{2t}$$

substitution in equation 13.36 gives:

$$\Delta_c = \frac{PD^2}{4tE}(2 - \nu) \tag{13.37}$$

For a sphere (or hemisphere)

$$\sigma_1 = \sigma_2 = \frac{PD}{4t}$$

and

$$\Delta_s = \frac{PD^2}{4tE}(1 - \nu) \tag{13.38}$$

So for a cylinder closed by a hemispherical head of the same thickness the difference in dilation of the two sections, if they were free to expand separately, would be:

$$\Delta_c - \Delta_s = \frac{PD^2}{4tE}$$

13.3.7. Secondary stresses

In the stress analysis of pressure vessels and pressure vessel components stresses are classified as primary or secondary. Primary stresses can be defined as those stresses that are necessary to satisfy the conditions of static equilibrium. The membrane stresses induced by the applied pressure and the bending stresses due to wind loads are examples of primary stresses. Primary stresses are not self-limiting; if they exceed the yield point of the material, gross distortion, and in the extreme situation, failure of the vessel will occur.

Secondary stresses are those stresses that arise from the constraint of adjacent parts of the vessel. Secondary stresses are self-limiting; local yielding or slight distortion will satisfy the conditions causing the stress, and failure would not be expected to occur in one application of the loading. The "thermal stress" set up by the differential expansion of parts of the vessel, due to different temperatures or the use of different materials, is an example of a secondary stress. The discontinuity that occurs between the head and the cylindrical section of a vessel is a major source of secondary stress. If free, the dilation of the head would be different from that of the cylindrical section (see Section 13.3.6); they are constrained to the same dilation by the welded joint between the two parts. The induced bending moment and shear force due to the constraint give rise to secondary bending and shear stresses at the junction. The magnitude of these discontinuity stresses can be estimated by analogy with the behaviour of beams on elastic foundations; see Hetenyi (1958) and Harvey (1974). The estimation of the stresses arising from discontinuities is covered in the books by Bednar (1990), and Jawad and Farr (1989).

Other sources of secondary stresses are the constraints arising at flanges, supports, and the change of section due to reinforcement at a nozzle or opening (see Section 13.6).

Though secondary stresses do not affect the "bursting strength" of the vessel, they are an important consideration when the vessel is subject to repeated pressure loading. If local yielding has occurred, residual stress will remain when the pressure load is removed, and repeated pressure cycling can lead to fatigue failure.

13.4. GENERAL DESIGN CONSIDERATIONS: PRESSURE VESSELS

13.4.1. Design pressure

A vessel must be designed to withstand the maximum pressure to which it is likely to be subjected in operation.

For vessels under internal pressure, the design pressure is normally taken as the pressure at which the relief device is set. This will normally be 5 to 10 per cent above the normal working pressure, to avoid spurious operation during minor process upsets. When deciding the design pressure, the hydrostatic pressure in the base of the column should be added to the operating pressure, if significant.

Vessels subject to external pressure should be designed to resist the maximum differential pressure that is likely to occur in service. Vessels likely to be subjected to vacuum should be designed for a full negative pressure of 1 bar, unless fitted with an effective, and reliable, vacuum breaker.

13.4.2. Design temperature

The strength of metals decreases with increasing temperature (see Chapter 7) so the maximum allowable design stress will depend on the material temperature. The design temperature at which the design stress is evaluated should be taken as the maximum working temperature of the material, with due allowance for any uncertainty involved in predicting vessel wall temperatures.

13.4.3. Materials

Pressure vessels are constructed from plain carbon steels, low and high alloy steels, other alloys, clad plate, and reinforced plastics.

Selection of a suitable material must take into account the suitability of the material for fabrication (particularly welding) as well as the compatibility of the material with the process environment.

The pressure vessel design codes and standards include lists of acceptable materials; in accordance with the appropriate material standards.

13.4.4. Design stress (nominal design strength)

For design purposes it is necessary to decide a value for the maximum allowable stress (nominal design strength) that can be accepted in the material of construction.

This is determined by applying a suitable "design stress factor" (factor of safety) to the maximum stress that the material could be expected to withstand without failure under standard test conditions. The design stress factor allows for any uncertainty in the design methods, the loading, the quality of the materials, and the workmanship.

For materials not subject to high temperatures the design stress is based on the yield stress (or proof stress), or the tensile strength (ultimate tensile stress) of the material at the design temperature.

For materials subject to conditions at which the creep is likely to be a consideration, the design stress is based on the creep characteristics of the material: the average stress to produce rupture after 10^5 hours, or the average stress to produce a 1 per cent strain after 10^5 hours, at the design temperature. Typical design stress factors for pressure components are shown in Table 13.1.

Table 13.1. Design stress factors

Property	Material		
	Carbon Carbon-manganese, low alloy steels	Austenitic stainless steels	Non-ferrous metals
Minimum yield stress or 0.2 per cent proof stress, at the design temperature	1.5	1.5	1.5
Minimum tensile strength, at room temperature	2.35	2.5	4.0
Mean stress to produce rupture at 10^5 h at the design temperature	1.5	1.5	1.0

In the British Standard, PD 5500, the nominal design strengths (allowable design stresses), for use with the design methods given, are listed in the standard, for the range of materials covered by the standard. The standard should be consulted for the principles and design stress factors used in determining the nominal design strengths.

Typical design stress values for some common materials are shown in Table 13.2. These may be used for preliminary designs. The standards and codes should be consulted for the values to be used for detailed vessel design.

Table 13.2. Typical design stresses for plate
(The appropriate material standards should be consulted for particular grades and plate thicknesses)

Material	Tensile strength (N/mm^2)	Design stress at temperature °C (N/mm^2)									
		0 to 50	100	150	200	250	300	350	400	450	500
Carbon steel (semi-killed or silicon killed)	360	135	125	115	105	95	85	80	70		
Carbon-manganese steel (semi-killed or silicon killed)	460	180	170	150	140	130	115	105	100		
Carbon-molybdenum steel, 0.5 per cent Mo	450	180	170	145	140	130	120	110	110		
Low alloy steel (Ni, Cr, Mo, V)	550	240	240	240	240	240	235	230	220	190	170
Stainless steel 18Cr/8Ni unstabilised (304)	510	165	145	130	115	110	105	100	100	95	90
Stainless steel 18Cr/8Ni Ti stabilised (321)	540	165	150	140	135	130	130	125	120	120	115
Stainless steel 18Cr/8Ni Mo $2\frac{1}{2}$ per cent (316)	520	175	150	135	120	115	110	105	105	100	95

13.4.5. Welded joint efficiency, and construction categories

The strength of a welded joint will depend on the type of joint and the quality of the welding.

The soundness of welds is checked by visual inspection and by non-destructive testing (radiography).

The possible lower strength of a welded joint compared with the virgin plate is usually allowed for in design by multiplying the allowable design stress for the material by a "welded joint factor" J. The value of the joint factor used in design will depend on the type of joint and amount of radiography required by the design code. Typical values are shown in Table 13.3. Taking the factor as 1.0 implies that the joint is equally as strong as the virgin plate; this is achieved by radiographing the complete weld length, and cutting out and remaking any defects. The use of lower joint factors in design, though saving costs on radiography, will result in a thicker, heavier, vessel, and the designer must balance any cost savings on inspection and fabrication against the increased cost of materials.

Table 13.3. Maximum allowable joint efficiency

Type of joint	Degree of radiography		
	100 per cent	spot	none
Double-welded butt or equivalent	1.0	0.85	0.7
Single-weld butt joint with bonding strips	0.9	0.80	0.65

The national codes and standards divide vessel construction into different categories, depending on the amount of non-destructive testing required. The higher categories require 100 per cent radiography of the welds, and allow the use of highest values for the weld-joint factors. The lower-quality categories require less radiography, but allow only lower joint-efficiency factors, and place restrictions on the plate thickness and type of materials that can be used. The highest category will invariably be specified for process-plant pressure vessels.

The standards should be consulted to determine the limitations and requirements of the construction categories specified. Welded joint efficiency factors are not used, as such, in the design equations given in BS PD 5500; instead limitations are placed on the values of the nominal design strength (allowable design stress) for materials in the lower construction category. The standard specifies three construction categories:

Category 1: the highest class, requires 100 per cent non-destructive testing (NDT) of the welds; and allows the use of all materials covered by the standard, with no restriction on the plate thickness.

Category 2: requires less non-destructive testing but places some limitations on the materials which can be used and the maximum plate thickness.

Category 3: the lowest class, requires only visual inspection of the welds, but is restricted to carbon and carbon-manganese steels, and austenitic stainless steel; and limits are placed on the plate thickness and the nominal design stress. For carbon and carbon-manganese steels the plate thickness is restricted to less than 13 mm and the design stress is about half that allowed for categories 1 and 2. For stainless steel the thickness is restricted to less than 25 mm and the allowable design stress is around 80 per cent of that for the other categories.

13.4.6. Corrosion allowance

The "corrosion allowance" is the additional thickness of metal added to allow for material lost by corrosion and erosion, or scaling (see Chapter 7). The allowance to be used should be agreed between the customer and manufacturer. Corrosion is a complex phenomenon, and it is not possible to give specific rules for the estimation of the corrosion allowance required for all circumstances. The allowance should be based on experience with the material of construction under similar service conditions to those for the proposed design. For carbon and low-alloy steels, where severe corrosion is not expected, a minimum allowance of 2.0 mm should be used; where more severe conditions are anticipated this should be increased to 4.0 mm. Most design codes and standards specify a minimum allowance of 1.0 mm.

13.4.7. Design loads

A structure must be designed to resist gross plastic deformation and collapse under all the conditions of loading. The loads to which a process vessel will be subject in service are listed below. They can be classified as major loads, that must always be considered in vessel design, and subsidiary loads. Formal stress analysis to determine the effect of the subsidiary loads is only required in the codes and standards where it is not possible to demonstrate the adequacy of the proposed design by other means; such as by comparison with the known behaviour of existing vessels.

Major loads

1. Design pressure: including any significant static head of liquid.
2. Maximum weight of the vessel and contents, under operating conditions.
3. Maximum weight of the vessel and contents under the hydraulic test conditions.
4. Wind loads.
5. Earthquake (seismic) loads.
6. Loads supported by, or reacting on, the vessel.

Subsidiary loads

1. Local stresses caused by supports, internal structures and connecting pipes.
2. Shock loads caused by water hammer, or by surging of the vessel contents.
3. Bending moments caused by eccentricity of the centre of the working pressure relative to the neutral axis of the vessel.
4. Stresses due to temperature differences and differences in the coefficient expansion of materials.
5. Loads caused by fluctuations in temperature and pressure.

A vessel will not be subject to all these loads simultaneously. The designer must determine what combination of possible loads gives the worst situation, and design for that loading condition.

13.4.8. Minimum practical wall thickness

There will be a minimum wall thickness required to ensure that any vessel is sufficiently rigid to withstand its own weight, and any incidental loads. As a general guide the wall thickness of any vessel should not be less than the values given below; the values include a corrosion allowance of 2 mm:

Vessel diameter (m)	Minimum thickness (mm)
1	5
1 to 2	7
2 to 2.5	9
2.5 to 3.0	10
3.0 to 3.5	12

13.5. THE DESIGN OF THIN-WALLED VESSELS UNDER INTERNAL PRESSURE

13.5.1. Cylinders and spherical shells

For a cylindrical shell the minimum thickness required to resist internal pressure can be determined from equation 13.7; the cylindrical stress will be the greater of the two principal stresses.

If D_i is internal diameter and e the minimum thickness required, the mean diameter will be $(D_i + e)$; substituting this for D in equation 13.7 gives:

$$e = \frac{P_i(D_i + e)}{2f}$$

where f is the design stress and P_i the internal pressure. Rearranging gives:

$$e = \frac{P_i D_i}{2f - P_i} \tag{13.39}$$

This is the form of the equation given in the British Standard PD 5500.

An equation for the minimum thickness of a sphere can be obtained from equation 13.9:

$$e = \frac{P_i D_i}{4f - P_i} \tag{13.40}$$

The equation for a sphere given in BS 5500 is:

$$e = \frac{P_i D_i}{4f - 1.2P_i} \tag{13.41}$$

The equation given in the British Standard PD 5500 differs slightly from equation 13.40, as it is derived from the formula for thick-walled vessels; see Section 13.15.

If a welded joint factor is used equations 13.39 and 13.40 are written:

$$e = \frac{P_i D_i}{2Jf - P_i} \tag{13.39a}$$

and

$$e = \frac{P_i D_i}{4Jf - 1.2P_i} \tag{13.40b}$$

where J is the joint factor.

Any consistent set of units can be used for equations 13.39*a* to 13.40*b*.

13.5.2. Heads and closures

The ends of a cylindrical vessel are closed by heads of various shapes. The principal types used are:

1. Flat plates and formed flat heads; Figure 13.9.
2. Hemispherical heads; Figure 13.10*a*.
3. Ellipsoidal heads; Figure 13.10*b*.
4. Torispherical heads; Figure 13.10*c*.

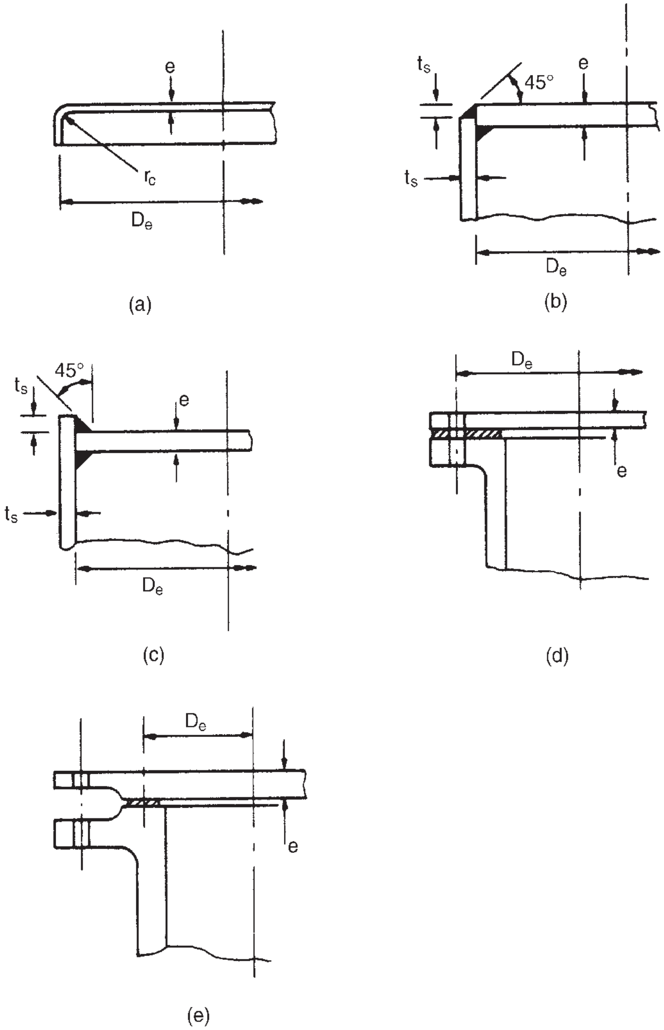


Figure 13.9. Flat-end closures (*a*) Flanged plate (*b*) Welded plate (*c*) Welded plate (*d*) Bolted cover (*e*) Bolted cover

Hemispherical, ellipsoidal and torispherical heads are collectively referred to as domed heads. They are formed by pressing or spinning; large diameters are fabricated from formed sections. Torispherical heads are often referred to as dished ends.

The preferred proportions of domed heads are given in the standards and codes.

Choice of closure

Flat plates are used as covers for manways, and as the channel covers of heat exchangers. Formed flat ends, known as "flange-only" ends, are manufactured by turning over a flange with a small radius on a flat plate, Figure 13.9*a*. The corner radius reduces the abrupt

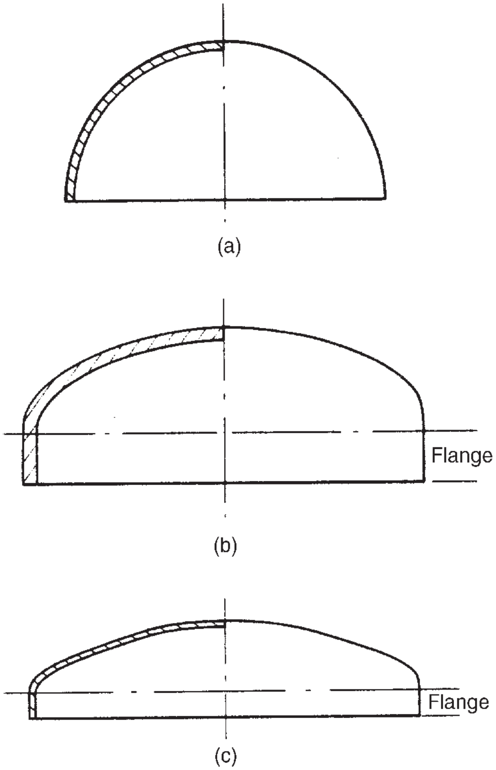


Figure 13.10. Domed heads (*a*) Hemispherical (*b*) Ellipsoidal (*c*) Torispherical

change of shape, at the junction with the cylindrical section; which reduces the local stresses to some extent: "Flange-only" heads are the cheapest type of formed head to manufacture, but their use is limited to low-pressure and small-diameter vessels.

Standard torispherical heads (dished ends) are the most commonly used end closure for vessels up to operating pressures of 15 bar. They can be used for higher pressures, but above 10 bar their cost should be compared with that of an equivalent ellipsoidal head. Above 15 bar an ellipsoidal head will usually prove to be the most economical closure to use.

A hemispherical head is the strongest shape; capable of resisting about twice the pressure of a torispherical head of the same thickness. The cost of forming a hemispherical head will, however, be higher than that for a shallow torispherical head. Hemispherical heads are used for high pressures.

13.5.3. Design of flat ends

Though the fabrication cost is low, flat ends are not a structurally efficient form, and very thick plates would be required for high pressures or large diameters.

The design equations used to determine the thickness of flat ends are based on the analysis of stresses in flat plates; Section 13.3.5.

The thickness required will depend on the degree of constraint at the plate periphery. The minimum thickness required is given by:

$$e = C_p D_e \sqrt{\frac{P_i}{f}} \tag{13.42}$$

where C_p = a design constant, dependent on the edge constraint,
D_e = nominal plate diameter,
f = design stress.

Any consistent set of units can be used.

Values for the design constant C_p and the nominal plate diameter D_e are given in the design codes and standards for various arrangements of flat end closures.

The values of the design constant and nominal diameter for the typical designs shown in Figure 13.9 are given below:

(*a*) Flanged-only end, for diameters less than 0.6 m and corner radii at least equal to $0.25e$, C_p can be taken as 0.45; D_e is equal to D_i.
(*b*, *c*) Plates welded to the end of the shell with a fillet weld, angle of fillet 45° and depth equal to the plate thickness, take C_p as 0.55 and $D_e = D_i$.
(*d*) Bolted cover with a full face gasket (see Section 13.10), take $C_p = 0.4$ and D_e equal to the bolt circle diameter.
(*e*) Bolted end cover with a narrow-face gasket, take $C_p = 0.55$ and D_e equal to the mean diameter of the gasket.

13.5.4. Design of domed ends

Design equations and charts for the various types of domed heads are given in the codes and standards and should be used for detailed design. The codes and standards cover both unpierced and pierced heads. Pierced heads are those with openings or connections. The head thickness must be increased to compensate for the weakening effect of the holes where the opening or branch is not locally reinforced (see Section 13.6).

For convenience, simplified design equations are given in this section. These are suitable for the preliminary sizing of unpierced heads and for heads with fully compensated openings or branches.

Hemispherical heads

It can be seen by examination of equations 13.7 and 13.9, that for equal stress in the cylindrical section and hemispherical head of a vessel the thickness of the head need only be half that of the cylinder. However, as the dilation of the two parts would then be different, discontinuity stresses would be set up at the head and cylinder junction. For no difference in dilation between the two parts (equal diametrical strain) it can be shown that for steels (Poisson's ratio = 0.3) the ratio of the hemispherical head thickness to cylinder thickness should be 7/17. However, the stress in the head would then be greater than that in the cylindrical section; and the optimum thickness ratio is normally taken as 0.6; see Brownell and Young (1959).

Ellipsoidal heads

Most standard ellipsoidal heads are manufactured with a major and minor axis ratio of 2 : 1. For this ratio, the following equation can be used to calculate the minimum thickness required:

$$e = \frac{P_i D_i}{2Jf - 0.2P_i} \tag{13.43}$$

Torispherical heads

There are two junctions in a torispherical end closure: that between the cylindrical section and the head, and that at the junction of the crown and the knuckle radii. The bending and shear stresses caused by the differential dilation that will occur at these points must be taken into account in the design of the heads. One approach taken is to use the basic equation for a hemisphere and to introduce a stress concentration, or shape, factor to allow for the increased stress due to the discontinuity. The stress concentration factor is a function of the knuckle and crown radii.

$$e = \frac{P_i R_c C_s}{2fJ + P_i(C_s - 0.2)} \tag{13.44}$$

where C_s = stress concentration factor for torispherical heads $= \frac{1}{4}(3 + \sqrt{R_c/R_k})$,
R_c = crown radius,
R_k = knuckle radius.

The ratio of the knuckle to crown radii should not be less than 0.06, to avoid buckling; and the crown radius should not be greater than the diameter of the cylindrical section. Any consistent set of units can be used with equations 13.43 and 13.44. For formed heads (no joints in the head) the joint factor J is taken as 1.0.

Flanges (skirts) on domed heads

Formed domed heads are made with a short straight cylindrical section, called a flange or skirt; Figure 13.10. This ensures that the weld line is away from the point of discontinuity between the head and the cylindrical section of the vessel.

13.5.5. Conical sections and end closures

Conical sections (reducers) are used to make a gradual reduction in diameter from one cylindrical section to another of smaller diameter.

Conical ends are used to facilitate the smooth flow and removal of solids from process equipment; such as, hoppers, spray-dryers and crystallisers.

From equation 13.10 it can be seen that the thickness required at any point on a cone is related to the diameter by the following expression:

$$e = \frac{P_i D_c}{2fJ - P_i} \cdot \frac{1}{\cos\alpha} \tag{13.45}$$

where D_c is the diameter of the cone at the point,
α = half the cone apex angle.

This equation will only apply at points away from the cone to cylinder junction. Bending and shear stresses will be caused by the different dilation of the conical and cylindrical sections. This can be allowed for by introducing a stress concentration factor, in a similar manner to the method used for torispherical heads,

$$e = \frac{C_c P_i D_c}{2fJ - P_i} \tag{13.46}$$

The design factor C_c is a function of the half apex angle α:

α	20°	30°	45°	60°
C_c	1.00	1.35	2.05	3.20

A formed section would normally be used for the transition between a cylindrical section and conical section; except for vessels operating at low pressures, or under hydrostatic pressure only. The transition section would be made thicker than the conical or cylindrical section and formed with a knuckle radius to reduce the stress concentration at the transition, Figure 13.11. The thickness at the knuckle can be calculated using equation 13.46, and that for the conical section away from the transition from equation 13.45.

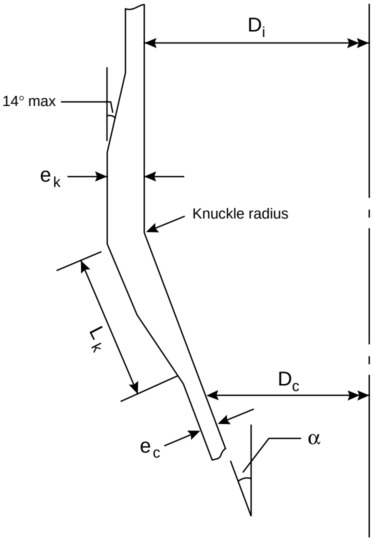


Figure 13.11. Conical transition section

The length of the thicker section L_k depends on the cone angle and is given by:

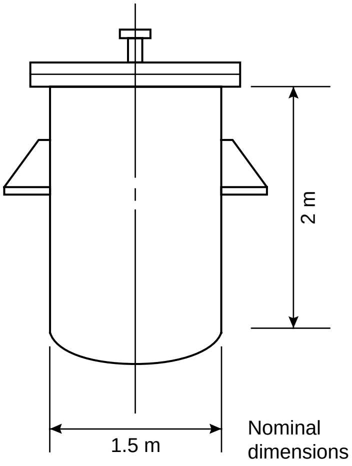
$$L_k = \sqrt{\frac{D_i e_k}{4\cos\alpha}} \tag{13.47}$$

where e_k is the thickness at the knuckle.

Design procedures for conical sections are given in the codes and standards.

Example 13.1

Estimate the thickness required for the component parts of the vessel shown in the diagram. The vessel is to operate at a pressure of 14 bar (absolute) and temperature of 300°C. The material of construction will be plain carbon steel. Welds will be fully radiographed. A corrosion allowance of 2 mm should be used.



Solution

Design pressure, take as 10 per cent above operating pressure,

$$= (14 - 1) \times 1.1$$

$$= 14.3 \text{ bar}$$

$$= 1.43 \text{ N/mm}^2$$

Design temperature 300°C.
From Table 13.2, typical design stress = 85 N/mm^2.

Cylindrical section

$$e = \frac{1.43 \times 1.5 \times 10^3}{2 \times 85 - 1.43} = 12.7 \text{ mm} \tag{13.39}$$

add corrosion allowance $12.7 + 2 = 14.7$
say $\underline{\underline{\text{15 mm plate}}}$

Domed head

(i) Try a standard dished head (torisphere):

$$\text{crown radius } R_c = D_i = 1.5 \text{ m}$$

$$\text{knuckle radius} = 6 \text{ per cent } R_c = 0.09 \text{ m}$$

A head of this size would be formed by pressing: no joints, so $J = 1$.

$$C_s = \tfrac{1}{4}\left(3 + \sqrt{\frac{R_c}{R_k}}\right) = \tfrac{1}{4}\left(3 + \sqrt{\frac{1.5}{0.09}}\right) = 1.77 \qquad (13.44)$$

$$e = \frac{1.43 \times 1.5 \times 10^3 \times 1.77}{2 \times 85 + 1.43(1.77 - 0.2)} = \underline{\underline{22.0 \text{ mm}}} \qquad (13.44)$$

(ii) Try a "standard" ellipsoidal head, ratio major : minor axes = 2 : 1

$$e = \frac{1.43 \times 1.5 \times 10^3}{2 \times 85 - 0.2 \times 1.43} \qquad (13.43)$$

$$= \underline{\underline{12.7 \text{ mm}}}$$

So an ellipsoidal head would probably be the most economical. Take as same thickness as wall 15 mm.

Flat head

Use a full face gasket $C_p = 0.4$

D_e = bolt circle diameter, take as approx. 1.7 m.

$$e = 0.4 \times 1.7 \times 10^3 \sqrt{\frac{1.43}{85}} = \underline{88.4 \text{ mm}} \qquad (13.42)$$

Add corrosion allowance and round-off to $\underline{\underline{90 \text{ mm}}}$.

This shows the inefficiency of a flat cover. It would be better to use a flanged domed head.

13.6. COMPENSATION FOR OPENINGS AND BRANCHES

All process vessels will have openings for connections, manways, and instrument fittings. The presence of an opening weakens the shell, and gives rise to stress concentrations. The stress at the edge of a hole will be considerably higher than the average stress in the surrounding plate. To compensate for the effect of an opening, the wall thickness is increased in the region adjacent to the opening. Sufficient reinforcement must be provided to compensate for the weakening effect of the opening without significantly altering the general dilation pattern of the vessel at the opening. Over-reinforcement will reduce the flexibility of the wall, causing a "hard spot", and giving rise to secondary stresses; typical arrangements are shown in Figure 13.12.

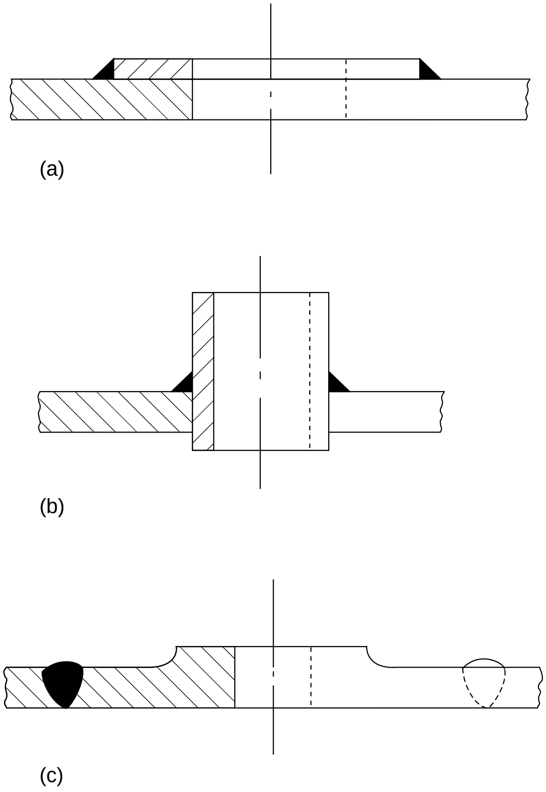


Figure 13.12. Types of compensation for openings (*a*) Welded pad (*b*) Inset nozzle (*c*) Forged ring

The simplest method of providing compensation is to weld a pad or collar around the opening, Figure 13.12*a*. The outer diameter of the pad is usually between $1\frac{1}{2}$ to 2 times the diameter of the hole or branch. This method, however, does not give the best disposition of the reinforcing material about the opening, and in some circumstances high thermal stress can arise due to the poor thermal conductivity of the pad to shell junction.

At a branch, the reinforcement required can be provided, with or without a pad, by allowing the branch, to protrude into the vessel, Figure 13.12*b*. This arrangement should be used with caution for process vessels, as the protrusion will act as a trap for crud, and local corrosion can occur. Forged reinforcing rings, Figure 13.12*c*, provide the most effective method of compensation, but are expensive. They would be used for any large openings and branches in vessels operating under severe conditions.

Calculation of reinforcement required

The "equal area method" is the simplest method used for calculating the amount of reinforcement required, and is allowed in most design codes and standards. The principle used is to provide reinforcement local to the opening, equal in cross-sectional area to the area removed in forming the opening, Figure 13.13. If the actual thickness of the vessel

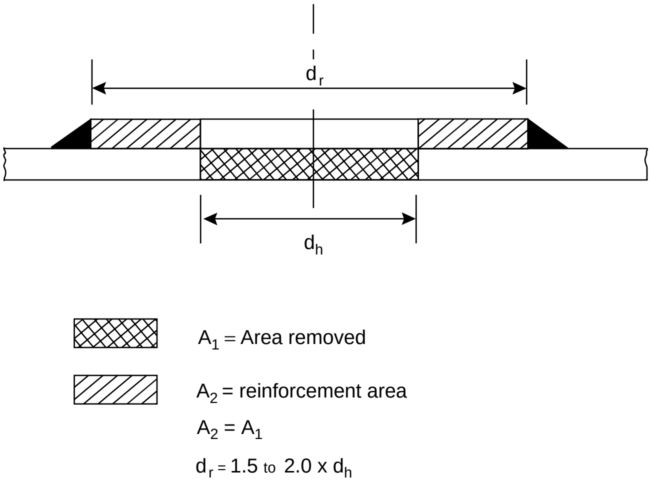
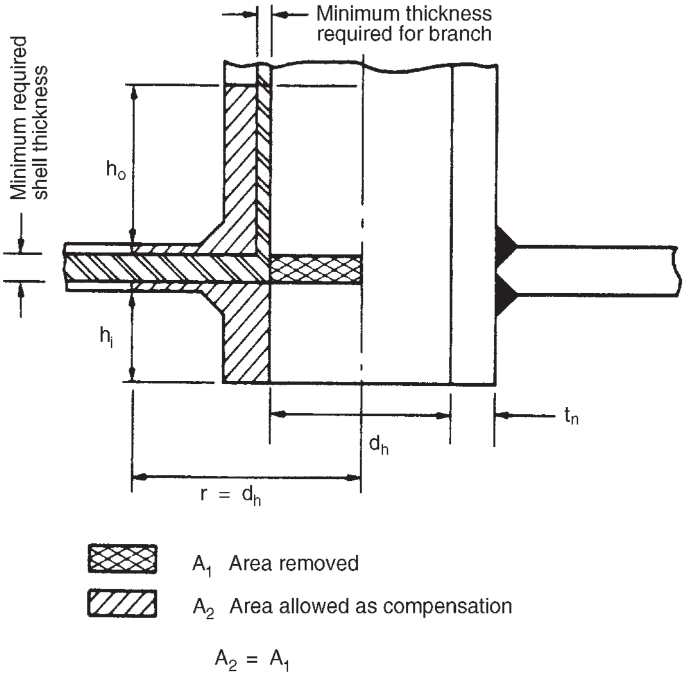


Figure 13.13. Equal-area method of compensation



Max. allowed h_0 and $h_i = 0.64\sqrt{(d_h + t_n)t_n}$

All dimensions shown are in the fully corroded condition (i.e. less corrosion allowance)

Figure 13.14. Branch compensation

wall is greater than the minimum required to resist the loading, the excess thickness can be taken into account when estimating the area of reinforcement required. Similarly with a branch connection, if the wall thickness of the branch or nozzle is greater than the minimum required, the excess material in the branch can be taken into account. Any corrosion allowance must be deducted when determining the excess thickness available as compensation. The standards and codes differ in the areas of the branch and shell considered to be effective for reinforcement, and should be consulted to determine the actual area allowed and the disposition of the various types of reinforcement. Figure 13.14 can be used for preliminary calculations. For branch connections of small diameter the reinforcement area can usually be provided by increasing the wall thickness of the branch pipe. Some design codes and standards do not require compensation for connections below 89 mm (3 in.) diameter.

If anything, the equal area method tends to over-estimate the compensation required and in some instances the additional material can reduce the fatigue life of the vessel. More sophisticated methods for determining the compensation required have been introduced into the latest editions of the codes and standards.

The equal-area method is generally used for estimating the increase in thickness required to compensate for multiple openings.

13.7. DESIGN OF VESSELS SUBJECT TO EXTERNAL PRESSURE

13.7.1. Cylindrical shells

Two types of process vessel are likely to be subjected to external pressure: those operated under vacuum, where the maximum pressure will be 1 bar (atm); and jacketed vessels, where the inner vessel will be under the jacket pressure. For jacketed vessels, the maximum pressure difference should be taken as the full jacket pressure, as a situation may arise in which the pressure in the inner vessel is lost. Thin-walled vessels subject to external pressure are liable to failure through elastic instability (buckling) and it is this mode of failure that determines the wall thickness required.

For an open-ended cylinder, the critical pressure to cause buckling P_c is given by the following expression; see Windenburg and Trilling (1934):

$$P_c = \frac{1}{3}\left[n^2 - 1 + \frac{2n^2 - 1 - v}{n^2\left(\dfrac{2L}{\pi D_0}\right)^2 - 1}\right]\frac{2E}{(1 - v^2)}\left(\frac{t}{D_0}\right)^3 + \frac{2Et/D_0}{(n^2 - 1)\left[n^2\left(\dfrac{2L}{\pi D_0}\right)^2 + 1\right]^2} \tag{13.48}$$

where L = the unsupported length of the vessel, the effective length,

D_0 = external diameter,

t = wall thickness,

E = Young's modulus,

v = Poisson's ratio,

n = the number of lobes formed at buckling.

For long tubes and cylindrical vessels this expression can be simplified by neglecting terms with the group $(2L/\pi D_0)^2$ in the denominator; the equation then becomes:

$$P_c = \tfrac{1}{3}\left[(n^2 - 1)\frac{2E}{(1 - v^2)}\right]\left(\frac{t}{D_0}\right)^3 \tag{13.49}$$

The minimum value of the critical pressure will occur when the number of lobes is 2, and substituting this value into equation 13.49 gives:

$$P_c = \frac{2E}{1 - v^2}\left(\frac{t}{D_0}\right)^3 \tag{13.50}$$

For most pressure-vessel materials Poisson's ratio can be taken as 0.3; substituting this in equation 13.50 gives:

$$P_c = 2.2E\left(\frac{t}{D_0}\right)^3 \tag{13.51}$$

For short closed vessels, and long vessels with stiffening rings, the critical buckling pressure will be higher than that predicted by equation 13.51. The effect of stiffening can be taken into account by introducing a "collapse coefficient", K_c, into equation 13.51.

$$P_c = K_c E\left(\frac{t}{D_0}\right)^3 \tag{13.52}$$

where K_c is a function of the diameter and thickness of the vessel, and the effective length L' between the ends or stiffening rings; and is obtained from Figure 13.16. The effective length for some typical arrangements is shown in Figure 13.15.

It can be shown (see Southwell, 1913) that the critical distance between stiffeners, L_c, beyond which stiffening will not be effective is given by:

$$L_c = \frac{4\pi\sqrt{6}D_0}{27}\left[(1 - v^2)^{1/4}\right]\left(\frac{D_0}{t}\right)^{1/2} \tag{13.53}$$

Substituting $v = 0.3$ gives:

$$L_c = 1.11D_0\left(\frac{D_0}{t}\right)^{1/2} \tag{13.54}$$

Any stiffening rings used must be spaced closer than L_c. Equation 13.52 can be used to determine the critical buckling pressure and hence the thickness required to resist a given external pressure; see Example 13.2. A factor of safety of at least 3 should be applied to the values predicted using equation 13.52.

The design methods and design curves given in the standards and codes should be used for the detailed design of vessels subject to external pressure.

Out of roundness

Any out-of-roundness in a shell after fabrication will significantly reduce the ability of the vessel to resist external pressure. A deviation from a true circular cross-section equal

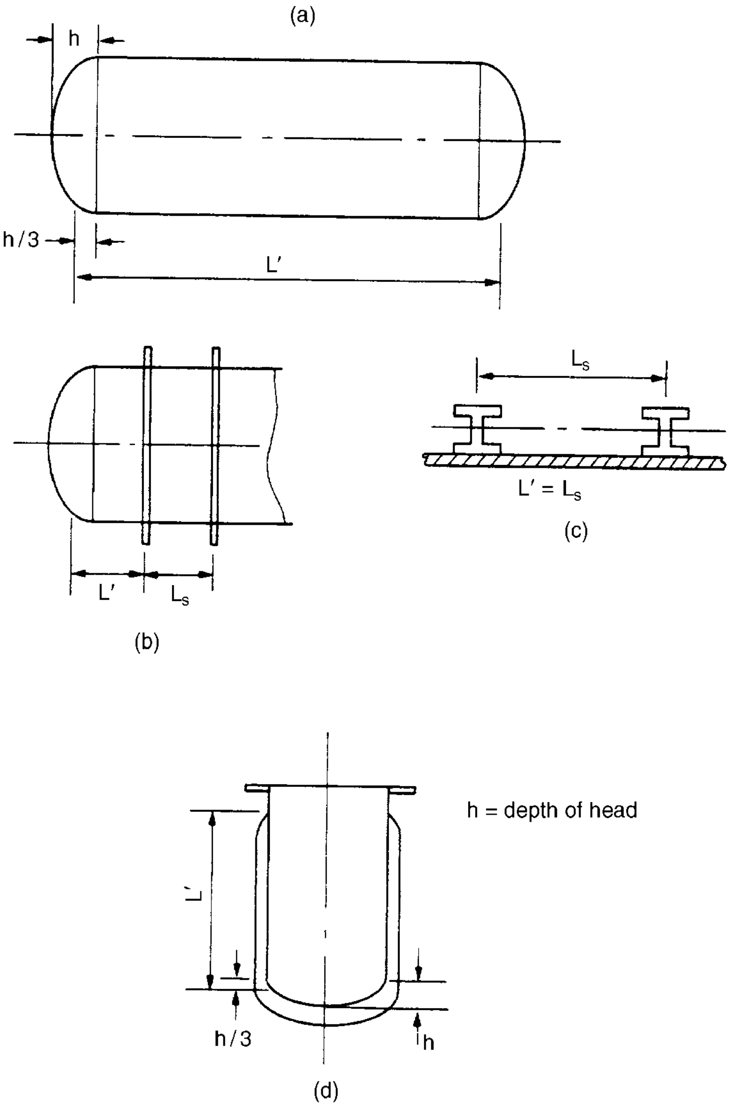


Figure 13.15. Effective length, vessel under external pressure (*a*) Plain vessel (*b*) With stiffeners (use smaller of L′ and L_S) (*c*) I—section stiffening rings (*d*) Jacketed vessel

to the shell thickness will reduce the critical buckling pressure by about 50 per cent. The ovality (out-of-roundness) of a cylinder is measured by:

$$\text{Ovality} = \frac{2(D_{\max} - D_{\min})}{(D_{\max} + D_{\min})} \times 100, \quad \text{per cent}$$

For vessels under external pressure this should not normally exceed 1.5 per cent.

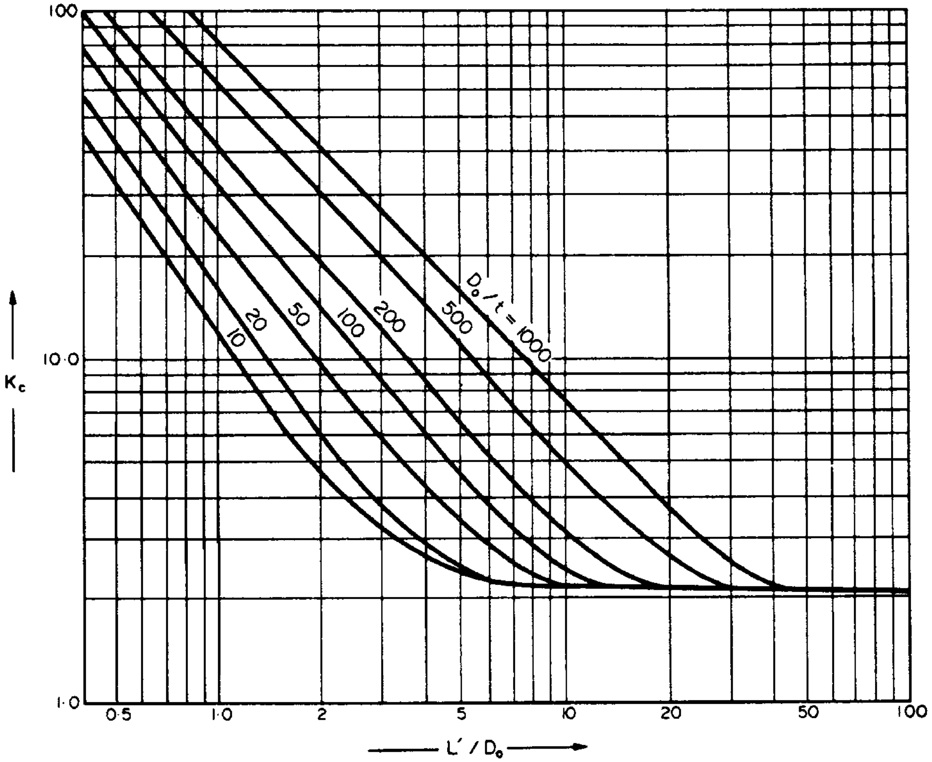


Figure 13.16. Collapse coefficients for cylindrical shells (after Brownell and Young, 1959)

13.7.2. Design of stiffness rings

The usual procedure is to design stiffening rings to carry the pressure load for a distance of $\frac{1}{2}L_s$ on each side of the ring, where L_s is the spacing between the rings. So, the load per unit length on a ring F_r will be given by:

$$F_r = P_e L_s \tag{13.55}$$

where P_e is the external pressure.

The critical load to cause buckling in a ring under a uniform radial load F_c is given by the following expression

$$F_c = \frac{24EI_r}{D_r^3} \tag{13.56}$$

where I_r = second moment of area of the ring cross-section,

D_r = diameter of the ring (approximately equal to the shell outside diameter).

Combining equations 13.55 and 13.56 will give an equation from which the required dimensions of the ring can be determined:

$$P_e L_s \not> \frac{24EI_r}{D_r^3} \div (\text{factor of safety}) \tag{13.57}$$

In calculating the second moment of area of the ring some allowance is normally made for the vessel wall; the use of I_r calculated for the ring alone will give an added factor of safety.

In vacuum distillation columns, the plate-support rings will act as stiffening rings and strengthen the vessel; see Example 13.2.

13.7.3. Vessel heads

The critical buckling pressure for a sphere subject to external pressure is given by (see Timoshenko, 1936):

$$P_c = \frac{2Et^2}{R_s^2\sqrt{3(1 - v^2)}} \tag{13.58}$$

where R_s is the outside radius of the sphere. Taking Poisson's ratio as 0.3 gives:

$$P_c = 1.21E\left(\frac{t}{R_s}\right)^2 \tag{13.59}$$

This equation gives the critical pressure required to cause general buckling; local buckling can occur at a lower pressure. Karman and Tsien (1939) have shown that the pressure to cause a "dimple" to form is about one-quarter of that given by equation 13.59, and is given by:

$$P'_c = 0.365E\left(\frac{t}{R_s}\right)^2 \tag{13.60}$$

A generous factor of safety is needed when applying equation 13.60 to the design of heads under external pressure. A value of 6 is typically used, which gives the following equation for the minimum thickness:

$$e = 4R_s\sqrt{\left(\frac{P_e}{E}\right)} \tag{13.61}$$

Any consistent system of units can be used with equation 13.61.

Torispherical and ellipsoidal heads can be designed as equivalent hemispheres. For a torispherical head the radius R_s is taken as equivalent to the crown radius R_c. For an ellipsoidal head the radius can be taken as the maximum radius of curvature; that at the top, given by:

$$R_s = \frac{a^2}{b} \tag{13.62}$$

where $2a$ = major axis = D_0 (shell o.d.),
$2b$ = minor axis = $2h$,
h = height of the head from the tangent line.

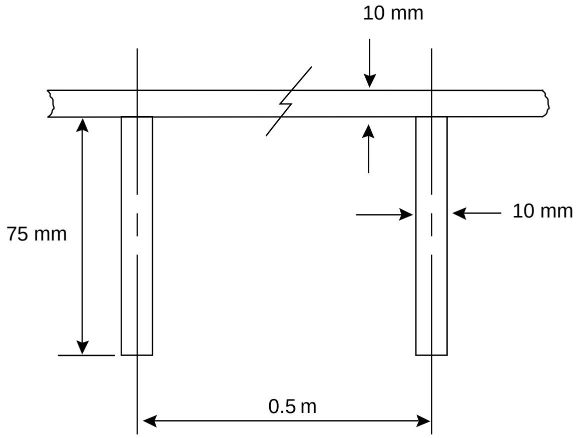
Because the radius of curvature of an ellipse is not constant the use of the maximum radius will over-size the thickness required.

Design methods for heads under external pressure are given in the standards and codes.

Example 13.2

A vacuum distillation column is to operate under a top pressure of 50 mmHg. The plates are supported on rings 75 mm wide, 10 mm deep. The column diameter is 1 m and the plate spacing 0.5 m. Check if the support rings will act as effective stiffening rings. The material of construction is carbon steel and the maximum operating temperature 50°C. If the vessel thickness is 10 mm, check if this is sufficient.

Solution



Take the design pressure as 1 bar external.

From equation 13.55 the load on each ring = 0.5×10^5 N/m.

Taking E for steel at 50°C as 200,000 N/mm^2 = 2×10^{11} N/m^2, and using a factor of safety of 6, the second moment of area of the ring to avoid buckling is given by: equation 13.57

$$0.5 \times 10^5 = \frac{24 \times 2 \times 10^{11} \times I_r}{1^3 \times 6}$$

$$I_r = 6.25 \times 10^{-8} \text{ m}^4$$

For a rectangular section, the second moment of area is given by

$$I = \frac{\text{breadth} \times \text{depth}^3}{12}$$

$$\text{so } I_r \text{ for the support rings} = \frac{10 \times (75)^3 \times 10^{-12}}{12}$$

$$= 3.5 \times 10^{-7} \text{ m}^4$$

and the support ring is of an adequate size to be considered as a stiffening ring.

$$\frac{L'}{D_0} = \frac{0.5}{1} = 0.5$$

$$\frac{D_0}{t} = \frac{1000}{10} = 100$$

From Figure 13.16 $K_c = 75$
From equation 13.52

$$P_c = 75 \times 2 \times 10^{11}\left(\frac{1}{100}\right)^3 = \underline{\underline{15 \times 10^6\ \text{N/m}^2}}$$

which is well above the maximum design pressure of 10^5 N/m^2.

13.8. DESIGN OF VESSELS SUBJECT TO COMBINED LOADING

Pressure vessels are subjected to other loads in addition to pressure (see Section 13.4.7) and must be designed to withstand the worst combination of loading without failure It is not practical to give an explicit relationship for the vessel thickness to resist combined loads. A trial thickness must be assumed (based on that calculated for pressure alone) and the resultant stress from all loads determined to ensure that the maximum allowable stress intensity is not exceeded at any point.

The main sources of load to consider are:

1. Pressure.
2. Dead weight of vessel and contents.
3. Wind.
4. Earthquake (seismic).
5. External loads imposed by piping and attached equipment.

The primary stresses arising from these loads are considered in the following paragraphs, for cylindrical vessels; Figure 13.17.

Primary stresses

1. The longitudinal and circumferential stresses due to pressure (internal or external), given by:

$$\sigma_h = \frac{PD_i}{2t} \tag{13.63}$$

$$\sigma_L = \frac{PD_i}{4t} \tag{13.64}$$

2. The direct stress σ_w due to the weight of the vessel, its contents, and any attachments. The stress will be tensile (positive) for points below the plane of the vessel supports, and compressive (negative) for points above the supports, see Figure 13.18. The dead-weight stress will normally only be significant, compared to the magnitude of the other stresses, in tall vessels.

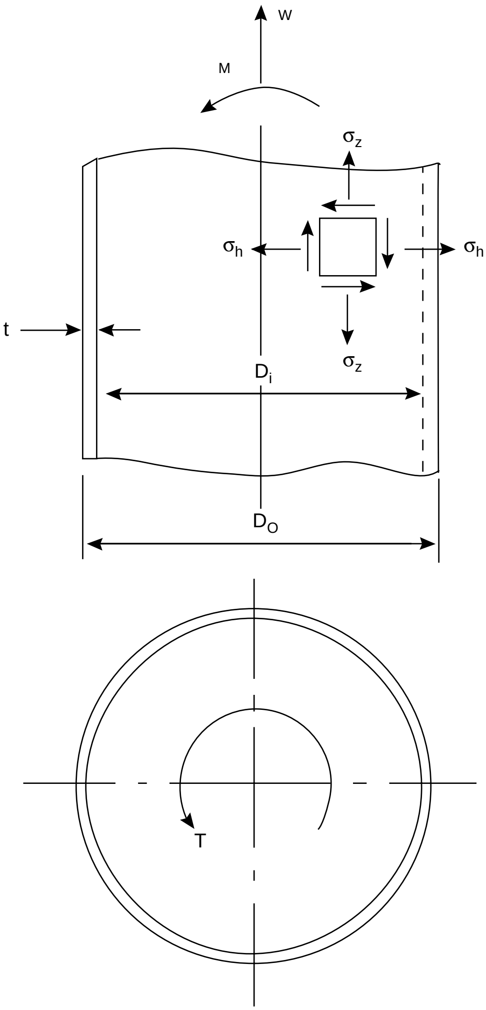


Figure 13.17. Stresses in a cylindrical shell under combined loading

$$\sigma_w = \frac{W}{\pi(D_i + t)t} \tag{13.65}$$

where W is the total weight which is supported by the vessel wall at the plane considered, see Section 13.8.1.

3. Bending stresses resulting from the bending moments to which the vessel is subjected. Bending moments will be caused by the following loading conditions:
   (a) The wind loads on tall self-supported vessels (Section 13.8.2).
   (b) Seismic (earthquake) loads on tall vessels (Section 13.8.3).
   (c) The dead weight and wind loads on piping and equipment which is attached to the vessel, but offset from the vessel centre line (Section 13.8.4).

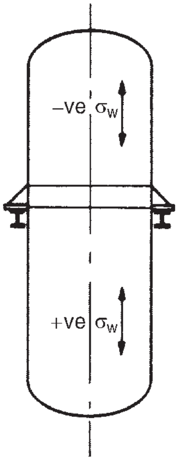


Figure 13.18. Stresses due to dead-weight loads

(d) For horizontal vessels with saddle supports, from the disposition of dead-weight load (see Section 13.9.1).

The bending stresses will be compressive or tensile, depending on location, and are given by:

$$\sigma_b = \pm\frac{M}{I_v}\left(\frac{D_i}{2} + t\right) \tag{13.66}$$

where M_v is the total bending moment at the plane being considered and I_v the second moment of area of the vessel about the plane of bending.

$$I_v = \frac{\pi}{64}(D_0^4 - D_i^4) \tag{13.67}$$

4. Torsional shear stresses τ resulting from torque caused by loads offset from the vessel axis. These loads will normally be small, and need not be considered in preliminary vessel designs.

   The torsional shear stress is given by:

$$\tau = \frac{T}{I_p}\left(\frac{D_i}{2} + t\right) \tag{13.68}$$

where T = the applied torque,
I_p = polar second moment of area = $(\pi/32)(D_0^4 - D_i^4)$

Principal stresses

The principal stresses will be given by:

$$\sigma_1 = \tfrac{1}{2}[\sigma_h + \sigma_z + \sqrt{(\sigma_h - \sigma_z)^2 + 4\tau^2}] \tag{13.69}$$

$$\sigma_2 = \frac{1}{2}[\sigma_h + \sigma_z - \sqrt{(\sigma_h - \sigma_z)^2 + 4\tau^2}] \tag{13.70}$$

where σ_z = total longitudinal stress
$= \sigma_L + \sigma_w \pm \sigma_b$

σ_w should be counted as positive if tension and negative if compressive.

τ is not usually significant.

The third principal stress, that in the radial direction σ_3, will usually be negligible for thin-walled vessels (see Section 13.1.1). As an approximation it can be taken as equal to one-half the pressure loading

$$\sigma_3 = 0.5P \tag{13.71}$$

σ_3 will be compressive (negative).

Allowable stress intensity

The maximum intensity of stress allowed will depend on the particular theory of failure adopted in the design method (see Section 13.3.2). The maximum shear-stress theory is normally used for pressure vessel design.

Using this criterion the maximum stress intensity at any point is taken for design purposes as the numerically greatest value of the following:

$$(\sigma_1 - \sigma_2)$$
$$(\sigma_1 - \sigma_3)$$
$$(\sigma_2 - \sigma_3)$$

The vessel wall thickness must be sufficient to ensure the maximum stress intensity does not exceed the design stress (nominal design strength) for the material of construction, at any point.

Compressive stresses and elastic stability

Under conditions where the resultant axial stress σ_z due to the combined loading is compressive, the vessel may fail by elastic instability (buckling) (see Section 13.3.3). Failure can occur in a thin-walled process column under an axial compressive load by buckling of the complete vessel, as with a strut (Euler buckling); or by local buckling, or wrinkling, of the shell plates. Local buckling will normally occur at a stress lower than that required to buckle the complete vessel. A column design must be checked to ensure that the maximum value of the resultant axial stress does not exceed the critical value at which buckling will occur.

For a curved plate subjected to an axial compressive load the critical buckling stress σ_c is given by (see Timoshenko, 1936):

$$\sigma_c = \frac{E}{\sqrt{3(1 - v^2)}}\left(\frac{t}{R_p}\right) \tag{13.72}$$

where R_p is the radius of curvature.

Taking Poisson's ratio as 0.3 gives:

$$\sigma_c = 0.60E\left(\frac{t}{R_p}\right) \tag{13.73}$$

By applying a suitable factor of safety, equation 13.72 can be used to predict the maximum allowable compressive stress to avoid failure by buckling. A large factor of safety is required, as experimental work has shown that cylindrical vessels will buckle at values well below that given by equation 13.72. For steels at ambient temperature $E = 200{,}000$ N/mm^2, and equation 13.72 with a factor of safety of 12 gives:

$$\sigma_c = 2 \times 10^4 \left(\frac{t}{D_o}\right) \text{ N/mm}^2 \tag{13.74}$$

The maximum compressive stress in a vessel wall should not exceed that given by equation 13.74; or the maximum allowable design stress for the material, whichever is the least.

Stiffening

As with vessels under external pressure, the resistance to failure buckling can be increased significantly by the use of stiffening rings, or longitudinal strips. Methods for estimating the critical buckling stress for stiffened vessels are given in the standards and codes.

Loading

The loads to which a vessel may be subjected will not all occur at the same time. For example, it is the usual practice to assume that the maximum wind load will not occur simultaneously with a major earthquake.

The vessel must be designed to withstand the worst combination of the loads likely to occur in the following situations:

1. During erection (or dismantling) of the vessel.
2. With the vessel erected but not operating.
3. During testing (the hydraulic pressure test).
4. During normal operation.

13.8.1. Weight loads

The major sources of dead weight loads are:

1. The vessel shell.
2. The vessel fittings: manways, nozzles.
3. Internal fittings: plates (plus the fluid on the plates); heating and cooling coils.
4. External fittings: ladders, platforms, piping.
5. Auxiliary equipment which is not self-supported; condensers, agitators.
6. Insulation.

7. The weight of liquid to fill the vessel. The vessel will be filled with water for the hydraulic pressure test; and may fill with process liquid due to misoperation.

Note: for vessels on a skirt support (see Section 13.9.2), the weight of the liquid to fill the vessel will be transferred directly to the skirt.

The weight of the vessel and fittings can be calculated from the preliminary design sketches. The weights of standard vessel components: heads, shell plates, manways, branches and nozzles, are given in various handbooks; Megyesy (2001) and Brownell and Young (1959).

For preliminary calculations the approximate weight of a cylindrical vessel with domed ends, and uniform wall thickness, can be estimated from the following equation:

$$W_v = C_v \pi \rho_m D_m g (H_v + 0.8 D_m) t \times 10^{-3} \tag{13.75}$$

where W_v = total weight of the shell, excluding internal fittings, such as plates, N,

C_v = a factor to account for the weight of nozzles, manways, internal supports, etc; which can be taken as

= 1.08 for vessels with only a few internal fittings,

= 1.15 for distillation columns, or similar vessels, with several manways, and with plate support rings, or equivalent fittings,

H_v = height, or length, between tangent lines (the length of the cylindrical section), m,

g = gravitational acceleration, 9.81 m/s^2,

t = wall thickness, mm

ρ_m = density of vessel material, kg/m^3,

D_m = mean diameter of vessel = $(D_i + t \times 10^{-3})$, m.

For a steel vessel, equation 13.75 reduces to:

$$W_v = 240 C_v D_m (H_v + 0.8 D_m) t \tag{13.76}$$

The following values can be used as a rough guide to the weight of fittings; see Nelson (1963):

(a) caged ladders, steel, 360 N/m length,
(b) plain ladders, steel, 150 N/m length,
(c) platforms, steel, for vertical columns, 1.7 kN/m^2 area,
(d) contacting plates, steel, including typical liquid loading, 1.2 kN/m^2 plate area.

Typical values for the density of insulating materials are (all kg/m^3):

Foam glass	150
Mineral wool	130
Fibreglass	100
Calcium silicate	200

These densities should be doubled to allow for attachment fittings, sealing, and moisture absorption.

13.8.2. Wind loads (tall vessels)

Wind loading will only be important on tall columns installed in the open. Columns and chimney-stacks are usually free standing, mounted on skirt supports, and not attached to structural steel work. Under these conditions the vessel under wind loading acts as a cantilever beam, Figure 13.19. For a uniformly loaded cantilever the bending moment at any plane is given by:

$$M_x = \frac{wx^2}{2} \tag{13.77}$$

where x is the distance measured from the free end and w the load per unit length (Newtons per metre run).

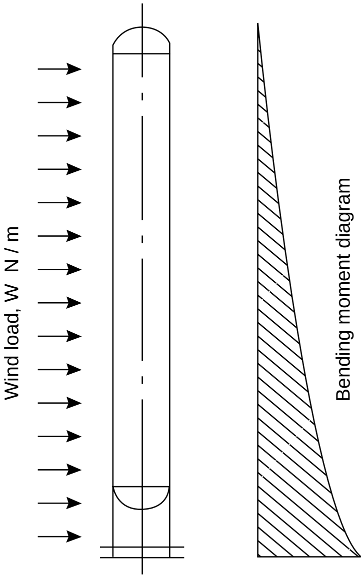


Figure 13.19. Wind loading on a tall column

So the bending moment, and hence the bending stress, will vary parabolically from zero at the top of the column to a maximum value at the base. For tall columns the bending stress due to wind loading will often be greater than direct stress due to pressure, and will determine the plate thickness required. The most economical design will be one in which the plate thickness is progressively increased from the top to the base of the column. The thickness at the top being sufficient for the pressure load, and that at the base sufficient for the pressure plus the maximum bending moment.

Any local increase in the column area presented to the wind will give rise to a local, concentrated, load, Figure 13.20. The bending moment at the column base caused by a concentrated load is given by:

$$M_p = F_p H_p \tag{13.78}$$

where F_p = local, concentrated, load,

H_p = the height of the concentrated load above the column base.

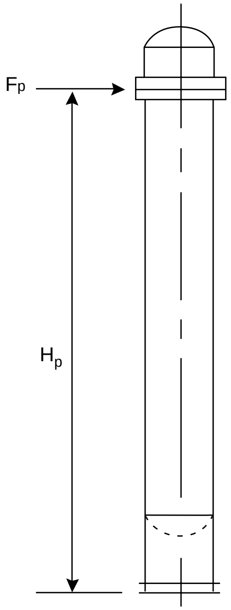


Figure 13.20. Local wind loading

Dynamic wind pressure

The load imposed on any structure by the action of the wind will depend on the shape of the structure and the wind velocity.

$$P_w = \frac{1}{2}C_d \rho_a u_w^2 \tag{13.79}$$

where P_w = wind pressure (load per unit area),
C_d = drag coefficient (shape factor),
ρ_a = density of air,
u_w = wind velocity.

The drag coefficient is a function of the shape of the structure and the wind velocity (Reynolds number).

For a smooth cylindrical column or stack the following semi-empirical equation can be used to estimate the wind pressure:

$$P_w = 0.05 u_w^2 \tag{13.79a}$$

where P_w = wind pressure, N/m^2,
u_w = wind speed, km/h.

If the column outline is broken up by attachments, such as ladders or pipe work, the factor of 0.05 in equation 13.79*a* should be increased to 0.07, to allow for the increased drag.

A column must be designed to withstand the highest wind speed that is likely to be encountered at the site during the life of the plant. The probability of a given wind speed occurring can be predicted by studying meteorological records for the site location.

Data and design methods for wind loading are given in the Engineering Sciences Data Unit (ESDU) Wind Engineering Series (www.ihsedsu.com).

Design loadings for locations in the United States are given by Moss (2003), Megyesy (2001) and Escoe (1994).

A wind speed of 160 km/h (100 mph) can be used for preliminary design studies; equivalent to a wind pressure of 1280 N/m^2 (25 lb/ft^2).

At any site, the wind velocity near the ground will be lower than that higher up (due to the boundary layer), and in some design methods a lower wind pressure is used at heights below about 20 m; typically taken as one-half of the pressure above this height.

The loading per unit length of the column can be obtained from the wind pressure by multiplying by the effective column diameter: the outside diameter plus an allowance for the thermal insulation and attachments, such as pipes and ladders.

$$F_w = P_w D_{\text{eff}} \tag{13.80}$$

An allowance of 0.4 m should be added for a caged ladder. The calculation of the wind load on a tall column, and the induced bending stresses, is illustrated in Example 13.3. Further examples of the design of tall columns are given by Brownell (1963), Henry (1973), Bednar (1990), Escoe (1994) and Jawad and Farr (1989).

Deflection of tall columns

Tall columns sway in the wind. The allowable deflection will normally be specified as less than 150 mm per 30 metres of height (6 in. per 100 ft).

For a column with a uniform cross-section, the deflection can be calculated using the formula for the deflection of a uniformly loaded cantilever. A method for calculating the deflection of a column where the wall thickness is not constant is given by Tang (1968).

Wind-induced vibrations

Vortex shedding from tall thin columns and stacks can induce vibrations which, if the frequency of shedding of eddies matches the natural frequency of the column, can be severe enough to cause premature failure of the vessel by fatigue. The effect of vortex shedding should be investigated for free standing columns with height to diameter ratios greater than 10. Methods for estimating the natural frequency of columns are given by Freese (1959) and DeGhetto and Long (1966).

Helical strakes (strips) are fitted to the tops of tall smooth chimneys to change the pattern of vortex shedding and so prevent resonant oscillation. The same effect will be achieved on a tall column by distributing any attachments (ladders, pipes and platforms) around the column.

13.8.3. Earthquake loading

The movement of the earth's surface during an earthquake produces horizontal shear forces on tall self-supported vessels, the magnitude of which increases from the base upward. The total shear force on the vessel will be given by:

$$F_s = a_e \left(\frac{W}{g}\right) \tag{13.81}$$

where a_e = the acceleration of the vessel due to the earthquake,
g = the acceleration due to gravity,
W = total weight of the vessel.

The term (a_e/g) is called the seismic constant C_e, and is a function of the natural period of vibration of the vessel and the severity of the earthquake. Values of the seismic constant have been determined empirically from studies of the damage caused by earthquakes, and are available for those geographical locations which are subject to earthquake activity. Values for sites in the United States, and procedures for determining the stresses induced in tall columns are given by Megyesy (2001), Escoe (1994) and Moss (2003).

A seismic stress analysis is not made as a routine procedure in the design of vessels for sites in the United Kingdom, except for nuclear installations, as the probability of an earthquake occurring of sufficient severity to cause significant damage is negligible. However, the possibility of earthquake damage may be considered if the site is a Major Hazards installation, see Chapter 9, Section 9.9.

13.8.4. Eccentric loads (tall vessels)

Ancillary equipment attached to a tall vessel will subject the vessel to a bending moment if the centre of gravity of the equipment does not coincide with the centre line of the vessel (Figure 13.21). The moment produced by small fittings, such as ladders, pipes and manways, will be small and can be neglected. That produced by heavy equipment, such as reflux condensers and side platforms, can be significant and should be considered. The moment is given by:

$$M_e = W_e L_o \tag{13.82}$$

where W_e = dead weight of the equipment,
L_o = distance between the centre of gravity of the equipment and the column centre line.

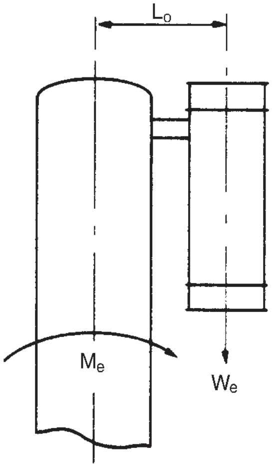


Figure 13.21. Bending moment due to offset equipment

13.8.5. Torque

Any horizontal force imposed on the vessel by ancillary equipment, the line of thrust of which does not pass through the centre line of the vessel, will produce a torque on the vessel. Such loads can arise through wind pressure on piping and other attachments. However, the torque will normally be small and usually can be disregarded. The pipe work and the connections for any ancillary equipment will be designed so as not to impose a significant load on the vessel.

Example 13.3

Make a preliminary estimate of the plate thickness required for the distillation column specified below:

Height, between tangent lines	50 m
Diameter	2 m
Skirt support, height	3 m
100 sieve plates, equally spaced	
Insulation, mineral wool	75 mm thick

Material of construction, stainless steel, design stress 135 N/mm^2 at design temperature 200°C

Operating pressure 10 bar (absolute)

Vessel to be fully radiographed (joint factor 1).

Solution

Design pressure; take as 10 per cent above operating pressure

$$= (10 - 1) \times 1.1 = 9.9 \text{ bar, say } 10 \text{ bar}$$

$$= 1.0 \text{ N/mm}^2$$

Minimum thickness required for pressure loading

$$= \frac{1 \times 2 \times 10^3}{2 \times 135 - 1} = 7.4 \text{ mm} \tag{13.39}$$

A much thicker wall will be needed at the column base to withstand the wind and dead weight loads.

As a first trial, divide the column into five sections (courses), with the thickness increasing by 2 mm per section. Try 10, 12, 14, 16, 18 mm.

Dead weight of vessel

Though equation 13.76 only applies strictly to vessels with uniform thickness, it can be used to get a rough estimate of the weight of this vessel by using the average thickness in the equation, 14 mm.

Take $C_v = 1.15$, vessel with plates,

$D_m = 2 + 14 \times 10^{-3} = 2.014$ m,

$$
\begin{aligned}
H_v &= 50 \text{ m},\\
t &= 14 \text{ mm}\\
W_v &= 240 \times 1.15 \times 2.014(50 + 0.8 \times 2.014)14 \qquad (13.76)\\
&= 401643 \text{ N}\\
&= 402 \text{ kN}
\end{aligned}
$$

Weight of plates:

plate area $= \pi/4 \times 2^2 = 3.14\ \text{m}^2$
weight of a plate (see page 761) $= 1.2 \times 3.14 = 3.8$ kN
100 plates $= 100 \times 3.8 = 380$ kN

Weight of insulation:

mineral wool density $= 130\ \text{kg/m}^3$
approximate volume of insulation $= \pi \times 2 \times 50 \times 75 \times 10^{-3}$
$= 23.6\ \text{m}^3$
weight $= 23.6 \times 130 \times 9.81 = 30{,}049$ N
double this to allow for fittings, etc. $= 60$ kN

Total weight:

shell	402
plates	380
insulation	60
	842 kN

Wind loading

Take dynamic wind pressure as $1280\ \text{N/m}^2$.

Mean diameter, including insulation $= 2 + 2(14 + 75) \times 10^{-3}$
$= 2.18$ m

$$\text{Loading (per linear metre) } F_w = 1280 \times 2.18 = 2790 \text{ N/m} \qquad (13.80)$$

Bending moment at bottom tangent line:

$$M_x = \frac{2790}{2} \times 50^2 = 3{,}487{,}500 \text{ Nm} \qquad (13.77)$$

Analysis of stresses

At bottom tangent line

Pressure stresses:

$$\sigma_L = \frac{1.0 \times 2 \times 10^3}{4 \times 18} = 27.8 \text{ N/mm}^2 \qquad (13.64)$$

$$\sigma_h = \frac{1 \times 2 \times 10^3}{2 \times 18} = 55.6 \text{ N/mm}^2 \qquad (13.63)$$

Dead weight stress:

$$\sigma_w = \frac{W_v}{\pi(D_i + t)t} = \frac{842 \times 10^3}{\pi(2000 + 18)18} \tag{13.65}$$

$$= 7.4 \text{ N/mm}^2 \text{ (compressive)}$$

Bending stresses:

$$D_o = 2000 + 2 \times 18 = 2036 \text{ mm}$$

$$I_v = \frac{\pi}{64}(2036^4 - 2000^4) = 5.81 \times 10^{10} \text{ mm}^4 \tag{13.67}$$

$$\sigma_b = \pm\frac{3{,}487{,}500 \times 10^3}{5.81 \times 10^{10}}\left(\frac{2000}{2} + 18\right) \tag{13.66}$$

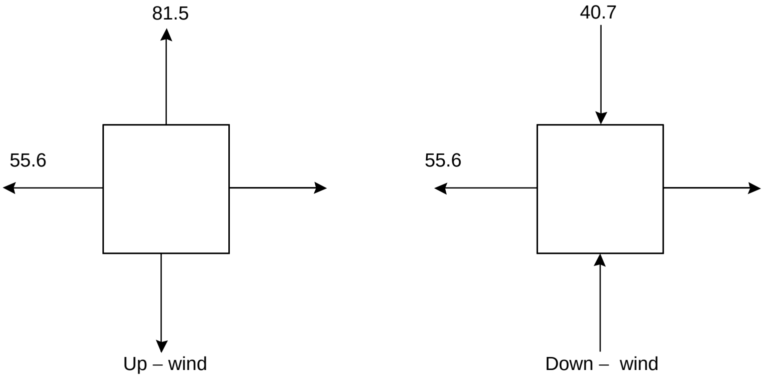
$$= \pm 61.1 \text{ N/mm}^2$$

The resultant longitudinal stress is:

$$\sigma_z = \sigma_L + \sigma_w \pm \sigma_b$$

σ_w is compressive and therefore negative.
σ_z (upwind) $= 27.8 - 7.4 + 61.1 = +81.5$ N/mm^2.
σ_z (downwind) $= 27.8 - 7.4 - 61.1 = -40.7$ N/mm^2.

As there is no torsional shear stress, the principal stresses will be σ_z and σ_h.
The radial stress is negligible, $\simeq (P_i/2) = 0.5$ N/mm^2.



The greatest difference between the principal stresses will be on the down-wind side

$$(55.6 - (-40.7)) = \underline{\underline{96.5 \text{ N/mm}^2}},$$

well below the maximum allowable design stress

Check elastic stability (buckling)

Critical buckling stress:

$$\sigma_c = 2 \times 10^4 \left(\frac{18}{2036}\right) = \underline{\underline{176.8 \text{ N/mm}^2}} \tag{13.74}$$

The maximum compressive stress will occur when the vessel is not under pressure $= 7.4 + 61.1 = 68.5$, well below the critical buckling stress.

So design is satisfactory. Could reduce the plate thickness and recalculate.

13.9. VESSEL SUPPORTS

The method used to support a vessel will depend on the size, shape, and weight of the vessel; the design temperature and pressure; the vessel location and arrangement; and the internal and external fittings and attachments. Horizontal vessels are usually mounted on two saddle supports; Figure 13.22. Skirt supports are used for tall, vertical columns; Figure 13.23. Brackets, or lugs, are used for all types of vessel; Figure 13.24. The supports must be designed to carry the weight of the vessel and contents, and any superimposed loads, such as wind loads. Supports will impose localised loads on the vessel wall, and the design must be checked to ensure that the resulting stress concentrations are below the maximum allowable design stress. Supports should be designed to allow easy access to the vessel and fittings for inspection and maintenance.

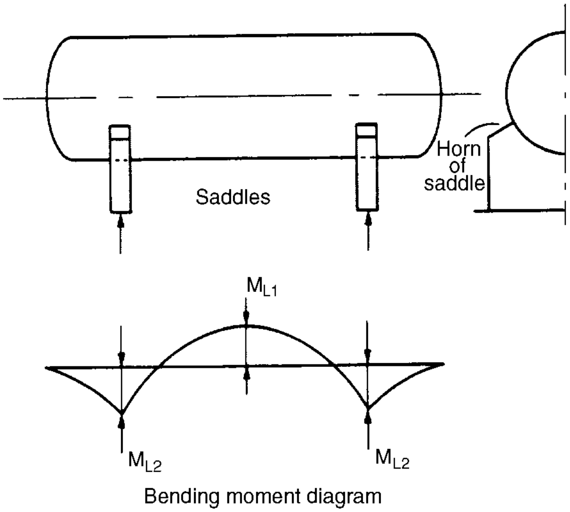


Figure 13.22. Horizontal cylindrical vessel on saddle supports

13.9.1. Saddle supports

Though saddles are the most commonly used support for horizontal cylindrical vessels, legs can be used for small vessels. A horizontal vessel will normally be supported at two cross-sections; if more than two saddles are used the distribution of the loading is uncertain.

A vessel supported on two saddles can be considered as a simply supported beam, with an essentially uniform load, and the distribution of longitudinal axial bending moment will be as shown in Figure 13.22. Maxima occur at the supports and at mid-span. The

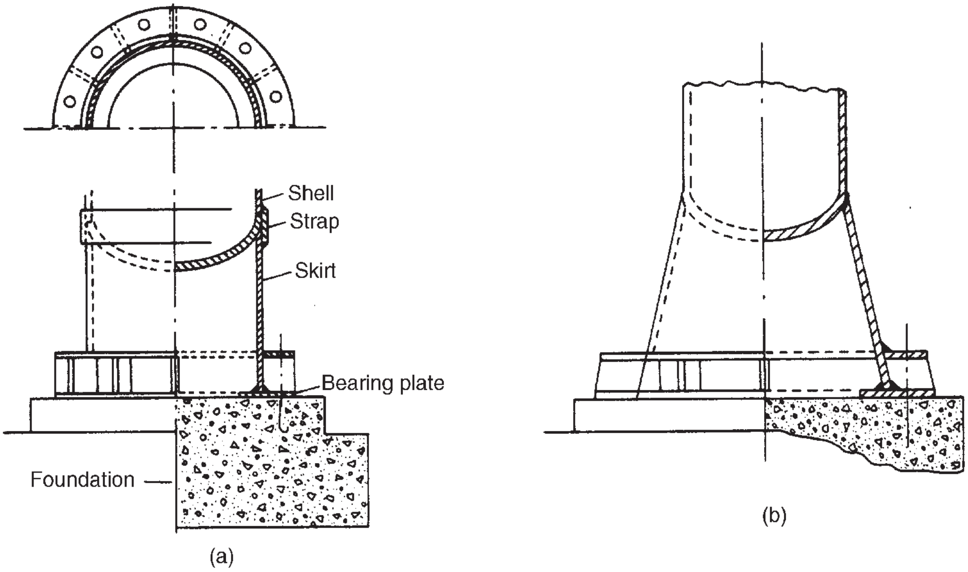


Figure 13.23. Typical skirt-support designs (*a*) Straight skirt (*b*) Conical skirt

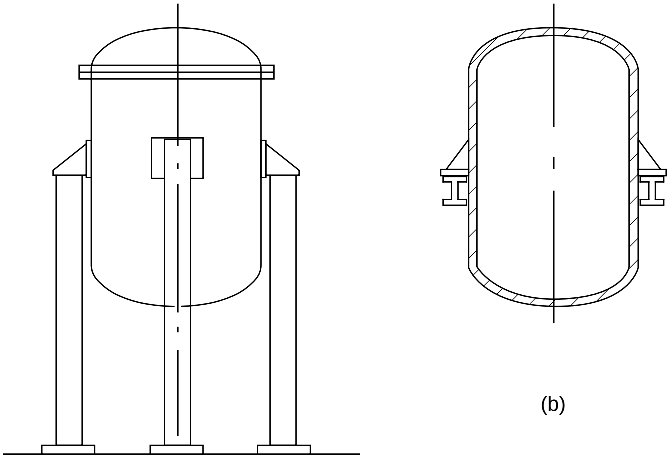


Figure 13.24. Bracket supports (*a*) Supported on legs (*b*) Supported from steel-work

theoretical optimum position of the supports to give the least maximum bending moment will be the position at which the maxima at the supports and at mid-span are equal in magnitude. For a uniformly loaded beam the position will be at 21 per cent of the span, in from each end. The saddle supports for a vessel will usually be located nearer the ends than this value, to make use of the stiffening effect of the ends.

Stress in the vessel wall

The longitudinal bending stress at the mid-span of the vessel is given by:

$$\sigma_{b1} = \frac{M_{L1}}{I_h} \times \frac{D}{2} \simeq \frac{4M_{L1}}{\pi D^2 t} \tag{13.83}$$

where M_{L1} = longitudinal bending stress at the mid-span,
I_h = second moment of area of the shell,
D = shell diameter,
t = shell thickness.

The resultant axial stress due to bending and pressure will be given by:

$$\sigma_z = \frac{PD}{4t} \pm \frac{4M_{L1}}{\pi D^2 t} \tag{13.84}$$

The magnitude of the longitudinal bending stress at the supports will depend on the local stiffness of the shell; if the shell does not remain circular under load a portion of the upper part of the cross-section is ineffective against longitudinal bending; see Figure 13.25. The stress is given by:

$$\sigma_{b2} = \frac{4M_{L2}}{C_h \pi D^2 t} \tag{13.85}$$

where M_{L2} = longitudinal bending moment at the supports,
C_h = an empirical constant; varying from 1.0 for a completely stiff shell to about 0.1 for a thin, unstiffened, shell.

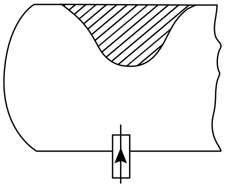


Figure 13.25. Saddle supports: shaded area is ineffective against longitudinal bending in an unstiffened shell

The ends of the vessels will stiffen the shell if the position of the saddles is less than $D/4$ from the ends. Ring stiffeners, located at the supports, are used to stiffen the shells of long thin vessels. The rings may be fitted inside or outside the vessel.

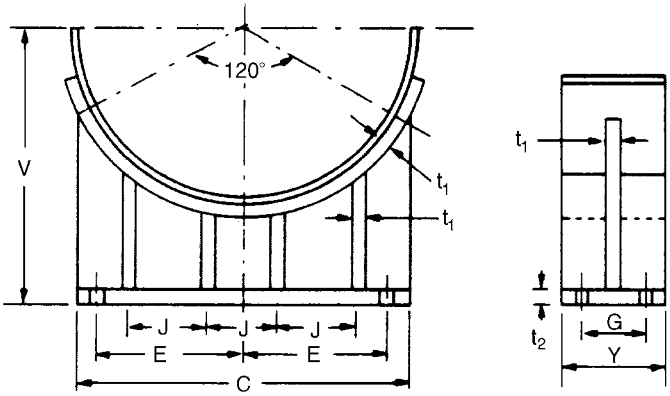
In addition to the longitudinal bending stress, a vessel supported on saddles will be subjected to tangential shear stresses, which transfer the load from the unsupported sections of the vessel to the supports; and to circumferential bending stresses. All these stresses need to be considered in the design of large, thin-walled, vessels, to ensure that the resultant stress does not exceed the maximum allowable design stress or the critical buckling stress for the material. A detailed stress analysis is beyond the scope of this book. A complete analysis of the stress induced in the shell by the supports is given by Zick (1951). Zick's method forms the basis of the design methods given in the national codes and standards. The method is also given by Brownell and Young (1959), Escoe (1994) and Megyesy (2001).

Design of saddles

The saddles must be designed to withstand the load imposed by the weight of the vessel and contents. They are constructed of bricks or concrete, or are fabricated from steel plate. The contact angle should not be less than 120°, and will not normally be greater than 150°. Wear plates are often welded to the shell wall to reinforce the wall over the area of contact with the saddle.

The dimensions of typical "standard" saddle designs are given in Figure 13.26. To take up any thermal expansion of the vessel, such as that in heat exchangers, the anchor bolt holes in one saddle can be slotted.

Procedures for the design of saddle supports are given by Brownell and Young (1959), Megyesy (2001), Escoe (1994) and Moss (2003).

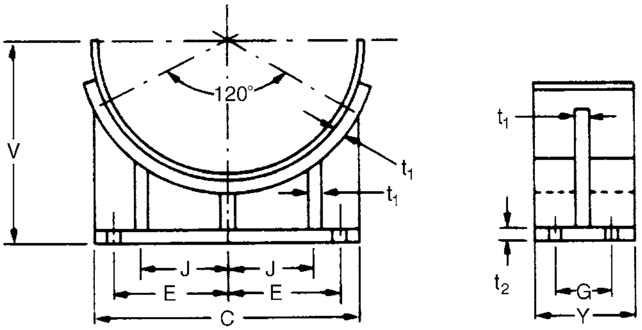


Vessel diam. (m)	Maximum weight (kN)	Dimensions (m)						mm			
		V	Y	C	E	J	G	t_2	t_1	Bolt diam.	Bolt holes
0.6	35	0.48	0.15	0.55	0.24	0.190	0.095	6	5	20	25
0.8	50	0.58	0.15	0.70	0.29	0.225	0.095	8	5	20	25
0.9	65	0.63	0.15	0.81	0.34	0.275	0.095	10	6	20	25
1.0	90	0.68	0.15	0.91	0.39	0.310	0.095	11	8	20	25
1.2	180	0.78	0.20	1.09	0.45	0.360	0.140	12	10	24	30

All contacting edges fillet welded

(a)

Figure 13.26. Standard steel saddles (adapted from Bhattacharyya, 1976). (*a*) for vessels up to 1.2 m



Vessel diam. (m)	Maximum weight (kN)	Dimensions (m)						mm			
		V	Y	C	E	J	G	t_2	t_1	Bolt diam.	Bolt holes
1.4	230	0.88	0.20	1.24	0.53	0.305	0.140	12	10	24	30
1.6	330	0.98	0.20	1.41	0.62	0.350	0.140	12	10	24	30
1.8	380	1.08	0.20	1.59	0.71	0.405	0.140	12	10	24	30
2.0	460	1.18	0.20	1.77	0.80	0.450	0.140	12	10	24	30
2.2	750	1.28	0.225	1.95	0.89	0.520	0.150	16	12	24	30
2.4	900	1.38	0.225	2.13	0.98	0.565	0.150	16	12	27	33
2.6	1000	1.48	0.225	2.30	1.03	0.590	0.150	16	12	27	33
2.8	1350	1.58	0.25	2.50	1.10	0.625	0.150	16	12	27	33
3.0	1750	1.68	0.25	2.64	1.18	0.665	0.150	16	12	27	33
3.2	2000	1.78	0.25	2.82	1.26	0.730	0.150	16	12	27	33
3.6	2500	1.98	0.25	3.20	1.40	0.815	0.150	16	12	27	33

All contacting edges fillet welded

(b)

Figure 13.26. (*b*) for vessels greater than 1.2 m

13.9.2. Skirt supports

A skirt support consists of a cylindrical or conical shell welded to the base of the vessel. A flange at the bottom of the skirt transmits the load to the foundations. Typical designs are shown in Figure 13.23. Openings must be provided in the skirt for access and for any connecting pipes; the openings are normally reinforced. The skirt may be welded to the bottom head of the vessel. Figure 13.27*a*; or welded flush with the shell, Figure 13.27*b*; or welded to the outside of the vessel shell, Figure 13.27*c*. The arrangement shown in Figure 13.27*b* is usually preferred.

Skirt supports are recommended for vertical vessels as they do not impose concentrated loads on the vessel shell; they are particularly suitable for use with tall columns subject to wind loading.

Skirt thickness

The skirt thickness must be sufficient to withstand the dead-weight loads and bending moments imposed on it by the vessel; it will not be under the vessel pressure.

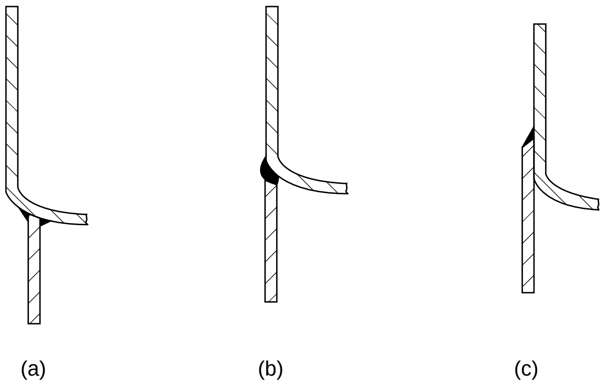


Figure 13.27. Skirt-support welds

The resultant stresses in the skirt will be:

$$\sigma_s \text{ (tensile)} = \sigma_{bs} - \sigma_{ws} \tag{13.86}$$

and

$$\sigma_s \text{ (compressive)} = \sigma_{bs} + \sigma_{ws} \tag{13.87}$$

where σ_{bs} = bending stress in the skirt

$$= \frac{4M_s}{\pi(D_s + t_s)t_s D_s}, \tag{13.88}$$

σ_{ws} = the dead weight stress in the skirt,

$$= \frac{W}{\pi(D_s + t_s)t_s} \tag{13.89}$$

where M_s = maximum bending moment, evaluated at the base of the skirt (due to wind, seismic and eccentric loads, see Section 13.8),

W = total weight of the vessel and contents (see Section 13.8),

D_s = inside diameter of the skirt, at the base,

t_s = skirt thickness.

The skirt thickness should be such that under the worst combination of wind and dead-weight loading the following design criteria are not exceeded:

$$\sigma_s \text{ (tensile)} \not> f_s J \sin\theta_s \tag{13.90}$$

$$\sigma_s \text{ (compressive)} \not> 0.125E\left(\frac{t_s}{D_s}\right)\sin\theta_s \tag{13.91}$$

where f_s = maximum allowable design stress for the skirt material, normally taken at ambient temperature, 20°C,

J = weld joint factor, if applicable,
θ_s = base angle of a conical skirt, normally 80° to 90°.

The minimum thickness should be not less than 6 mm.

Where the vessel wall will be at a significantly higher temperature than the skirt, discontinuity stresses will be set up due to differences in thermal expansion. Methods for calculating the thermal stresses in skirt supports are given by Weil and Murphy (1960) and Bergman (1963).

Base ring and anchor bolt design

The loads carried by the skirt are transmitted to the foundation slab by the skirt base ring (bearing plate). The moment produced by wind and other lateral loads will tend to overturn the vessel; this will be opposed by the couple set up by the weight of the vessel and the tensile load in the anchor bolts. A variety of base ring designs is used with skirt supports. The simplest types, suitable for small vessels, are the rolled angle and plain flange rings shown in Figure 13.28*a* and *b*. For larger columns a double ring stiffened by gussets, Figure 13.18*c*, or chair supports, Figure 13.30, are used. Design methods for base rings, and methods for sizing the anchor bolts, are given by Brownell and Young (1959). For preliminary design, the short-cut method and nomographs given by Scheiman (1963) can be used. Scheiman's method is based on a more detailed procedure for the design of base rings and foundations for columns and stacks given by Marshall (1958). Scheiman's method is outlined below and illustrated in Example 13.4.

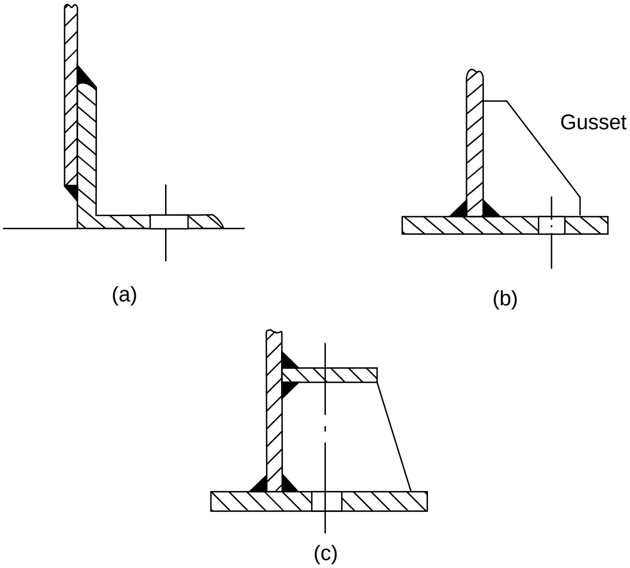


Figure 13.28. Flange ring designs (*a*) Rolled-angle (*b*) Single plate with gusset (*c*) Double plate with gusset

The anchor bolts are assumed to share the overturning load equally, and the bolt area required is given by:

$$A_b = \frac{1}{N_b f_b}\left[\frac{4M_s}{D_b} - W\right] \tag{13.92}$$

where A_b = area of one bolt at the root of the thread, mm^2,
N_b = number of bolts,
f_b = maximum allowable bolt stress, N/mm^2;
typical design value 125 N/mm^2 (18,000 psi),
M_s = bending (overturning) moment at the base, Nm,
W = weight of the vessel, N,
D_b = bolt circle diameter, m.

Scheiman gives the following guide rules which can be used for the selection of the anchor bolts:

1. Bolts smaller than 25 mm (1 in.) diameter should not be used.
2. Minimum number of bolts 8.
3. Use multiples of 4 bolts.
4. Bolt pitch should not be less than 600 mm (2 ft).

If the minimum bolt pitch cannot be accommodated with a cylindrical skirt, a conical skirt should be used.

The base ring must be sufficiently wide to distribute the load to the foundation. The total compressive load on the base ring is given by:

$$F_b = \left[\frac{4M_s}{\pi D_s^2} + \frac{W}{\pi D_s}\right] \tag{13.93}$$

where F_b = the compressive load on the base ring, Newtons per linear metre,
D_s = skirt diameter, m.

The minimum width of the base ring is given by:

$$L_b = \frac{F_b}{f_c} \times \frac{1}{10^3} \tag{13.94}$$

where L_b = base ring width, mm (Figure 13.29),
f_c = the maximum allowable bearing pressure on the concrete foundation pad, which will depend on the mix used, and will typically range from 3.5 to 7 N/mm^2 (500 to 1000 psi).

The required thickness for the base ring is found by treating the ring as a cantilever beam.

The minimum thickness is given by:

$$t_b = L_r\sqrt{\frac{3f'_c}{f_r}} \tag{13.95}$$

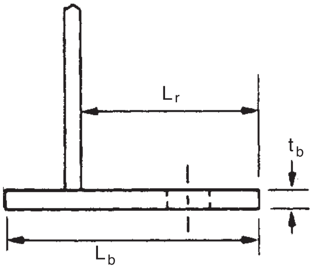
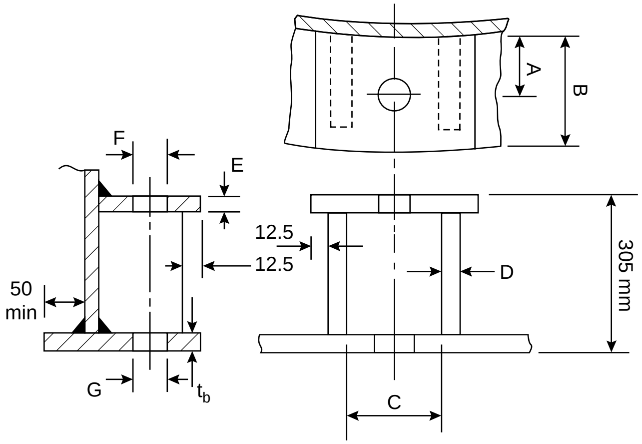


Figure 13.29. Flange ring dimensions



All contacting edges fillet welded

Dimensions mm								
Bolt size	Root area	*A*	*B*	*C*	*D*	*E*	*F*	*G*
M24	353	45	76	64	13	19	30	36
M30	561	50	76	64	13	25	36	42
M36	817	57	102	76	16	32	42	48
M42	1120	60	102	76	16	32	48	54
M48	1470	67	127	89	19	38	54	60
M56	2030	75	150	102	25	45	60	66
M64	2680	83	152	102	25	50	70	76
70	—	89	178	127	32	64	76	83
76	—	95	178	127	32	64	83	89

Bolt size = Nominal dia. (BS 4190: 1967)

Figure 13.30. Anchor bolt chair design

where L_r = the distance from the edge of the skirt to the outer edge of the ring, mm; Figure 13.29,

t_b = base ring thickness, mm,

f'_c = actual bearing pressure on base, N/mm^2,

f_r = allowable design stress in the ring material, typically 140 N/mm^2.

Standard designs will normally be used for the bolting chairs. The design shown in Figure 13.30 has been adapted from that given by Scheiman.

Example 13.4

Design a skirt support for the column specified in Example 13.3.

Solution

Try a straight cylindrical skirt ($\theta_s = 90^\circ$) of plain carbon steel, design stress 135 N/mm^2 and Young's modulus 200,000 N/mm^2 at ambient temperature.

The maximum dead weight load on the skirt will occur when the vessel is full of water.

$$\text{Approximate weight} = \left(\frac{\pi}{4} \times 2^2 \times 50\right) 1000 \times 9.81$$

$$= 1{,}540{,}951 \text{ N}$$

$$= 1541 \text{ kN}$$

Weight of vessel, from Example 13.3 = 842 kN

Total weight = 1541 + 842 = 2383 kN

Wind loading, from Example 13.4 = 2.79 kN/m

$$\text{Bending moment at base of skirt} = 2.79 \times \frac{53^2}{2} \tag{13.77}$$

$$= 3919 \text{ kNm}$$

As a first trial, take the skirt thickness as the same as that of the bottom section of the vessel, 18 mm.

$$\sigma_{bs} = \frac{4 \times 3919 \times 10^3 \times 10^3}{\pi(2000 + 18)2000 \times 18} \tag{13.88}$$

$$= 68.7 \text{ N/mm}^2$$

$$\sigma_{ws} \text{ (test)} = \frac{1543 \times 10^3}{\pi(2000 + 18)18} = 13.5 \text{ N/mm}^2 \tag{13.89}$$

$$\sigma_{ws} \text{ (operating)} = \frac{842 \times 10^3}{\pi(2000 + 18)18} = 7.4 \text{ N/mm}^2 \tag{13.89}$$

Note: the "test" condition is with the vessel full of water for the hydraulic test. In estimating total weight, the weight of liquid on the plates has been counted twice. The weight has not been adjusted to allow for this as the error is small, and on the "safe side".

$$\text{Maximum } \hat{\sigma}_s \text{ (compressive)} = 68.7 + 13.5 = 82.2 \text{ N/mm}^2 \tag{13.87}$$

$$\text{Maximum } \hat{\sigma}_s \text{ (tensile)} = 68.7 - 7.4 = 61.3 \text{ N/mm}^2 \tag{13.86}$$

Take the joint factor J as 0.85.

Criteria for design:

$$\hat{\sigma}_s \text{ (tensile)} \not> f_s J \sin\theta \tag{13.90}$$

$$61.3 \not> 0.85 \times 135 \sin 90$$

$$61.3 \not> 115$$

$$\hat{\sigma}_s \text{ (compressive)} \not> 0.125E\left(\frac{t_s}{D_s}\right)\sin\theta \tag{13.91}$$

$$82.2 \not> 0.125 \times 200{,}000\left(\frac{18}{2000}\right)\sin 90$$

$$82.2 \not> 225$$

Both criteria are satisfied, add 2 mm for corrosion, gives a design thickness of 20 mm

Base ring and anchor bolts

Approximate pitch circle dia., say, 2.2 m
Circumference of bolt circle $= 2200\pi$
Number of bolts required, at minimum recommended bolt spacing

$$= \frac{2200\pi}{600} = 11.5$$

Closest multiple of $4 = 12$ bolts
Take bolt design stress $= 125\ \text{N/mm}^2$
$M_s = 3919$ kN m

Take W = operating value = 842 kN.

$$A_b = \frac{1}{12 \times 125}\left[\frac{4 \times 3919 \times 10^3}{2.2} - 842 \times 10^3\right] \tag{13.92}$$

$$= 4190\ \text{mm}^2$$

$$\text{Bolt root dia.} = \sqrt{\frac{4190 \times 4}{\pi}} = 73\ \text{mm, looks too large.}$$

Total compressive load on the base ring per unit length

$$F_b = \left[\frac{4 \times 3919 \times 10^3}{\pi \times 2.0^2} + \frac{842 \times 10^3}{\pi \times 2.0}\right] \tag{13.93}$$

$$= 1381 \times 10^3\ \text{N/m}$$

Taking the bearing pressure as $5\ \text{N/mm}^2$

$$L_b = \frac{1381 \times 10^3}{5 \times 10^3} = 276\ \text{mm} \tag{13.94}$$

Rather large — consider a flared skirt.

Take the skirt bottom dia. as 3 m

$$\text{Skirt base angle } \theta_s = \tan^{-1}\frac{3}{\frac{1}{2}(3-2)} = 80.5^\circ$$

Keep the skirt thickness the same as that calculated for the cylindrical skirt. Highest stresses will occur at the top of the skirt; where the values will be close to those calculated for the cylindrical skirt. Sin 80.5° = 0.99, so this term has little effect on the design criteria.

Assume bolt circle dia. = 3.2 m.

Take number of bolts as 16.

$$\text{Bolt spacing} = \frac{\pi \times 3.2 \times 10^3}{16} = 628 \text{ mm satisfactory.}$$

$$A_b = \frac{1}{16 \times 125}\left[\frac{4 \times 3919 \times 10^3}{3.2} - 842 \times 10^3\right]$$

$$= \underline{\underline{2029 \text{ mm}^2}}$$

Use M56 bolts (BS 4190:1967) root area = 2030 mm^2,

$$F_b = \left[\frac{4 \times 3919 \times 10^3}{\pi \times 3.0^2} + \frac{842 \times 10^3}{\pi \times 3.0}\right]$$

$$= 644 \text{ kN/m.}$$

$$L_b = \frac{644 \times 10^3}{5 \times 10^3} = 129 \text{ mm}$$

This is the minimum width required; actual width will depend on the chair design.

Actual width required (Figure 13.30):

$$= L_r + t_s + 50 \text{ mm}$$

$$= 150 + 20 + 50 = \underline{\underline{220 \text{ mm}}}$$

Actual bearing pressure on concrete foundation:

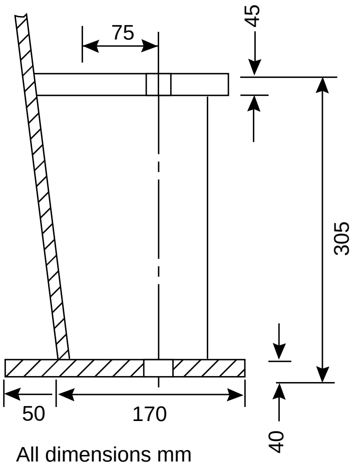
$$f'_c = \frac{644 \times 10^3}{220 \times 10^3} = 2.93 \text{ N/mm}^2$$

$$t_b = 150\sqrt{\frac{3 \times 2.93}{140}} = 37.6 \text{ mm} \qquad (13.95)$$

$$\text{round off to } \underline{\underline{40 \text{ mm}}}$$

Chair dimensions from Figure 13.30 for bolt size M56.

Skirt to be welded flush with outer diameter of column shell.



13.9.3. Bracket supports

Brackets, or lugs, can be used to support vertical vessels. The bracket may rest on the building structural steel work, or the vessel may be supported on legs; Figure 13.24.

The main load carried by the brackets will be the weight of the vessel and contents; in addition the bracket must be designed to resist the load due to any bending moment due to wind, or other loads. If the bending moment is likely to be significant skirt supports should be considered in preference to bracket supports.

As the reaction on the bracket is eccentric, Figure 13.31, the bracket will impose a bending moment on the vessel wall. The point of support, at which the reaction acts, should be made as close to the vessel wall as possible; allowing for the thickness of any insulation. Methods for estimating the magnitude of the stresses induced in the vessel

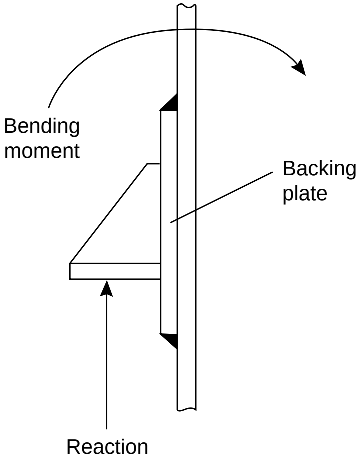


Figure 13.31. Loads on a bracket support

wall by bracket supports are given by Brownell and Young (1959) and by Wolosewick (1951). Backing plates are often used to carry the bending loads.

The brackets, and supporting steel work, can be designed using the usual methods for structural steelwork. Suitable methods are given by Bednar (1986) and Moss (2003).

A quick method for sizing vessel reinforcing rings (backing plates) for bracket supports is given by Mahajan (1977).

Typical bracket designs are shown in Figures 13.32*a* and *b*. The loads which steel brackets with these proportions will support are given by the following formula:

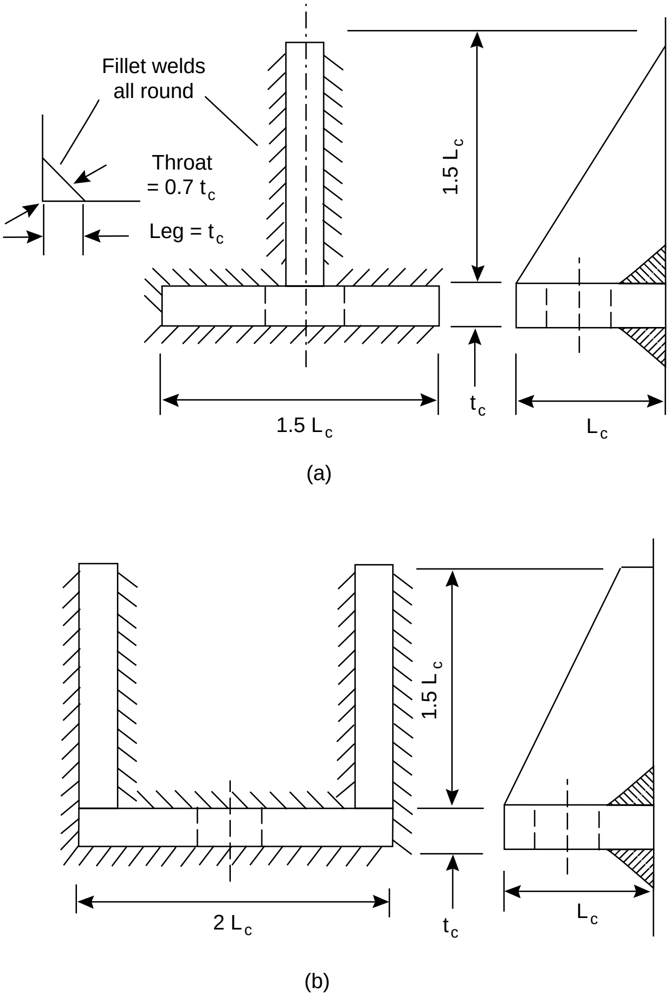


Figure 13.32. Bracket designs (*a*) Single gusset plate (*b*) Double gusset plate

Single-gusset plate design, Figure 13.32*a*:

$$F_{bs} = 60 L_c t_c \tag{13.96}$$

Double-gusset plate design, Figure 13.32*b*:

$$F_{bs} = 120 L_c t_c \tag{13.97}$$

where F_{bs} = maximum design load per bracket, N,
L_c = the characteristic dimension of bracket (depth), mm,
t_c = thickness of plate, mm.

13.10. BOLTED FLANGED JOINTS

Flanged joints are used for connecting pipes and instruments to vessels, for manhole covers, and for removable vessel heads when ease of access is required. Flanges may also be used on the vessel body, when it is necessary to divide the vessel into sections for transport or maintenance. Flanged joints are also used to connect pipes to other equipment, such as pumps and valves. Screwed joints are often used for small-diameter pipe connections, below 40 mm. Flanged joints are also used for connecting pipe sections where ease of assembly and dismantling is required for maintenance, but pipework will normally be welded to reduce costs.

Flanges range in size from a few millimetres diameter for small pipes, to several metres diameter for those used as body or head flanges on vessels.

13.10.1. Types of flange, and selection

Several different types of flange are used for various applications. The principal types used in the process industries are:

1. Welding-neck flanges.
2. Slip-on flanges, hub and plate types.
3. Lap-joint flanges.
4. Screwed flanges.
5. Blank, or blind, flanges.

Welding-neck flanges, Figure 13.33*a*: have a long tapered hub between the flange ring and the welded joint. This gradual transition of the section reduces the discontinuity stresses between the flange and branch, and increases the strength of the flange assembly. Welding-neck flanges are suitable for extreme service conditions; where the flange is likely to be subjected to temperature, shear and vibration loads. They will normally be specified for the connections and nozzles on process vessels and process equipment.

Slip-on flanges, Figure 13.33*b*: slip over the pipe or nozzle and are welded externally, and usually also internally. The end of the pipe is set back from 0 to 2.0 mm. The strength of a slip-on flange is from one-third to two-thirds that of the corresponding standard welding-neck flange. Slip-on flanges are cheaper than welding-neck flanges and are easier to align, but have poor resistance to shock and vibration loads. Slip-on flanges are generally used for pipe work. Figure 13.33*b* shows a forged flange with a hub; for light duties slip-on flanges can be cut from plate.

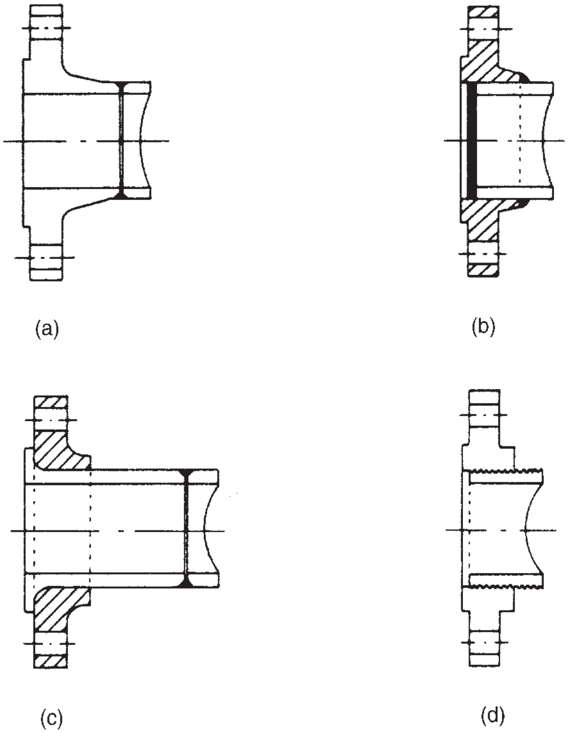


Figure 13.33. Flange types (*a*) Welding-neck (*b*) Slip-on (*c*) Lap-joint (*d*) Screwed

Lap-joint flanges, Figure 13.33*c*: are used for piped work. They are economical when used with expensive alloy pipe, such as stainless steel, as the flange can be made from inexpensive carbon steel. Usually a short lapped nozzle is welded to the pipe, but with some schedules of pipe the lap can be formed on the pipe itself, and this will give a cheap method of pipe assembly.

Lap-joint flanges are sometimes known as “Van-stone flanges”.

Screwed flanges, Figure 13.33*d*: are used to connect screwed fittings to flanges. They are also sometimes used for alloy pipe which is difficult to weld satisfactorily.

Blind flanges (blank flanges): are flat plates, used to blank off flange connections, and as covers for manholes and inspection ports.

13.10.2. Gaskets

Gaskets are used to make a leak-tight joint between two surfaces. It is impractical to machine flanges to the degree of surface finish that would be required to make a satisfactory seal under pressure without a gasket. Gaskets are made from “semi-plastic” materials; which will deform and flow under load to fill the surface irregularities between the flange faces, yet retain sufficient elasticity to take up the changes in the flange alignment that occur under load.

Table 13.4. Gasket materials
(Based on a similar table in BS 5500: 1991; see BS PD 5500–2003)

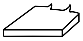
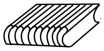
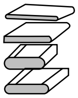
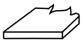
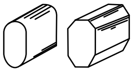
Gasket material		Gasket factor m	Min. design seating stress y(N/mm^2)	Sketches	Minimum gasket width (mm)
Rubber without fabric or a high percentage of asbestos fibre; hardness: below 75° IRH		0.50	0		10
75° IRH or higher		1.00	1.4		
Asbestos with a suitable binder for the operating conditions	3.2 mm thick	2.00	11.0		10
	1.6 mm thick	2.75	25.5		
	0.8 mm thick	3.50	44.8		
Rubber with cotton fabric insertion		1.25	2.8		10
Rubber with asbestos fabric insertion, with or without wire reinforcement	3-ply	2.25	15.2		10
	2-ply	2.50	20.0		
	1-ply	2.75	25.5		
Vegetable fibre		1.75	7.6		10
Spiral-wound metal, asbestos filled	Carbon	2.50	20.0		10
	Stainless or monel	3.00	31.0		
Corrugated metal, asbestos inserted or Corrugated metal, jacketed asbestos filled	Soft aluminium	2.50	20.0		10
	Soft copper or brass	2.75	25.5		
	Iron or soft steel	3.00	31.0		
	Monel or 4 to 6 per cent chrome	3.25	37.9		
	Stainless steels	3.50	44.8		
Corrugated metal	Soft aluminium	2.75	25.5		10
	Soft copper or brass	3.00	31.0		
	Iron or soft steel	3.25	37.9		
	Monel or 4 to 6 per cent chrome	3.50	44.8		
	Stainless steels	3.75	52.4		
Flat metal jacketed asbestos filled	Soft aluminium	3.25	37.9		10
	Soft copper or brass	3.50	44.8		
	Iron or soft steel	3.75	52.4		
	Monel	3.50	55.1		
	4 to 6 per cent chrome	3.75	62.0		
	Stainless steels	3.75	62.0		
Grooved metal	Soft aluminium	3.25	37.9		10
	Soft copper or brass	3.50	44.8		
	Iron or soft steel	3.75	52.4		
	Monel or 4 to 6 per cent chrome	3.75	62.0		
	Stainless steels	4.25	69.5		
	Soft aluminium	4.00	60.6		
	Soft copper or brass	4.75	89.5		

Table 13.4. (*continued*)

Gasket material		Gasket factor m	Min. design seating stress $y(\mathrm{N/mm^2})$	Sketches	Minimum gasket width (mm)
Solid flat metal	Iron or soft steel	5.50	124		6
	Monel or 4 to 6 per cent chrome	6.00	150		
	Stainless steels	6.50	179		
Ring joint	Iron or soft steel	5.50	124		
	Monel or 4 to 6 per cent chrome	6.00	150		6
	Stainless steels	6.50	179		

A great variety of proprietary gasket materials is used, and reference should be made to the manufacturers' catalogues and technical manuals when selecting gaskets for a particular application. Design data for some of the more commonly used gasket materials are given in Table 13.4. Further data can be found in the pressure vessel codes and standards and in various handbooks; Perry *et al.* (1997). The minimum seating stress y is the force per unit area (pressure) on the gasket that is required to cause the material to flow and fill the surface irregularities in the gasket face.

The gasket factor m is the ratio of the gasket stress (pressure) under the operating conditions to the internal pressure in the vessel or pipe. The internal pressure will force the flanges' faces apart, so the pressure on the gasket under operating conditions will be lower than the initial tightening-up pressure. The gasket factor gives the minimum pressure that must be maintained on the gasket to ensure a satisfactory seal.

The following factors must be considered when selecting a gasket material:

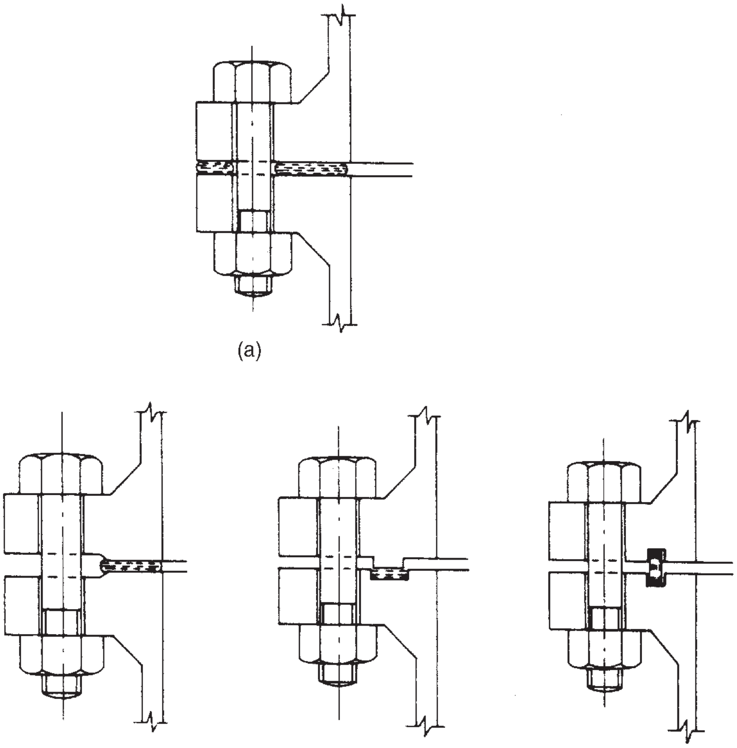
1. The process conditions: pressure, temperature, corrosive nature of the process fluid.
2. Whether repeated assembly and disassembly of the joint is required.
3. The type of flange and flange face (see Section 13.10.3).

Up to pressures of 20 bar, the operating temperature and corrosiveness of the process fluid will be the controlling factor in gasket selection. Vegetable fibre and synthetic rubber gaskets can be used at temperatures of up to 100°C. Solid polyfluorocarbon (Teflon) and compressed asbestos gaskets can be used to a maximum temperature of about 260°C. Metal-reinforced gaskets can be used up to around 450°C. Plain soft metal gaskets are normally used for higher temperatures.

13.10.3. Flange faces

Flanges are also classified according to the type of flange face used. There are two basic types:

1. Full-faced flanges, Figure 13.34*a*: where the face contact area extends outside the circle of bolts; over the full face of the flange.


(a)

(b) (c) (d)

Figure 13.34. Flange types and faces (*a*) Full-face (*b*) Gasket within bolt circle (*c*) Spigot and socket (*d*) Ring type joint

2. Narrow-faced flanges, Figure 13.34*b*, *c*, *d*: where the face contact area is located within the circle of bolts.

Full face, wide-faced, flanges are simple and inexpensive, but are only suitable for low pressures. The gasket area is large, and an excessively high bolt tension would be needed to achieve sufficient gasket pressure to maintain a good seal at high operating pressures.

The raised face, narrow-faced, flange shown in Figure 13.34*b* is probably the most commonly used type of flange for process equipment.

Where the flange has a plain face, as in Figure 13.34*b*, the gasket is held in place by friction between the gasket and flange surface. In the spigot and socket, and tongue and grooved faces, Figure 13.34*c*, the gasket is confined in a groove, which prevents failure by "blow-out". Matched pairs of flanges are required, which increases the cost, but this type is suitable for high pressure and high vacuum service. Ring joint flanges, Figure 13.34*d*, are used for high temperatures and high pressure services.

13.10.4. Flange design

Standard flanges will be specified for most applications (see Section 13.10.5). Special designs would be used only if no suitable standard flange were available; or for large flanges, such as the body flanges of vessels, where it may be cheaper to size a flange specifically for the duty required rather than to accept the nearest standard flange, which of necessity would be over-sized.

Figure 13.35 shows the forces acting on a flanged joint. The bolts hold the faces together, resisting the forces due to the internal pressure and the gasket sealing pressure. As these forces are offset the flange is subjected to a bending moment. It can be considered as a cantilever beam with a concentrated load. A flange assembly must be sized so as to have sufficient strength and rigidity to resist this bending moment. A flange that lacks sufficient rigidity will rotate slightly, and the joint will leak; Figure 13.36. The principles of flange design are discussed by Singh and Soler (1992), and Azbel and Cheremisinoff (1982). Singh and Soler give a computer programme for flange design.

Design procedures and work sheets for non-standard flanges are given in the national codes and standards.

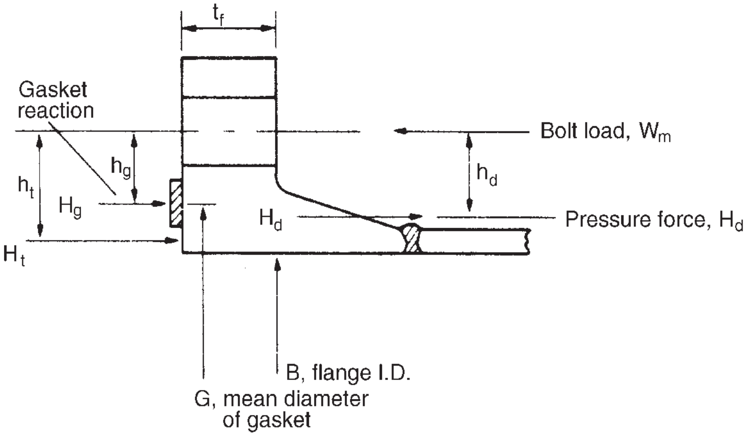


Figure 13.35. Forces acting on an integral flange

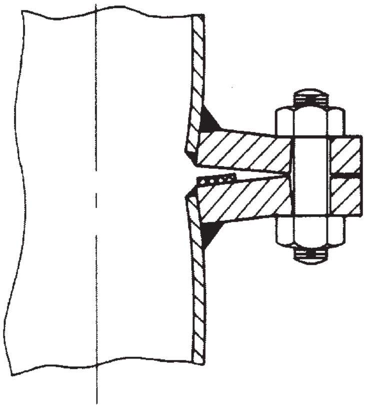


Figure 13.36. Deflection of a weak flange (exaggerated)

For design purposes, flanges are classified as integral or loose flanges.

Integral flanges are those in which the construction is such that the flange obtains support from its hub and the connecting nozzle (or pipe). The flange assembly and nozzle neck form an "integral" structure. A welding-neck flange would be classified as an integral flange.

Loose flanges are attached to the nozzle (or pipe) in such a way that they obtain no significant support from the nozzle neck and cannot be classified as an integral attachment. Screwed and lap-joint flanges are typical examples of loose flanges.

The design procedures given in the codes and standards can be illustrated by considering the forces and moments which act on an integral flange, Figure 13.35.

The total moment M_{op} acting on the flange is given by:

$$M_{op} = H_d h_d + H_t h_t + H_g h_g \tag{13.98}$$

Where H_g = gasket reaction (pressure force), = $\pi G(2b)mP_i$
H_t = pressure force on the flange face = $H - H_d$,
H = total pressure force = $(\pi/4)G^2P_i$,
H_d = pressure force on the area inside the flange = $(\pi/4)B^2P_i$,
G = mean diameter of the gasket,
B = inside diameter of the flange,
$2b$ = effective gasket pressure width,
b = effective gasket sealing width,
h_d, h_g and h_t are defined in Figure 13.35.

The minimum required bolt load under the operating conditions is given by:

$$W_{m1} = H + H_g \tag{13.99}$$

The forces and moments on the flange must also be checked under the bolting-up conditions.

The moment M_{atm} is given by:

$$M_{atm} = W_{m2} h_g \tag{13.100}$$

where W_{m2} is the bolt load required to seat the gasket, given by:

$$W_{m2} = y\pi G b \tag{13.101}$$

where y is the gasket seating pressure (stress).

The flange stresses are given by:

longitudinal hub stress, $$\sigma_{hb} = F_1 M \tag{13.102}$$

radial flange stress, $$\sigma_{rd} = F_2 M \tag{13.103}$$

tangential flange stress, $$\sigma_{tg} = F_3 M - F_4 \sigma_{rd} \tag{13.104}$$

where M is taken as M_{op} or M_{atm}, whichever is the greater; and the factors F_1 to F_4 are functions of the flange type and dimensions, and are obtained from equations and graphs given in the codes and standards (BS 5500, clause 3.8).

The flange must be sized so that the stresses given by equations 13.102 to 13.104 satisfy the following criteria:

$$\sigma_{hb} \not> 1.5 f_{f0} \tag{13.105}$$

$$\sigma_{rd} \not> f_{f0} \tag{13.106}$$

$$\tfrac{1}{2}(\sigma_{hb} + \sigma_{rd}) \not> f_{f0} \tag{13.107}$$

$$\tfrac{1}{2}(\sigma_{hb} + \sigma_{tg}) \not> f_{f0} \tag{13.108}$$

where f_{f0} is the maximum allowable design stress for the flange material at the operating conditions.

The minimum bolt area required A_{bf} will be given by:

$$A_{bf} = \frac{W_m}{f_b} \tag{13.109}$$

where W_m is the greater value of W_{m1} or W_{m2}, and f_b the maximum allowable bolt stress. Standard size bolts should be chosen, sufficient to give the required area. The bolt size will not normally be less than 12 mm, as smaller sizes can be sheared off by over-tightening.

The bolt spacing must be selected to give a uniform compression of the gasket. It will not normally be less than 2.5 times the bolt diameter, to give sufficient clearance for tightening with a wrench or spanner. The following formula can be used to determine the maximum bolt spacing:

$$p_b = 2d_b + \frac{6t_f}{(m + 0.5)} \tag{13.110}$$

where p_b = bolt pitch (spacing), mm,
d_b = bolt diameter, mm,
t_f = flange thickness, mm,
m = gasket factor.

13.10.5. Standard flanges

Standard flanges are available in a range of types, sizes and materials; and are used extensively for pipes, nozzles and other attachments to pressure vessels.

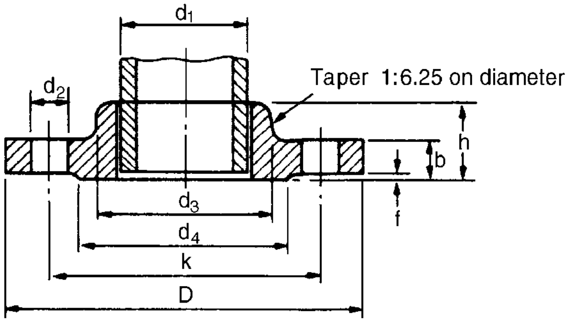
The proportions of standard flanges are set out in various codes and standards. A typical example of a standard flange design is shown in Figure 13.37. This was taken from BS 4504, which has now been superseded by the European standard BS EN 1092. The design of standard flanges is also specified in BS 1560.

In the United States, flanges are covered by the standards issued by the American National Standards Institute (ANSI). An abstract of the American standards is given by Perry *et al.* (1997).

Standard flanges are designated by class numbers, or rating numbers, which correspond to the primary service (pressure) rating of the flange at room temperature.

STEEL SLIP-ON BOSS FLANGE FOR WELDING

Nominal pressure 6 bar



Nom. size	Pipe o.d. d_1	Flange			Raised face		Bolting	Drilling			Boss
	$\approx$	D	b	h	d_4	f		No.	d_2	k	d_3
10	17.2	75	12	20	35	2	M10	4	11	50	25
15	21.3	80	12	20	40	2	M10	4	11	55	30
20	26.9	90	14	24	50	2	M10	4	11	65	40
25	33.7	100	14	24	60	2	M10	4	11	75	50
32	42.4	120	14	26	70	2	M12	4	14	90	60
40	48.3	130	14	26	80	3	M12	4	14	100	70
50	60.3	140	14	28	90	3	M12	4	14	110	80
65	76.1	160	14	32	110	3	M12	4	14	130	100
80	88.9	190	16	34	128	3	M16	4	18	150	110
100	114.3	210	16	40	148	3	M16	4	18	170	130
125	139.7	240	18	44	178	3	M16	8	18	200	160
150	168.3	265	18	44	202	3	M16	8	18	225	185
200	219.1	320	20	44	258	3	M16	8	18	280	240
250	273	375	22	44	312	3	M16	12	18	335	295
300	323.9	440	22	44	365	4	M20	12	22	395	355

Figure 13.37. Typical standard flange design (All dimensions mm)

The flange class number required for a particular application will depend on the design pressure and temperature, and the material of construction. The reduction in strength at elevated temperatures is allowed for by selecting a flange with a higher rating than the design pressure. For example, for a design pressure of 10 bar (150 psi) a BS 1560 carbon steel flange class 150 flange would be selected for a service temperature below 300°C; whereas for a service temperature of, say, 300°C a 300 pound flange would be specified. A typical pressure–temperature relationship for carbon steel flanges is shown in Table 13.5. Pressure–temperature ratings for a full range of materials can be obtained from the standards.

Typical designs, dimensioned, for welding-neck flanges over a range of pressure ratings are given in Appendix E. These can be used for preliminary designs. The current standards and suppliers' catalogues should be consulted before firming up the design.

Table 13.5. Typical pressure-temperature ratings for carbon steel flanges, BS 4504.

Nominal pressure (bar)	Design pressure at temperature, °C (bar)						
	up to 120	150	200	250	300	350	400
2.5	2.5	2.3	2.0	1.8	1.5	1.3	0.9
6	6.0	5.4	4.8	4.2	3.6	3.0	2.1
10	10	9.0	8.0	7.0	6.0	5.0	3.5
16	16	14.4	12.8	11.2	9.6	8.0	5.6
25	25	2.5	20.0	17.5	15.0	12.5	8.8
40	40	36.0	32.0	28.0	24.0	20.0	14.0

13.11. HEAT-EXCHANGER TUBE-PLATES

The tube-plates (tube-sheets) in shell and tube heat exchangers support the tubes, and separate the shell and tube side fluids (see Chapter 12). One side is subject to the shell-side pressure and the other the tube-side pressure. The plates must be designed to support the maximum differential pressure that is likely to occur. Radial and tangential bending stresses will be induced in the plate by the pressure load and, for fixed-head exchangers, by the load due to the differential expansion of the shell and tubes.

A tube-plate is essentially a perforated plate with an unperforated rim, supported at its periphery. The tube holes weaken the plate and reduce its flexual rigidity. The equations developed for the stress analysis of unperforated plates (Section 13.3.5) can be used for perforated plates by substituting "virtual" (effective) values for the elastic constants E and v, in place of the normal values for the plate material. The virtual elastic constants E' and v' are functions of the plate ligament efficiency, Figure 13.38; see O'Donnell and Langer (1962). The ligament efficiency of a perforated plate is defined as:

$$\lambda = \frac{p_h - d_h}{p_h} \tag{13.111}$$

where p_h = hole pitch,
d_h = hole diameter.

The "ligament" is the material between the holes (that which holds the holes together). In a tube-plate the presence of the tubes strengthens the plate, and this is taken into account when calculating the ligament efficiency by using the inside diameter of the tubes in place of the hole diameter in equation 13.111.

Design procedures for tube-plates are given in BS PD 5500, and in the TEMA heat exchanger standards (see Chapter 12). The tube-plate must be thick enough to resist the bending and shear stresses caused by the pressure load and any differential expansion of the shell and tubes. The minimum plate thickness to resist bending can be estimated using an equation of similar form to that for plate end closures (Section 13.5.3).

$$t_p = C_{ph} D_p \sqrt{\frac{\Delta P'}{\lambda f_p}} \tag{13.112}$$

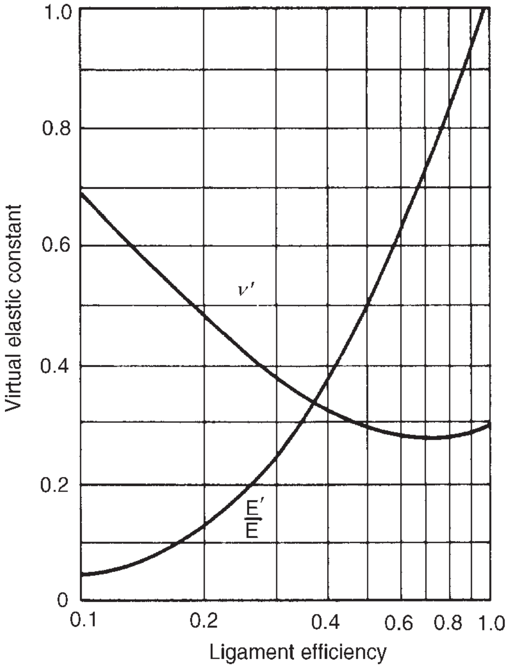


Figure 13.38. Virtual elastic constants

where t_p = the minimum plate thickness,
$\Delta P'$ = the effective tube plate design pressure,
λ = ligament efficiency,
f_p = maximum allowable design stress for the plate,
C_{ph} = a design factor,
D_p = plate diameter.

The value of the design factor C_{ph} will depend on the type of head, the edge support (clamped or simply supported), the plate dimensions, and the elastic constants for the plate and tube material.

The tube-sheet design pressure $\Delta P'$ depends on the type of exchanger. For an exchanger with confined heads or U-tubes it is taken as the maximum difference between the shell-side and tube-side operating pressures; with due consideration being given to the possible loss of pressure on either side. For exchangers with unconfined heads (plates fixed to the shell) the load on the tube-sheets due to differential expansion of the shell and tubes must be added to that due to the differential pressure.

The shear stress in the tube-plate can be calculated by equating the pressure force on the plate to the shear force in the material at the plate periphery. The minimum plate thickness to resist shear is given by:

$$t_p = \frac{0.155 D_p \Delta P'}{\lambda \tau_p} \tag{13.113}$$

where $\tau_p =$ the maximum allowable shear stress, taken as half the maximum allowable design stress for the material (see Section 13.3.2).

The design plate thickness is taken as the greater of the values obtained from equations 13.112 and 13.113 and must be greater than the minimum thickness given below:

Tube o.d. (mm)	Minimum plate thickness (mm)
25	0.75 × tube o.d.
25–30	22
30–40	25
40–50	30

For exchangers with fixed tube-plates the longitudinal stresses in the tubes and shell must be checked to ensure that the maximum allowable design stresses for the materials are not exceeded. Methods for calculating these stresses are given in the standards.

A detailed account of the methods used for the stresses analysis of tube sheets is given by Jawad and Farr (1989), and Singh and Soler (1992). Singh and Soler give computer programs for the design of the principal types of tube-plate.

13.12. WELDED JOINT DESIGN

Process vessels are built up from preformed parts: cylinders, heads, and fittings, joined by fusion welding. Riveted construction was used extensively in the past (prior to the 1940s) but is now rarely seen.

Cylindrical sections are usually made up from plate sections rolled to the required curvature. The sections (strakes) are made as large as is practicable to reduce the number of welds required. The longitudinal welded seams are offset to avoid a conjunction of welds at the corners of the plates.

Many different forms of welded joint are needed in the construction of a pressure vessel. Some typical forms are shown in Figures 13.39 to 13.41.

The design of a welded joint should satisfy the following basic requirements:

1. Give good accessibility for welding and inspection.
2. Require the minimum amount of weld metal.
3. Give good penetration of the weld metal; from both sides of the joint, if practicable.
4. Incorporate sufficient flexibility to avoid cracking due to differential thermal expansion.

The preferred types of joint, and recommended designs and profiles, are given in the codes and standards.

The correct form to use for a given joint will depend on the material, the method of welding (machine or hand), the plate thickness, and the service conditions. Double-sided V- or U-sections are used for thick plates, and single V- or U-profiles for thin plates. A backing strip is used where it is not possible to weld from both sides. Lap joints are seldom used for pressure vessels construction, but are used for atmospheric pressure storage tanks.

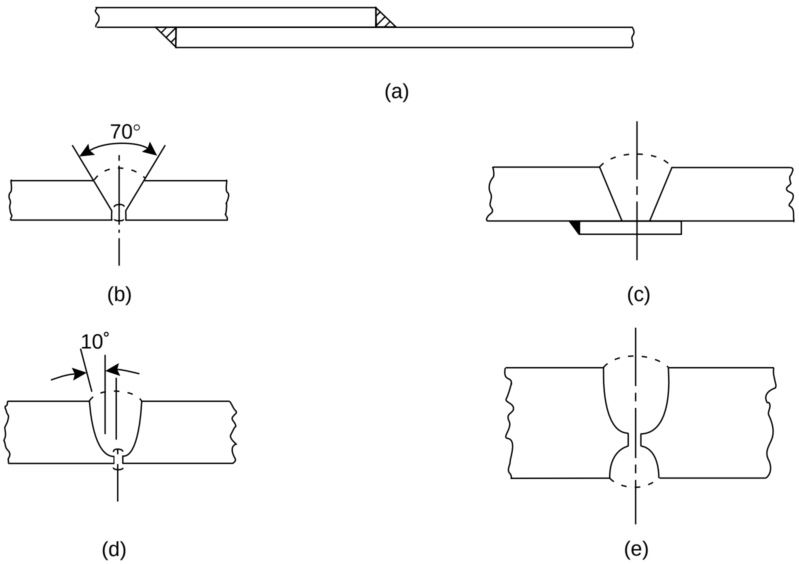


Figure 13.39. Weld profiles; (*b* to *e*) butt welds (*a*) Lap joint (*b*) Single ‘V’ (*c*) Backing strip (*d*) Single ‘U’ (*e*) Double ‘U’

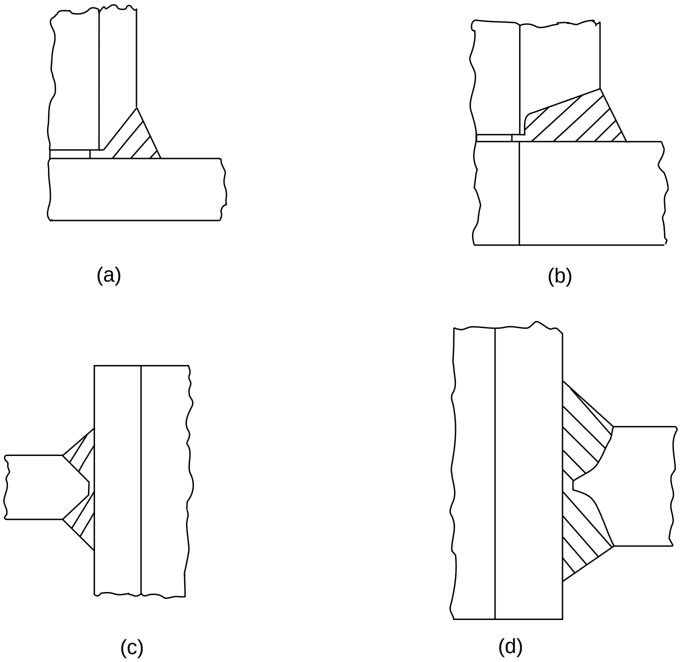


Figure 13.40. Typical weld profiles — Branches (*a*), (*b*) Set-on branches (*c*), (*d*) Set-in branches

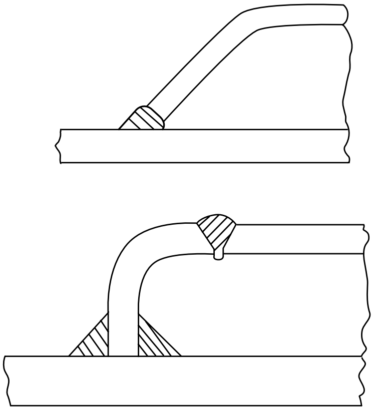


Figure 13.41. Typical construction methods for welded jackets

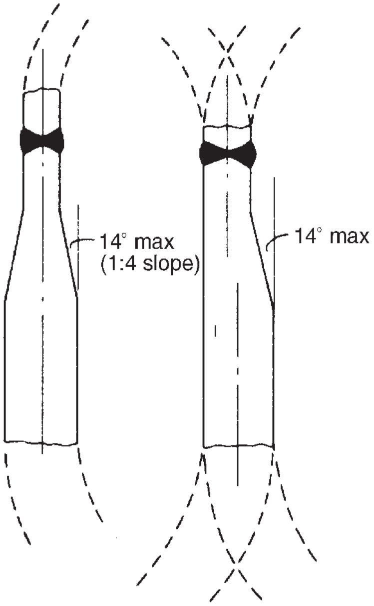


Figure 13.42. Transition between plates of unequal thickness

Where butt joints are made between plates of different thickness, the thicker plate is reduced in thickness with a slope of not greater than 1 in 4 (14°) (Figure 13.42).

The local heating, and consequent expansion, that occurs during welding can leave the joint in a state of stress. These stresses are relieved by post-welding heat treatment. Not all vessels will be stress relieved. Guidance on the need for post-welding heat treatment is given in the codes and standards, and will depend on the service and conditions, materials of construction, and plate thickness.

To ensure that a satisfactory quality of welding is maintained, welding-machine operators and welders working on the pressure parts of vessels are required to pass welder approval tests; which are designed to test their competence to make sound welds.

13.13. FATIGUE ASSESSMENT OF VESSELS

During operation the shell, or components of the vessel, may be subjected to cyclic stresses. Stress cycling can arise from the following causes:

1. Periodic fluctuations in operating pressure.
2. Temperature cycling.
3. Vibration.
4. "Water hammer".
5. Periodic fluctuation of external loads.

A detailed fatigue analysis is required if any of these conditions is likely to occur to any significant extent. Fatigue failure will occur during the service life of the vessel if the endurance limit (number of cycles for failure) at the particular value of the cyclic stress is exceeded. The codes and standards should be consulted to determine when a detailed fatigue analysis must be undertaken.

13.14. PRESSURE TESTS

The national pressure vessel codes and standards require that all pressure vessels be subjected to a pressure test to prove the integrity of the finished vessel. A hydraulic test is normally carried out, but a pneumatic test can be substituted under circumstances where the use of a liquid for testing is not practical. Hydraulic tests are safer because only a small amount of energy is stored in the compressed liquid. A standard pressure test is used when the required thickness of the vessel parts can be calculated in accordance with the particular code or standard. The vessel is tested at a pressure above the design pressure, typically 25 to 30 per cent. The test pressure is adjusted to allow for the difference in strength of the vessel material at the test temperature compared with the design temperature, and for any corrosion allowance.

Formulae for determining the appropriate test pressure are given in the codes and standards; such as that given below:

$$\text{Test pressure} = 1.25\left[P_d \frac{f_a}{f_n} \times \frac{t}{(t-c)}\right] \tag{13.114}$$

where P_d = design pressure, N/mm^2,
f_a = nominal design strength (design stress) at the test temperature, N/mm^2,
f_n = nominal design strength at the design temperature, N/mm^2,
c = corrosion allowance, mm,
t = actual plate thickness, mm.

When the required thickness of the vessel component parts cannot be determined by calculation in accordance with the methods given, the codes and standards require that a hydraulic proof test be carried out. In a proof test the stresses induced in the vessel during the test are monitored using strain gauges, or similar techniques. The requirements for the proof testing of vessels are set out in the codes and standards.

13.15. HIGH-PRESSURE VESSELS

High pressures are required for many commercial chemical processes. For example, the synthesis of ammonia is carried out at reactor pressures of up to 1000 bar, and high-density polyethylene processes operate up to 1500 bar.

Only a brief discussion of the design of vessels for operation at high pressures will be given in this section; sufficient to show the fundamental limitations of single-wall (monobloc) vessels, and the construction techniques that are used to overcome this limitation. A full discussion of the design and construction of high-pressure vessels and ancillary equipment (pumps, compressors, valves and fittings) is given in the books by Fryer and Harvey (1997) and Jawad and Farr (1989); see also the relevant ASME code, ASME (2004).

13.15.1. Fundamental equations

Thick walls are required to contain high pressures, and the assumptions made in the earlier sections of this chapter to develop the design equations for "thin-walled" vessels will not be valid. The radial stress will not be negligible and the tangential (hoop) stress will vary across the wall.

Consider the forces acting on the elemental section of the wall of the cylinder shown in Figure 13.43. The cylinder is under an internal pressure P_i and an external pressure P_e. The conditions for static equilibrium, with the forces resolved radially, give:

$$\sigma_r r\delta\phi - 2\sigma_t \delta r \sin\frac{\delta\phi}{2} - (\sigma_r + \delta\sigma_r)(r + \delta r)\delta\phi = 0$$

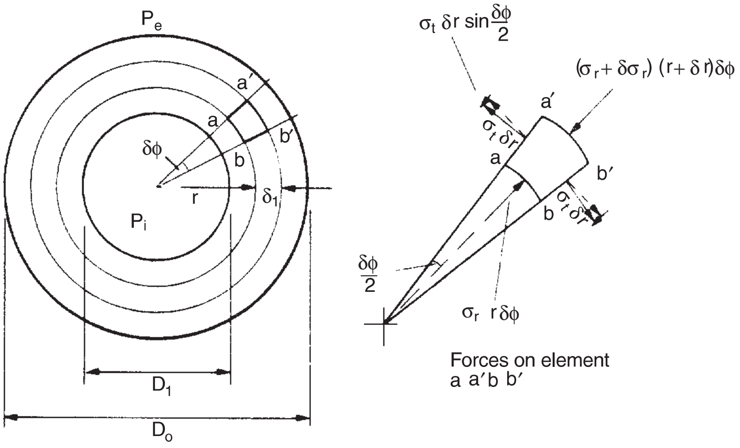


Figure 13.43. Thick cylinder

multiplying out taking the limit gives:

$$\sigma_t + r\frac{d\sigma_r}{dr} + \sigma_r = 0 \tag{13.115}$$

A second equation relating the radial and tangential stresses can be written if the longitudinal strain ε_L and stress σ_L are taken to be constant across the wall; that is, that there is no distortion of plane sections, which will be true for sections away from the ends. The longitudinal strain is given by:

$$\varepsilon_L = \frac{1}{E}[\sigma_L - (\sigma_t - \sigma_r)v] \tag{13.116}$$

If ε_L and σ_L are constant, then the term $(\sigma_t - \sigma_r)$ must also be constant, and can be written as:

$$(\sigma_t - \sigma_r) = 2A \tag{13.117}$$

where A is an arbitrary constant.

Substituting for σ_t in equation 13.115 gives:

$$2\sigma_r + r\frac{\mathrm{d}\sigma_r}{\mathrm{d}r} = -2A$$

and integrating

$$\sigma_r = -A + \frac{B'}{r^2} \tag{13.118}$$

where B' is the constant of integration.

In terms of the cylinder diameter, the equations can be written as:

$$\sigma_r = -A + \frac{B}{d^2} \tag{13.119}$$

$$\sigma_t = A + \frac{B}{d^2} \tag{13.120}$$

These are the fundamental equations for the design of thick cylinders and are often referred to as Lamé's equations, as they were first derived by Lamé and Clapeyron (1833). The constants A and B are determined from the boundary conditions for the particular loading condition.

Most high-pressure process vessels will be under internal pressure only, the atmospheric pressure outside a vessel will be negligible compared with the internal pressure. The boundary conditions for this loading condition will be:

$$\sigma_r = P_i \text{ at } d = D_i$$

$$\sigma_r = 0 \text{ at } d = D_o$$

Substituting these values in equation 13.119 gives

$$P_i = -A + \frac{B}{D_i^2}$$

and
$$0 = -A + \frac{B}{D_o^2}$$

subtracting gives
$$P_i = B\left[\frac{1}{D_i^2} - \frac{1}{D_o^2}\right]$$

hence
$$B = P_i \frac{(D_i^2 D_o^2)}{(D_o^2 - D_i^2)}$$

and
$$A = P_i \frac{D_i^2}{(D_o^2 - D_i^2)}$$

Substituting in equations 13.119 and 13.120 gives:

$$\sigma_r = P_i\left[\frac{D_i^2(D_o^2 - d^2)}{d^2(D_o^2 - D_i^2)}\right] \tag{13.121}$$

$$\sigma_t = P_i\left[\frac{D_i^2(D_o^2 + d^2)}{d^2(D_o^2 - D_i^2)}\right] \tag{13.122}$$

The stress distribution across the vessel wall is shown plotted in Figure 13.44. The maximum values will occur at the inside surface, at $d = D_i$.

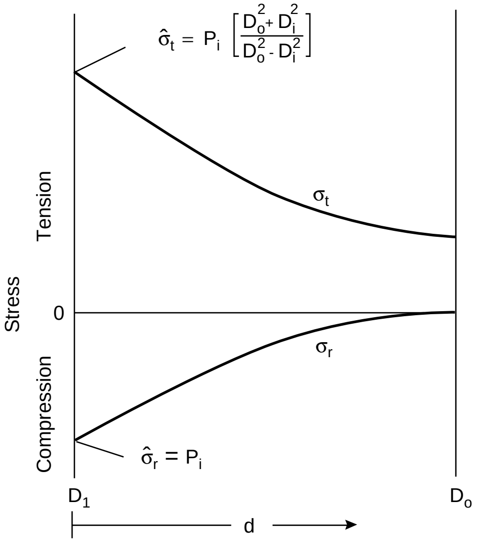


Figure 13.44. Stress distribution in wall of a monobloc cylinder

Putting $K = D_o/D_i$, the maximum values are given by:

$$\hat{\sigma}_r = P_i \text{ (compressive)} \tag{13.123}$$

$$\hat{\sigma}_t = P_i \left[\frac{K^2 + 1}{K^2 - 1}\right] \tag{13.124}$$

An expression for the longitudinal stress can be obtained by equating forces in the axial direction:

$$\sigma_L \frac{\pi}{4}(D_o^2 - D_i^2) = P_i \frac{\pi D_i^2}{4}$$

hence
$$\sigma_L = \frac{P_i D_i^2}{(D_o^2 - D_i^2)} = \frac{P_i}{(K^2 - 1)} \tag{13.125}$$

The maximum shear stress will be given by (see Section 13.3.1):

$$\hat{\tau} = \tfrac{1}{2}(\hat{\sigma}_t + \hat{\sigma}_r) = \frac{P_i K^2}{(K^2 - 1)} \tag{13.126}$$

Theoretical maximum pressure

If the maximum shear stress theory is taken as the criterion of failure (Section 13.3.2), then the maximum pressure that a monobloc vessel can be designed to withstand without failure is given by:

$$\hat{\tau} = \frac{\sigma'_e}{2} = \frac{P_i K^2}{(K^2 - 1)}$$

hence
$$\hat{P}_i = \frac{\sigma'_e}{2}\left[\frac{K^2 - 1}{K^2}\right] \tag{13.127}$$

where σ'_e is the elastic limit stress for the material of construction divided by a suitable factor of safety. As the wall thickness is increased the term $(K^2 - 1)/K^2$ tends to 1,

and
$$\hat{P}_i = \frac{\sigma'_e}{2} \tag{13.128}$$

which sets an upper limit on the pressure that can be contained in a monobloc cylinder.

Manning (1947) has shown that the maximum shear strain energy theory of failure (due to Mises (1913)) gives a closer fit to experimentally determined failure pressures for monobloc cylinders than the maximum shear stress theory. This criterion of failure gives:

$$\hat{P}_i = \frac{\sigma'_e}{\sqrt{3}} \tag{13.129}$$

From Figure (13.44) it can be seen that the stress falls off rapidly across the wall and that the material in the outer part of the wall is not being used effectively. The material can be used more efficiently by prestressing the wall. This will give a more uniform stress distribution under pressure. Several different “prestressing” techniques are used; the principal methods are described briefly in the following sections.

13.15.2. Compound vessels

Shrink-fitted cylinders

Compound vessels are made by shrinking one cylinder over another. The inside diameter of the outer cylinder is made slightly smaller than the outer diameter of the inner cylinder, and is expanded by heating to fit over the inner. On cooling the outer cylinder contracts and places the inner under compression. The stress distribution in a two-cylinder compound vessel is shown in Figure 13.45; more than two cylinders may be used.

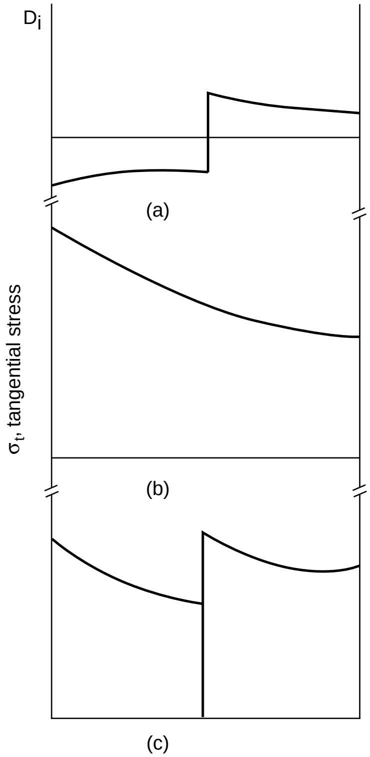


Figure 13.45. Stress distribution in a shrink-fitted compound cylinder (*a*) Due to shrinkage (*b*) Due to pressure (*c*) Combined ($a + b$)

Shrink-fitted compound cylinders are used for small-diameter vessels, such as compressor cylinder barrels. The design of shrink-fitted compound cylinders is discussed by Manning (1947) and Jawad and Farr (1989).

Multilayer vessels

Multilayer vessels are made by wrapping several layers of relatively thin plate round a central tube. The plates are heated, tightened and welded, and this gives the desired stress distribution in the compound wall. The vessel is closed with forged heads. A typical

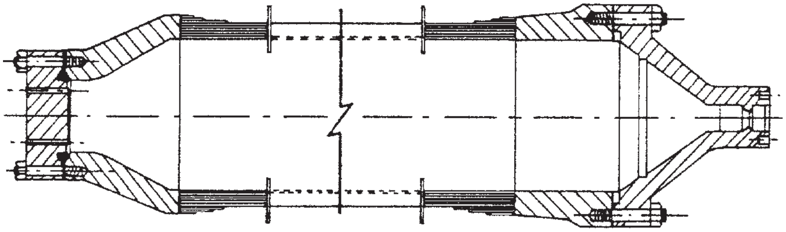


Figure 13.46. Multilayer construction

design is shown in Figure 13.46. This construction technique is discussed by Jasper and Scudder (1941) and Jawad and Farr (1989).

Wound vessels

Cylindrical vessels can be reinforced by winding on wire or thin ribbons. Winding on the wire under tension places the cylinder under compression. For high-pressure vessels special interlocking strips are used, such as those shown in Figure 13.47. The interlocking gives strength in the longitudinal direction and a more uniform stress distribution. The strips may be wound on hot to increase the prestressing. This type of construction is described by Birchall and Lake (1947). Wire winding was used extensively for the barrels of large guns.

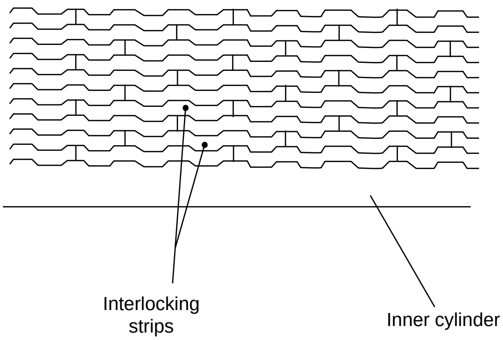


Figure 13.47. Strip wound vessel

13.15.3. Autofrettage

Autofrettage is a technique used to prestress the inner part of the wall of a monobloc vessel, to give a similar stress distribution to that obtained in a shrink-fitted compound cylinder. The finished vessel is deliberately over pressurised by hydraulic pressure. During this process the inner part of the wall will be more highly stressed than the outer part and will undergo plastic strain. On release of the “autofrettage” pressure the inner part, which is now over-size, will be placed under compression by the elastic contraction of the outer part, which gives a residual stress distribution similar to that obtained in a two-layer shrink-fitted compound cylinder. After straining the vessel is annealed at a relatively low temperature, approximately 300°C. The straining also work-hardens the inner part of the wall. The vessel can be used at pressures up to the "autofrettage" pressure without further permanent distortion.

The autofrettage technique is discussed by Manning (1950) and Jawad and Farr (1989).

13.16. LIQUID STORAGE TANKS

Vertical cylindrical tanks, with flat bases and conical roofs, are universally used for the bulk storage of liquids at atmospheric pressure. Tank sizes vary from a few hundred gallons (tens of cubic metres) to several thousand gallons (several hundred cubic metres).

The main load to be considered in the design of these tanks is the hydrostatic pressure of the liquid, but the tanks must also be designed to withstand wind loading and, for some locations, the weight of snow on the tank roof.

The minimum wall thickness required to resist the hydrostatic pressure can be calculated from the equations for the membrane stresses in thin cylinders (Section 13.3.4):

$$e_s = \frac{\rho_L H_L g}{2 f_t J} \frac{D_t}{10^3} \qquad (13.130)$$

where e_s = tank thickness required at depth H_L, mm,
H_L = liquid depth, m,
ρ_L = liquid density, kg/m^3,
J = joint factor (if applicable),
g = gravitational acceleration, 9.81 m/s^2,
f_t = design stress for tank material, N/mm^2,
D_t = tank diameter, m.

The liquid density should be taken as that of water (1000 kg/m^3), unless the process liquid has a greater density.

For small tanks a constant wall thickness would normally be used, calculated at the maximum liquid depth.

With large tanks, it is economical to take account of the variation in hydrostatic pressure with depth, by increasing the plate thickness progressively from the top to bottom of the tank. Plate widths of 2 m (6 ft) are typically used in tank construction.

The roofs of large tanks need to be supported by a steel framework; supported on columns in very large-diameter tanks.

The design and construction of atmospheric storage tanks for the petroleum industry are covered by British Standard BS 2654, and the American Petroleum Industry standards API 650 (2003) and 620 (2002). The design of storage tanks is covered in the books by Myers (1997), and Jawad and Farr (1989). See also the papers by Debham *et al.* (1968) and Zick and McGarth (1968).

13.17. MECHANICAL DESIGN OF CENTRIFUGES

13.17.1. Centrifugal pressure

The fluid in a rotating centrifuge exerts pressure on the walls of the bowl or basket. The minimum wall thickness required to contain this pressure load can be determined in a similar manner to that used for determining the wall thickness of a pressure vessel under internal pressure. If the bowl contains a single homogeneous liquid, Figure 13.48*a*, the fluid pressure is given by:

$$P_f = \tfrac{1}{2}\rho_L\omega^2(R_1^2 - R_2^2) \tag{13.131}$$

where P_f = centrifugal pressure, N/m^2,
ρ_L = liquid density, kg/m^3,
ω = rotational speed of the centrifuge, radians/s,
R_1 = inside radius of the bowl, m,
R_2 = radius of the liquid surface, m.

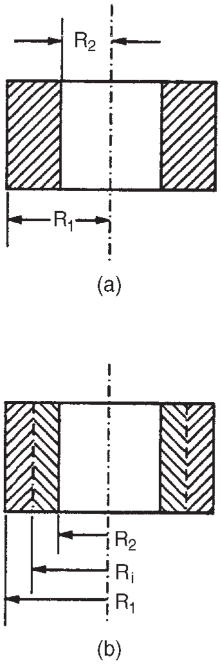


Figure 13.48. Centrifugal fluid pressure (*a*) Single fluid (*b*) Two fluids

For design, the maximum fluid pressure will occur when the bowl is full, $R_2 = 0$.

If the centrifuge is separating two immiscible liquids, Figure 13.48*b*, the pressure will be given by:

$$P_f = \tfrac{1}{2}\omega^2[\rho_{L1}(R_1^2 - R_i^2) + \rho_{L2}(R_i^2 - R_2^2)] \tag{13.132}$$

where ρ_{L1} = density of the heavier liquid, kg/m^3,
ρ_{L2} = density of the lighter liquid, kg/m^3,
R_i = radius of the interface between the two liquids, m.

If the machine is separating a solid-liquid mixture, the mean density of the slurry in the bowl should be used in equation 13.131.

The shell of an empty centrifuge bowl will be under stress due to the rotation of the bowl's own mass; this "self-pressure" P_m is given by:

$$P_m = \tfrac{1}{2}\omega^2\rho_m[(R_1 + t)^2 - R_1^2] \tag{13.133}$$

where ρ_m = density of the bowl material, kg/m^3,
t = bowl wall thickness, m.

The minimum wall thickness required can be estimated using the equations for membrane stress derived in Section 13.3.4. For a solid bowl

$$e_c = \frac{P_t R_1}{f_m \times 10^3} \tag{13.134}$$

where P_t = the total (maximum) pressure (fluid + self-pressure), N/m^2,
f_m = maximum allowable design stress for the bowl material, N/mm^2,
e_c = wall thickness, mm.

With a perforated basket the presence of the holes will weaken the wall. This can be allowed for by introducing a "ligament efficiency" into equation 13.134 (see Section 13.11)

$$e_c = \frac{P_t R_1}{f_m \times 10^3 \lambda} \tag{13.135}$$

where λ = ligament efficiency = $(p_h - d_h)/(p_h)$,
p_h = hole pitch,
d_h = hole diameter.

Equations 13.134 and 13.135 can also be used to estimate the maximum safe load (or speed) for an existing centrifuge, if the service is to be changed.

In deriving these equations no account was taken of the strengthening effect of the bottom and top rings of the bowl or basket; so the equations will give estimates that are on the safe side. Strengthening hoops or bands are used on some basket designs.

13.17.2. Bowl and spindle motion: critical speed

Centrifuges are classified according to the form of mounting used: fixed or free spindle. With fixed-spindle machines, the bearings are rigidly mounted; whereas, in a free spindle, or self-balancing, machine a degree of "free-play" is allowed in the spindle mounting. The amount of movement of the spindle is restrained by some device, such as a rubber buffer. This arrangement allows the centrifuge to operate with a certain amount of out-of-balance loading without imposing an undue load on the bearings. Self-balancing centrifuges can be under or over-driven; that is, with the drive mounted below or above the bowl. Severe vibration can occur in the operation of fixed-spindle centrifuges and these are often suspended on rods, supported from columns mounted on an independent base, to prevent the vibration being transmitted to the building structure.

Critical speed

If the centre of gravity of the rotating load does not coincide with the axis of rotation of the bowl an uneven force will be exerted on the machine spindle. In a self-balancing machine (or a suspended fixed-spindle machine) this will cause the spindle to deflect from the vertical position and the bowl will develop a whirling vibration. The phenomenon is analogous with the whirling of the shafts in other rotating machinery; such as compressors, pumps, and agitators; which is considered under the general heading of the "whirling of shafts" in standard texts on the "Theory of Machines".

The simple analysis given below is based on that used to determine the whirling speed of a shaft with a single concentrated mass. Figure 13.49 shows the position of the centre of gravity of a rotating mass m_c with an initial displacement h_c. Let x_c be the additional displacement caused by the action of centrifugal force, and s the restoring force, assumed to be proportional to the displacement. The radial outward centrifugal force due to the displacement of the centre of the gravity from the axis of rotation will be $= m_c\omega^2(x + h_c)$. This is balanced by the inward action of the restoring force $= sx_c$.

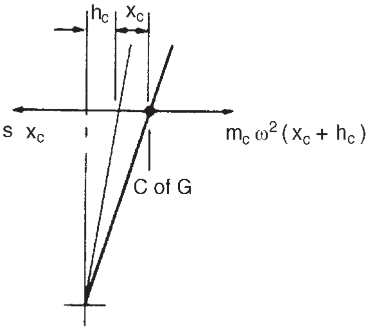


Figure 13.49. Displacement of centre of gravity of a centrifuge bowl

Equating the two forces:

$$m_c\omega^2(x_c + h_c) = sx_c$$

from which

$$\frac{x_c}{h_c} = \frac{1}{\left(\dfrac{s}{m_c\omega^2}\right) - 1} \tag{13.136}$$

It can be seen by inspection of equation 13.136 that the deflection (the ratio x_c/h_c) will become indefinitely large when the term $s/m_c\omega^2 = 1$; the corresponding value of ω is known as the critical, or whirling, speed. Above the critical speed the term $s/m_c\omega^2$ becomes negative, and x_c/h_c tends to a limiting value of -1 at high speeds. This shows that if the centrifuge is run at speeds in excess of the critical speed the tendency is for the spindle to deflect so that the axis of rotation passes through the centre of gravity of the system. The sequence of events as a self-balancing centrifuge run up to speed is shown in Figure 13.50. In practice, a centrifuge is accelerated rapidly to get through the critical speed range quickly, and the observed deflections are not great.

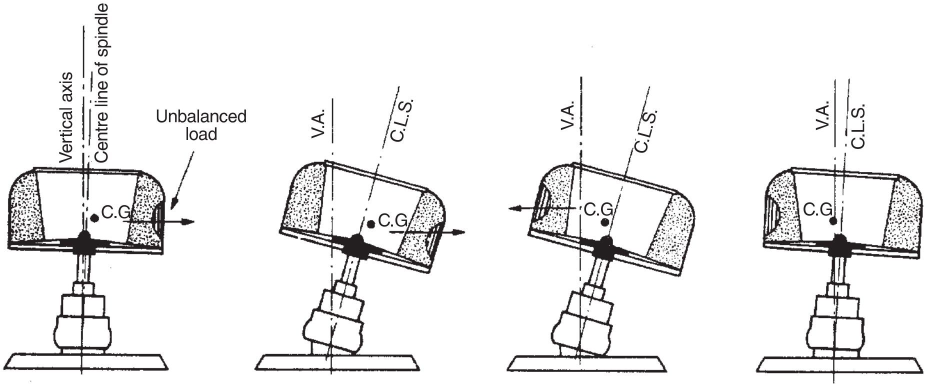
It can be seen from equation 13.136 that the critical speed of a centrifuge will depend on the mass of the bowl and the magnitude of the restoring force; it will also depend on the dimensions of the machine and the length of the spindle. The critical speed of a simple system can be calculated, but for a complex system, such as loaded centrifuges, the critical speed must be determined by experiment. It can be shown that the critical speed of a rotating system corresponds with the natural frequency of vibration of the system.

A low critical speed is desired, as less time is then spent accelerating the bowl through the critical range. Suspended fixed-spindle centrifuges generally have a low critical speed.

Precession

In addition to the whirling vibration due to an out-of-balance force, another type of motion can occur in a free-spindle machine. When the bowl or basket is tilted the spindle may move in a circle. This slow gyratory motion is known as "precession", and is similar to the "precession" of a gyroscope. It is usually most pronounced at high speeds, above the critical speed.

A complete analysis of the motion of centrifuges is given by Alliott (1924, 1926).



Just after starting unbalanced load pulls spindle out of centre

Just below critical speed unbalanced load tends to pull spindle very much out of centre

Just above critical speed deflection of spindle lags half a turn behind unbalanced load

At high speeds deflection decreases till centre of gravity comes into vertical axis

Figure 13.50. Diagram of action of self-balancing centrifuge, showing motion of centre of gravity and unbalanced load with increasing speed

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ASME Boiler and pressure vessel code (2204)

13.19. NOMENCLATURE

		Dimensions in **MLT**
A	Arbitrary constant in equation 13.117	$\mathbf{ML^{-1}T^{-2}}$
A_{bf}	Total bolt area required for a flange	$\mathbf{L}^2$
A_1	Area removed in forming hole	$\mathbf{L}^2$
A_2	Area of compensation	$\mathbf{L}^2$
a	Diameter of flat plate	$\mathbf{L}$
$2a$	Major axis of ellipse	$\mathbf{L}$
a_e	Acceleration due to an earthquake	$\mathbf{LT}^{-2}$

B	Inside diameter of flange	$\mathbf{L}$
B	Arbitrary constant in equation 13.120	$\mathbf{MLT}^{-2}$
B'	Constant of integration in equation 13.118	$\mathbf{MLT}^{-2}$
b	Effective sealing width of gasket	$\mathbf{L}$
$2b$	Minor axis of ellipse	$\mathbf{L}$
C	Constant in equation 13.34	—
C_c	Design factor in equation 13.46	—
C_d	Drag coefficient in equation 13.79	—
C_e	Seismic constant	—
C_h	Constant in equation 13.85	—
C_p	Constant in equation 13.34	—
C_{ph}	Design factor in equation 13.112	—
C_s	Design factor in equation 13.44	—
c	Corrosion allowance	$\mathbf{L}$
D	Diameter	$\mathbf{L}$
$\mathbf{D}$	Flexual rigidity	$\mathbf{ML}^{2}\mathbf{T}^{-2}$
D_b	Bolt circle diameter	$\mathbf{L}$
D_c	Diameter of cone at point of interest	$\mathbf{L}$
D_e	Nominal diameter of flat end	$\mathbf{L}$
D_{eff}	Effective diameter of column for wind loading	$\mathbf{L}$
D_i	Internal diameter	$\mathbf{L}$
D_m	Mean diameter	$\mathbf{L}$
D_o	Outside diameter	$\mathbf{L}$
D_p	Plate diameter, tube-sheet	$\mathbf{L}$
D_r	Diameter of stiffening ring	$\mathbf{L}$
D_s	Skirt internal diameter	$\mathbf{L}$
D_t	Tank diameter	$\mathbf{L}$
d	Diameter at point of interest, thick cylinder	$\mathbf{L}$
d_b	Bolt diameter	$\mathbf{L}$
d_h	Hole diameter	$\mathbf{L}$
d_r	Diameter of reinforcement pad	$\mathbf{L}$
E	Young’s modulus	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
e	Minimum plate thickness	$\mathbf{L}$
e_c	Minimum thickness of conical section	$\mathbf{L}$
e_k	Minimum thickness of conical transition section	$\mathbf{L}$
e_m	Minimum wall thickness, centrifuge	$\mathbf{L}$
e_s	Minimum thickness of tank	$\mathbf{L}$
F_b	Compressive load on base ring, per unit length	$\mathbf{MT}^{-2}$
F_{bs}	Load supported by bracket	$\mathbf{MLT}^{-2}$
F_c	Critical buckling load for a ring, per unit length	$\mathbf{MT}^{-2}$
F_p	Local, concentrated, wind load	$\mathbf{MLT}^{-2}$
F_r	Load on stiffening ring, per unit length	$\mathbf{MT}^{-2}$
F_s	Shear force due an earthquake	$\mathbf{MLT}^{-2}$
F_w	Loading due to wind pressure, per unit length	$\mathbf{MT}^{-2}$
F_1	Factor in equation 13.102	$\mathbf{L}^{-3}$
F_2	Factor in equation 13.103	$\mathbf{L}^{-3}$
F_3	Factor in equation 13.104	$\mathbf{L}^{-3}$
F_4	Factor in equation 13.104	—
f	Maximum allowable stress (design stress)	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_a	Nominal design strength at test temperature	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_b	Maximum allowable bolt stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_c	Maximum allowable bearing pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f'_c	Actual bearing pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_f	Maximum allowable design stress for flange material	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_m	Maximum allowable stress for centrifuge material	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_n	Nominal design strength at design temperature	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_p	Maximum allowable design stress for plate	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_r	Maximum allowable design stress for ring material	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
f_s	Maximum allowable design stress for skirt material	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$

f_t	Maximum allowable design stress for tank material	$\mathbf{ML^{-1}T^{-2}}$
G	Mean diameter of gasket	$\mathbf{L}$
g	Gravitational acceleration	$\mathbf{LT^{-2}}$
H	Total pressure force on flange	$\mathbf{MLT^{-2}}$
H_d	Pressure force on area inside flange	$\mathbf{MLT^{-2}}$
H_g	Gasket reaction	$\mathbf{MLT^{-2}}$
H_L	Liquid depth	$\mathbf{L}$
H_p	Height of local load above base	$\mathbf{L}$
H_t	Pressure force on flange face	$\mathbf{MLT^{-2}}$
H_v	Height (length) of cylindrical section between tangent lines	$\mathbf{L}$
h	Height of domed head from tangent line	$\mathbf{L}$
h_c	Initial displacement of shaft	$\mathbf{L}$
h_d	Moment arm of force H_d	$\mathbf{L}$
h_g	Moment arm of force H_g	$\mathbf{L}$
h_i	Internal height of branch allowed as compensation	$\mathbf{L}$
h_o	External height of branch allowed as compensation	$\mathbf{L}$
h_t	Moment arm of force H_t	$\mathbf{L}$
I	Second moment of area (moment of inertia)	$\mathbf{L^4}$
I'	Second moment of area per unit length	$\mathbf{L^3}$
I_h	Second moment of area of shell, horizontal vessel	$\mathbf{L^4}$
I_p	Polar second moment of area	$\mathbf{L^4}$
I_r	Second moment of area of ring	$\mathbf{L^4}$
I_v	Second moment of area of vessel	$\mathbf{L^4}$
J	Joint factor, welded joint	—
K	Ratio of diameters of thick cylinder $= D_o/D_i$	—
K_c	Collapse coefficient in equation 13.52	—
L	Unsupported length of vessel	$\mathbf{L}$
L'	Effective length between stiffening rings	$\mathbf{L}$
L_c	Critical distance between stiffening rings	$\mathbf{L}$
L_k	Length of conical transition section	$\mathbf{L}$
L_o	Distance between centre line of equipment and column	$\mathbf{L}$
L_r	Distance between edge of skirt to outer edge of flange	$\mathbf{L}$
M	Bending moment	$\mathbf{ML^2T^{-2}}$
M_{atm}	Moment acting on flange during bolting up	$\mathbf{ML^2T^{-2}}$
M_e	Bending moment due to offset equipment	$\mathbf{ML^2T^{-2}}$
M_{L1}	Longitudinal bending moment at mid-span	$\mathbf{ML^2T^{-2}}$
M_{L2}	Longitudinal bending moment at saddle support	$\mathbf{ML^2T^{-2}}$
M_{op}	Total moment acting on flange	$\mathbf{ML^2T^{-2}}$
M_s	Bending moment at base of skirt	$\mathbf{ML^2T^{-2}}$
M_v	Bending moment acting on vessel	$\mathbf{ML^2T^{-2}}$
M_x	Bending moment at point x from free end of column	$\mathbf{ML^2T^{-2}}$
M_1	Bending moment acting along cylindrical sections	$\mathbf{ML^2T^{-2}}$
M_2	Bending moment acting along diametrical sections	$\mathbf{ML^2T^{-2}}$
m_c	Displaced mass, centrifuge	$\mathbf{M}$
N_b	Number of bolts	—
n	Number of lobes	—
P	Pressure	$\mathbf{ML^{-1}T^{-2}}$
P_c	Critical buckling pressure	$\mathbf{ML^{-1}T^{-2}}$
P'_c	Critical pressure to cause local buckling in a spherical shell	$\mathbf{ML^{-1}T^{-2}}$
P_d	Design pressure	$\mathbf{ML^{-1}T^{-2}}$
P_e	External pressure	$\mathbf{ML^{-1}T^{-2}}$
P_f	Centrifugal pressure	$\mathbf{ML^{-1}T^{-2}}$
P_i	Internal pressure	$\mathbf{ML^{-1}T^{-2}}$
P_m	Self-pressure, centrifuge	$\mathbf{ML^{-1}T^{-2}}$
P_t	Total pressure acting on centrifuge wall	$\mathbf{ML^{-1}T^{-2}}$
P_w	Wind pressure loading	$\mathbf{ML^{-1}T^{-2}}$
$\Delta P'$	Effective tube-plate design pressure difference	$\mathbf{ML^{-1}T^{-2}}$
p_b	Bolt pitch	$\mathbf{L}$

p_h	Hole pitch	$\mathbf{L}$
R_c	Crown radius	$\mathbf{L}$
R_k	Knuckle radius	$\mathbf{L}$
R_i	Radius of interface	$\mathbf{L}$
R_o	Major radius of torus	$\mathbf{L}$
R_p	Radius of curvature of plate	$\mathbf{L}$
R_s	Outside radius of sphere	$\mathbf{L}$
R_1	Inside radius of centrifuge bowl	$\mathbf{L}$
R_2	Radius of liquid surface	$\mathbf{L}$
r	Radius	$\mathbf{L}$
r_1	Meridional radius of curvature	$\mathbf{L}$
r_2	Circumferential radius of curvature	$\mathbf{L}$
s	Resisting force per unit displacement	$\mathbf{MT}^{-2}$
T	Torque	$\mathbf{ML}^{2}\mathbf{T}^{-2}$
t	Thickness of plate (shell)	$\mathbf{L}$
t_b	Thickness of base ring	$\mathbf{L}$
t_c	Thickness of bracket plate	$\mathbf{L}$
t_f	Thickness of flange	$\mathbf{L}$
t_n	Actual thickness of branch	$\mathbf{L}$
t_p	Tube-plate thickness	$\mathbf{L}$
t_s	Skirt thickness	$\mathbf{L}$
u_w	Wind velocity	$\mathbf{LT}^{-1}$
W	Total weight of vessel and contents	$\mathbf{MLT}^{-2}$
W_e	Weight of ancillary equipment	$\mathbf{MLT}^{-2}$
W_m	Greater value of W_{m1} and W_{m2} in equation 13.109	$\mathbf{MLT}^{-2}$
W_{m1}	Minimum bolt load required under operating conditions	$\mathbf{MLT}^{-2}$
W_{m2}	Minimum bolt load required to seal gasket	$\mathbf{MLT}^{-2}$
W_v	Weight of vessel	$\mathbf{MLT}^{-2}$
w	Deflection of flat plate	$\mathbf{L}$
w	Loading per unit length	$\mathbf{MT}^{-2}$
x	Radius from centre of flat plate to point of interest	$\mathbf{L}$
x	Distance from free end of cantilever beam	$\mathbf{L}$
x_c	Displacement caused by centrifugal force	$\mathbf{L}$
y	Minimum seating pressure for gasket	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
α	Cone half cone apex angle	—
Δ	Dilation	$\mathbf{L}$
Δ_c	Dilation of cylinder	$\mathbf{L}$
Δ_s	Dilation of sphere	$\mathbf{L}$
ε	Strain	—
ε_1, ε_2	Principal strains	—
θ	Angle	—
θ_s	Base angle of conical section	—
λ	Ligament efficiency	—
ν	Poisson’s ratio	—
ρ_m	Density of vessel material	$\mathbf{ML}^{-3}$
ρ_a	Density of air	$\mathbf{ML}^{-3}$
ρ_L	Liquid density	$\mathbf{ML}^{-3}$
ρ_{L1}	Density of heavier liquid	$\mathbf{ML}^{-3}$
ρ_{L2}	Density of lighter liquid	$\mathbf{ML}^{-3}$
σ	Normal stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_b	Bending stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_{b1}	Bending stress at mid-span	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_{b2}	Bending stress at saddle supports	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_e	Stress at elastic limit of material	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ'_e	Elastic limit stress divided by factor of safety	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_h	Circumferential (hoop) stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_{hb}	Longitudinal hub stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_L	Longitudinal stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_r	Radial stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$

σ_{rd}	Radial flange stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_s	Stress in skirt support	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_t	Tangential (hoop) stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_{tg}	Tangential flange stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_{ws}	Stress in skirt due to weight of vessel	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_x	Normal stress in x direction	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_y	Normal stress in y direction	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_z	Axial stresses in vessel	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
σ_1, σ_2, σ_3	Principal stresses	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
τ	Torsional shear stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
τ_{xy}	Shear stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
τ_1, τ_2, τ_3	Shear stress maxima	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
ϕ	Slope of flat plate	—
ϕ	Angle	—
ω	Rotational speed	$\mathbf{T}^{-1}$

Superscript

$\wedge$	Maximum

13.20. PROBLEMS

13.1. Calculate the maximum membrane stress in the wall of shells having the shapes listed below. The vessel walls are 2 mm thick and subject to an internal pressure of 5 bar.

1. An infinitely long cylinder, inside diameter 2 m.
2. A sphere, inside diameter 2 m.
3. An ellipsoid, major axis 2 m, minor axis 1.6 m.
4. A torus, mean diameter 2 m, diameter of cylinder 0.3 m.

13.2. Compare the thickness required for a 2 m diameter flat plate, designed to resist a uniform distributed load of 10 kN/m^2, if the plate edge is:

(a) completely rigid,
(b) free to rotate.

Take the allowable design stress for the material as 100 MN/m^2 and Poisson's ratio for the material as 0.3.

13.3. A horizontal, cylindrical, tank, with hemispherical ends, is used to store liquid chlorine at 10 bar. The vessel is 4 m internal diameter and 20 m long. Estimate the minimum wall thickness required to resist this pressure, for the cylindrical section and the heads. Take the design pressure as 12 bar and the allowable design stress for the material as 110 MN/m^2.

13.4. The thermal design of a heat exchanger to recover heat from a kerosene stream by transfer to a crude oil stream was carried in Chapter 12, Example 12.2. Make a preliminary mechanical design for this exchanger. Base your design on the specification obtained from the CAD design procedure used in the example. All material of construction to be carbon steel (semi-killed or silicon killed). Your design should cover:

(a) choice of design pressure and temperature,
(b) choice of the required corrosion allowances,

(c) choice of the type of end covers,
(d) determination of the minimum wall thickness for the shell, headers and ends,
(e) a check on the pressure rating of the tubes,
(f) a suggested thickness for the tube sheets — detailed stressing is not required,
(g) selection the flange types and dimensions — use standard flanges,
(h) design of the exchanger supports.

13.5. Make a preliminary mechanical design for the vertical thermosyphon reboiler for which the thermal design was done as Example 12.9 in Chapter 12. The inlet liquid nozzle and the steam connections will be 50 mm inside diameter. Flat plate end closures will be used on both headers. The reboiler will be hung from four bracket supports, positioned 0.5 m down from the top tube plate. The shell and tubes will be of semi-killed carbon steel.
Your design should cover:

(a) choice of design pressure and temperature,
(b) choice of the required corrosion allowances,
(c) selection of the header dimensions.
(d) determination of the minimum wall thickness for the shell, headers and ends,
(e) a check on the pressure rating of the tubes,
(f) a suggested thickness for the tube sheets — detailed stressing is not required,
(g) selection the flanges types and dimensions — use standard flanges,
(h) reinforcement at the nozzles, if required,
(i) design of the exchanger support brackets.

13.6. The specification for of a sieve plate column is given below. Make a preliminary mechanical design for the column. You design should include:

(a) column wall thickness,
(b) selection and sizing of vessel heads,
(c) reinforcement, if any, of openings,
(d) the nozzles and flanges (use standard flanges),
(e) column supporting skirt and base ring/flange.

You need not design the plates or plate supports.

You should consider the following design loads:

(a) internal pressure,
(b) wind loading,
(c) dead weight of vessel and contents (vessel full of water).

There will be no significant loading from piping and external equipment. Earthquake loading need not be considered.

Column specification:
Length of cylindrical section 37 m
Internal diameter 1.5 m
Heads, standard ellipsoidal
50 sieve plates
Nozzles: feed, at mid-point, 50 mm inside diameter,
vapour out, 0.7 m below top of cylindrical section, 250 mm

inside diameter
bottom product, centre of vessel head, 50 mm inside diameter
reflux return, 1.0 m below top of cylindrical section, 50 mm inside diameter

Two 0.6 m diameter access ports (manholes) situated 1.0 m above the bottom and 1.5 m below the top of the column
Support skirt height 2.5 m
Access ladder with platforms
Insulation, mineral wool, 50 mm thick
Materials of construction: vessel stainless steel, unstabilised (304)
nozzles as vessel
skirt carbon steel, silicon killed
Design pressure 1200 kN/m^2
Design temperature 150 °C
Corrosion allowance 2 mm.

Make a dimensioned sketch of your design and fill out the column specification sheet given in Appendix G.

13.7. A jacketed vessel is to be used as a reactor. The vessel has an internal diameter of 2 m and is fitted with a jacket over a straight section 1.5 m long. Both the vessel and jacket walls are 25 mm thick. The spacing between the vessel and jacket is 75 mm.

The vessel and jacket are made of carbon steel. The vessel will operate at atmospheric pressure and the jacket will be supplied with steam at 20 bar. Check if the thickness of the vessel and jacket is adequate for this duty.

Take the allowable design stress as 100 N/mm^2 and the value of Young's modulus at the operating temperature as 180,000 N/mm^2.

13.8. A high pressure steam pipe is 150 mm inside diameter and 200 mm outside diameter. If the steam pressure is 200 bar, what will be the maximum shear stress in the pipe wall?

13.9. A storage tank for concentrated nitric acid will be constructed from aluminium to resist corrosion. The tank is to have an inside diameter of 6 m and a height of 17 m. The maximum liquid level in the tank will be at 16 m. Estimate the plate thickness required at the base of the tank. Take the allowable design stress for aluminium as 90 N/mm^2.

CHAPTER 10

Equipment Selection, Specification and Design

10.1. INTRODUCTION

The first chapters of this book covered process design: the synthesis of the complete process as an assembly of units; each carrying out a specific process operation. In this and the following chapters, the selection, specification and design of the equipment required to carry out the function of these process units (unit operations) is considered in more detail. The equipment used in the chemical processes industries can be divided into two classes: proprietary and non-proprietary. Proprietary equipment, such as pumps, compressors, filters, centrifuges and dryers, is designed and manufactured by specialist firms. Non-proprietary equipment is designed as special, one-off, items for particular processes; for example, reactors, distillation columns and heat exchangers.

Unless employed by one of the specialist equipment manufacturers, the chemical engineer is not normally involved in the detailed design of proprietary equipment. His job will be to select and specify the equipment needed for a particular duty; consulting with the vendors to ensure that the equipment supplied is suitable. He may be involved with the vendor's designers in modifying standard equipment for particular applications; for example, a standard tunnel dryer designed to handle particulate solids may be adapted to dry synthetic fibres.

As was pointed out in Chapter 1, the use of standard equipment, whenever possible, will reduce costs.

Reactors, columns and other vessels are usually designed as special items for a given project. In particular, reactor designs are usually unique, except where more or less standard equipment is used; such as an agitated, jacketed, vessel.

Distillation columns, vessels and tubular heat exchangers, though non-proprietary items, will be designed to conform to recognised standards and codes; this reduces the amount of design work involved.

The chemical engineer's part in the design of "non-proprietary" equipment is usually limited to selecting and "sizing" the equipment. For example, in the design of a distillation column his work will typically be to determine the number of plates; the type and design of plate; diameter of the column; and the position of the inlet, outlet and instrument nozzles. This information would then be transmitted, in the form of sketches and specification sheets, to the specialist mechanical design group, or the fabricator's design team, for detailed design.

In this chapter the emphasis is put on equipment selection, rather than equipment design; as most of the equipment described is proprietary equipment. Design methods are given for some miscellaneous non-proprietary items. A brief discussion of reactor design is included. The design of two important classes of equipment, columns and heat exchangers, is covered separately in Chapters 11 and 12. A great variety of equipment is used in the process industries, and it is only possible to give very brief descriptions of the main types in this volume. Further details are given in Volume 2; and descriptions and illustrations of most of the equipment used can be found in various handbooks: Perry *et al*. (1997), Schweitzer (1988) and Walas (1990). Equipment manufacturers' advertisements in the technical press should also be studied. It is worthwhile building up a personal file of vendors' catalogues to supplement those that may be held in a firm's library. In the United Kingdom, a commercial organisation, Technical Indexes Ltd., publishes the Process Engineering Index; which contains on microfilm information from over 3000 manufacturers and suppliers of process equipment.

The scientific principles and theory that underlie the design of and operation of processing equipment is covered in Volume 2.

10.2. SEPARATION PROCESSES

As was discussed in Chapter 1, chemical processes consist essentially of reaction stages followed by separation stages in which the products are separated and purified.

The main techniques used to separate phases, and the components within phases, are listed in Table 10.1 and discussed in Sections 10.3 to 10.9.

10.3. SOLID-SOLID SEPARATIONS

Processes and equipment are required to separate valuable solids from unwanted material, and for size grading (classifying) solid raw materials and products.

The equipment used for solid-solid separation processes was developed primarily for the minerals processing and metallurgical industries for the benefication (up-grading) of ores. The techniques used depend on differences in physical, rather than chemical, properties, though chemical additives may be used to enhance separation. The principal techniques used are shown in Figure 10.1; which can be used to select the type of processes likely to be suitable for a particular material and size range.

Sorting material by appearance, by hand, is now rarely used due to the high cost of labour.

10.3.1. Screening (sieving)

The methods used for laboratory particle size analysis are discussed in detail in Volume 2, Chapter 1.

Screens separate particles on the basis of size. Their main application is in grading raw materials and products into size ranges, but they are also used for the removal of trash (over-and under-sized contaminants) and for dewatering. Industrial screening equipment is used over a wide range of particle sizes, from fine powders to large rocks. For small particles woven cloth or wire screens are used, and for larger sizes, perforated metal plates or grids.

Table 10.1. Separation processes

Numbers refer to the sections in this chapter. Processes in brackets are used for separating dissolved components (solutions). The terms major and minor component only apply where different phases are to be separated; i.e. not to those on the diagonal

		MINOR COMPONENT		
		Solid	Liquid	Gas/Vapour
MAJOR COMPONENT	Solid	Sorting 10.3 Screening 10.3.1 Hydrocyclones 10.3.2 Classifiers 10.3.3 Jigs 10.3.4 Tables 10.3.5 Centrifuges 10.3.6 Dense media 10.3.7 Flotation 10.3.8 Magnetic 10.3.9 Electrostatic 10.3.10	Pressing 10.4.5 Drying 10.4.6.	Crushing 10.10 Heating —
	Liquid	Thickeners 10.4.1 Clarifiers 10.4.1 Hydrocyclones 10.4.4 Filtration 10.4.2 Centrifuges 10.4.3 (Crystallisers) 10.5.2 (Evaporators) 10.5.1	Decanters 10.6.1 Coalescers 10.6.3 (Solvent extraction) 10.7.1 (Distillation) Chapter 11 (Adsorption) Volume 2 (Ion exchange) Volume 2	(Stripping) Volume 2
	Gas/Vapour	Gravity settlers 10.8.1 Impingement settlers 10.8.2 Cyclones 10.8.3 Filters 10.8.4 Wet scrubbers 10.8.5 Electrostatic precipitators 10.8.6	Separating vessels 10.9 Demisting pads 10.9 Cyclones 10.8.3 Wet scrubbers 10.8.5 Electrostatic precipitators 10.8.6	(Adsorption) Volume 2 (Absorption) Volume 2

Screen sizes are defined in two ways: by a mesh size number for small sizes and by the actual size of opening in the screen for the larger sizes. There are several different standards in use for mesh size, and it is important to quote the particular standard used when specifying particle size ranges by mesh size. In the UK the appropriate British Standards should be used; BS 410 and BS 1796. A comparison of the various international standard sieve mesh sizes is given in Volume 2, Chapter 1.

The simplest industrial screening equipment are stationary screens, over which the material to be screened flows. Typical of this type are “Grizzly” screens, which consist of rows of equally spaced parallel bars, and which are used to “scalp” off over-sized rocks in the feed to crushers.

Dynamic screening equipment can be categorised according to the type of motion used to shake-up and transport the material on the screen. The principal types used in the chemical process industries are described briefly below.

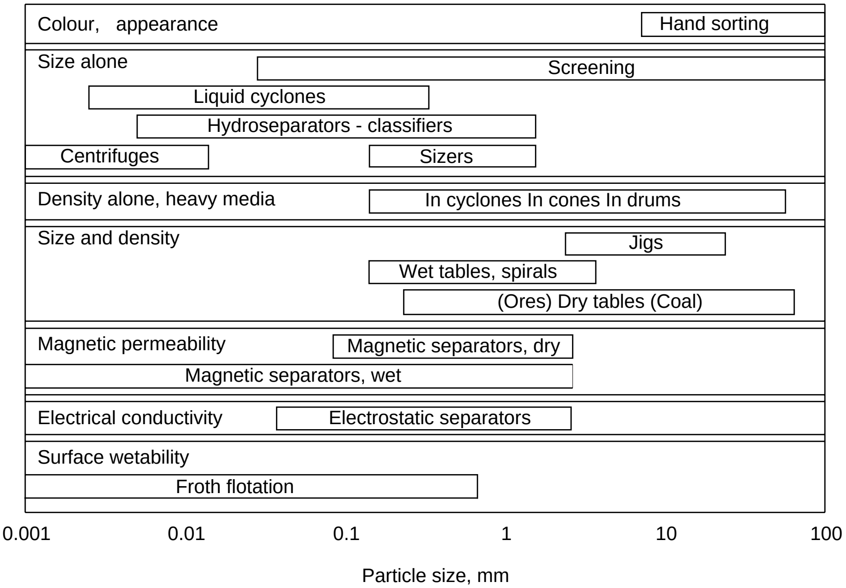


Figure 10.1. A particle size selection guide to solid-solid separation techniques and equipment (after Roberts *et al.* 1971)

Vibrating screens: horizontal and inclined screening surfaces vibrated at high frequencies (1000 to 7000 Hz). High capacity units, with good separating efficiency, which are used for a wide range of particle sizes.

Oscillating screens: operated at lower frequencies than vibrating screens (100–400 Hz) with a longer, more linear, stroke.

Reciprocating screens: operated with a shaking motion, a long stroke at low frequency (20–200 Hz). Used for conveying with size separation.

Shifting screens: operated with a circular motion in the plane of the screening surface. The actual motion may be circular, gyratory, or circularly vibrated. Used for the wet and dry screening of fine powders.

Revolving screens: inclined, cylindrical screens, rotated at low speeds (10–20 rpm). Used for the wet screening of relatively coarse material, but have now been largely replaced by vibrating screens.

Figure 10.2, which is based on a similar chart given by Matthews (1971), can be used to select the type of screening equipment likely to be suitable for a particular size range. Equipment selection will normally be based on laboratory and pilot scale screening tests, conducted with the co-operation of the equipment vendors. The main factors to be considered, and the information that would be required by the firms supplying proprietary screening equipment, are listed below:

1. Rate, throughput required.
2. Size range (test screen analysis).
3. Characteristics of the material: free-flowing or sticky, bulk density, abrasiveness.
4. Hazards: flammability, toxicity, dust explosion.
5. Wet or dry screening to be used.

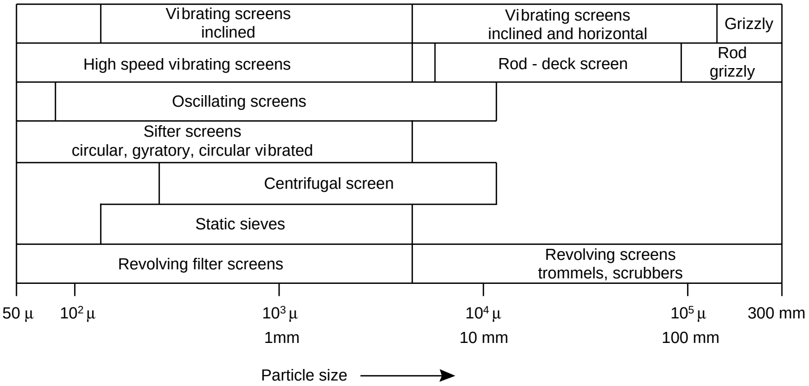


Figure 10.2. Screen selection by particle size range

10.3.2. Liquid-solid cyclones

Cyclones can be used for the classification of solids, as well as for liquid-solid, and liquid-liquid separations. The design and application of liquid cyclones (hydrocyclones) is discussed in Section 10.4.4. A typical unit is shown in Figure 10.3.

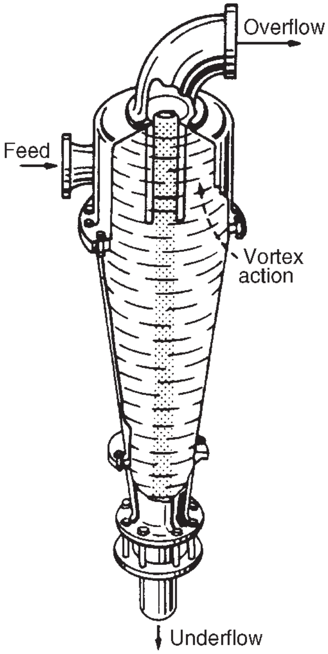


Figure 10.3. Liquid-solid cyclone (hydrocyclone)

Liquid cyclones can be used for the classification of solid particles over a size range from 5 to 100 μm. Commercial units are available in a wide range of materials of construction and sizes; from as small as 10 mm to up to 30 m diameter. The separating efficiency of liquid cyclones depends on the particle size and density, and the density and viscosity of the liquid medium.

10.3.3. Hydroseparators and sizers (classifiers)

Classifiers that depend on the difference in the settling rates of different size particles in water are frequently used for separating fine particles, in the 50 to 300 μm range. Various designs are used. The principal ones used in the chemical process industries are described below.

Thickeners: thickeners are primarily used for liquid-solid separation (see Section 10.4). When used for classification, the feed rate is such that the overflow rate is greater than the settling rate of the slurry, and the finer particles remain in the overflow stream.

Rake classifiers: are inclined, shallow, rectangular troughs, fitted with mechanical rakes at the bottom to rake the deposited solids to the top of the incline (Figure 10.4). Several rake classifiers can be used in series to separate the feed into different size ranges.

Bowl classifiers: are shallow bowls with concave bottoms, fitted with rakes. Their operation is similar to that of thickeners.

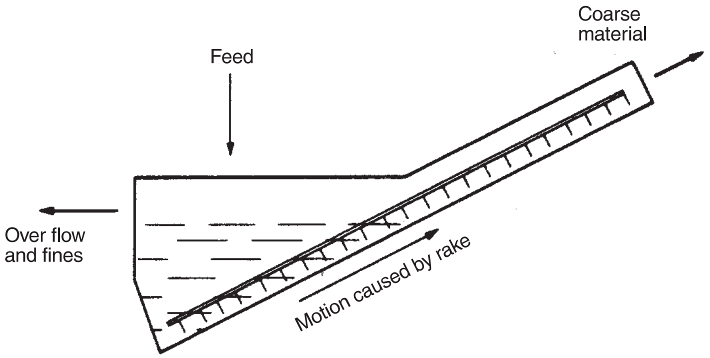


Figure 10.4. Rake classifier

10.3.4. Hydraulic jigs

Jigs separate solids by difference in density and size. The material is immersed in water, supported on a screen (Figure 10.5). Pulses of water are forced through the bed of material, either by moving the screen or by pulsating the water level. The flow of water fluidises the bed and causes the solids to stratify with the lighter material at the top and the heavier at the bottom.

10.3.5. Tables

Tables are used wet and dry. The separating action of a wet table resembles that of the traditional miner's pan. Riffled tables (Figure 10.6) are basically rectangular decks, inclined at a shallow angle to the horizontal (2 to 5°), with shallow slats (riffles) fitted to

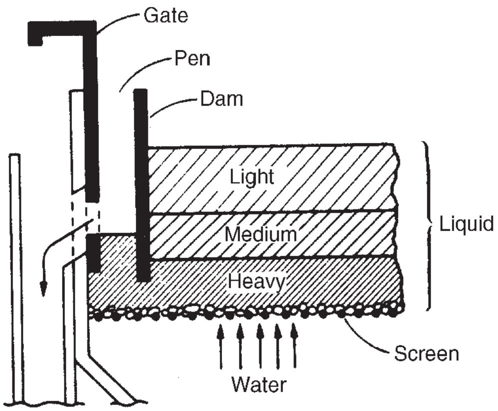


Figure 10.5. A hydraulic jig

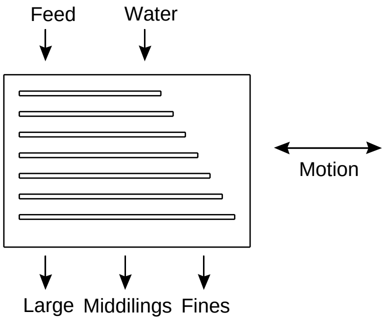


Figure 10.6. Wilfley riffled table

the surface. The table is mechanically shaken, with a slow stroke in the forward direction and a faster backward stroke. The particles are separated into different size ranges under the combined action of the vibration, water flow, and the resistance to flow over the riffles.

10.3.6. Classifying centrifuges

Centrifuges are used for the classification of particles in size ranges below 10 μm. Two types are used: solid bowl centrifuges, usually with a cylindrical, conical bowl, rotated about a horizontal axis; and "nozzle" bowl machines, fitted with discs.

These types are described in Section 10.4.3.

10.3.7. Dense-medium separators (sink and float processes)

Solids of different densities can be separated by immersing them in a fluid of intermediate density. The heavier solids sink to the bottom and the lighter float to the surface. Water suspensions of fine particles are often used as the dense liquid (heavy-medium). The technique is used extensively for the benefication (concentration) of mineral ores.

10.3.8. Flotation separators (froth-flotation)

Froth-flotation processes are used extensively for the separation of finely divided solids. Separation depends on differences in the surface properties of the materials. The particles are suspended in an aerated liquid (usually water), and air bubbles adhere preferentially to the particles of one component and bring them to the surface. Frothing agents are used so that the separated material is held on the surface as a froth and can be removed.

Froth-flotation is an extensively used separation technique, having a wide range of applications in the minerals processing industries and other industries. It can be used for particles in the size range from 50 to 400 μm.

10.3.9. Magnetic separators

Magnetic separators can be used for materials that are affected by magnetic fields; the principle is illustrated in Figure 10.7. Rotating-drum magnetic separators are used for a wide range of materials in the minerals processing industries. They can be designed to handle relatively high throughputs, up to 3000 kg/h per metre length of drum.

Simple magnetic separators are often used for the removal of iron from the feed to a crusher.

The various types of magnetic separators used and their applications are described by Bronkala (1988).

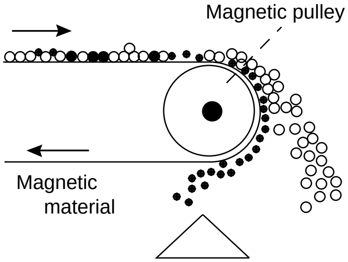


Figure 10.7. Magnetic separator

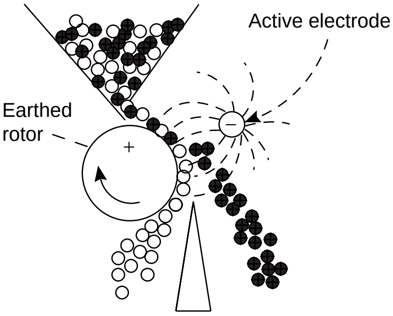


Figure 10.8. Electrostatic separator

10.3.10. Electrostatic separators

Electrostatic separation depends on differences in the electrical properties (conductivity) of the materials to be treated. In a typical process the material particles pass through a high-voltage electric field as it is fed on to a revolving drum, which is at earth potential (Figure 10.8). Those particles that acquire a charge adhere to the drum surface and are carried further around the drum before being discharged.

10.4. LIQUID-SOLID (SOLID-LIQUID) SEPARATORS

The need to separate solid and liquid phases is probably the most common phase separation requirement in the process industries, and a variety of techniques is used (Figure 10.9). Separation is effected by either the difference in density between the liquid and solids, using either gravity or centrifugal force, or, for filtration, depends on the particle size and shape. The most suitable technique to use will depend on the solids concentration and feed rate, as well as the size and nature of the solid particles. The range of application of various techniques and equipment, as a function of slurry concentration and particle size, is shown in Figure 10.10.

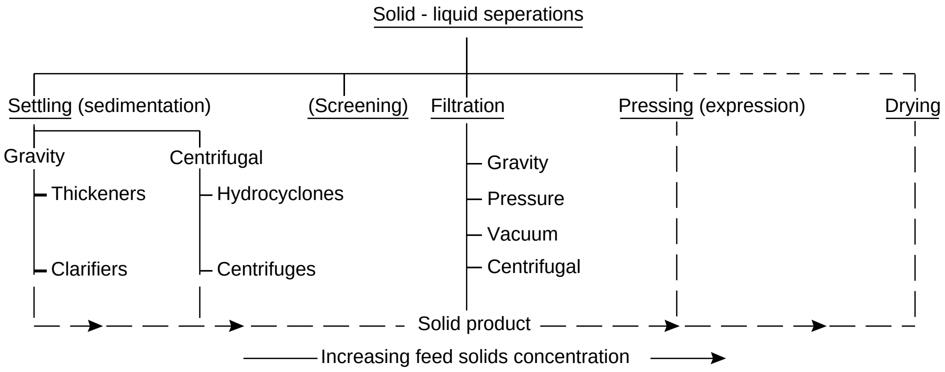


Figure 10.9. Solid-liquid separation techniques

The choice of equipment will also depend on whether the prime objective is to obtain a clear liquid or a solid product, and on the degree of dryness of the solid required.

The design, construction and application of thickeners, centrifuges and filters is a specialised subject, and firms who have expertise in these fields should be consulted when selecting and specifying equipment for new applications. Several specialist texts on the subject are available: Svarovsky (2001), Ward (2000) and Wakeman and Tarleton (1998). The theory of sedimentation processes is covered in Volume 2, Chapter 5 and filtration in Chapter 7.

10.4.1. Thickeners and clarifiers

Thickening and clarification are sedimentation processes, and the equipment used for the two techniques are similar. The primary purpose of thickening is to increase the concentration of a relatively large quantity of suspended solids; whereas that of clarifying,

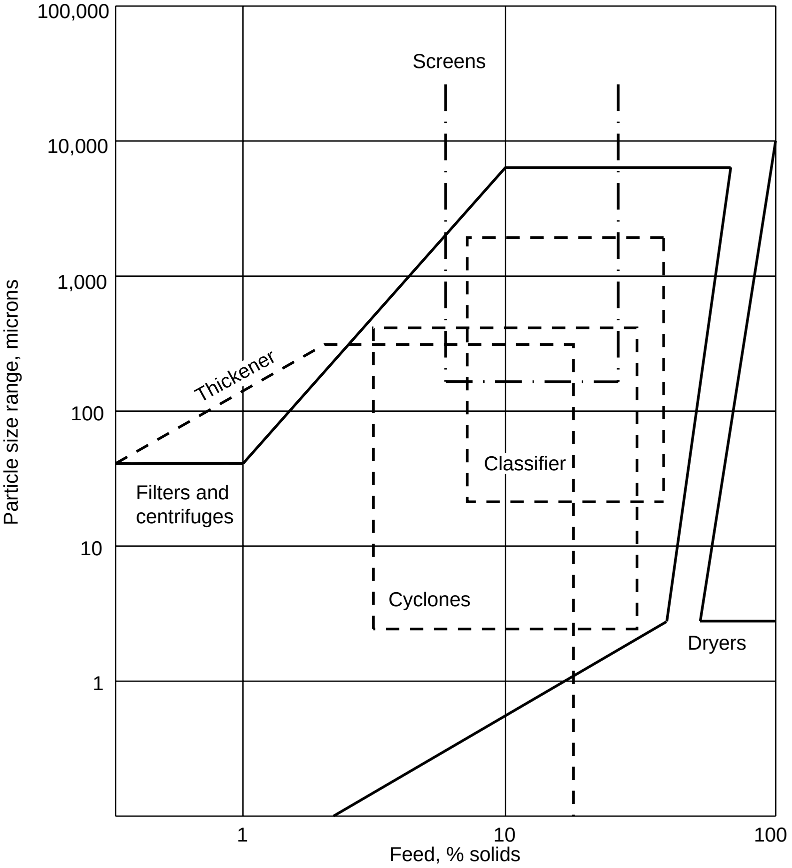


Figure 10.10. Solid-liquid separation techniques (after Dahlstrom and Cornell, 1971)

as the name implies, is to remove a small quantity of fine solids to produce a clear liquid effluent. Thickening and clarification are relatively cheap processes when used for the treatment of large volumes of liquid.

A thickener, or clarifier, consists essentially of a large circular tank with a rotating rake at the base. Rectangular tanks are also used, but the circular design is preferred. They can be classified according to the way the rake is supported and driven. The three basic designs are shown in Figure 10.11 (see p. 410). Various designs of rake are used, depending on the nature of the solids.

The design and construction of thickeners and clarifiers is described by Dahlstrom and Cornell (1971).

Flocculating agents are often added to promote the separating performance of thickeners.

10.4.2. Filtration

In filtration processes the solids are separated from the liquid by passing (filtering) the slurry through some form of porous filter medium. Filtration is a widely used separation

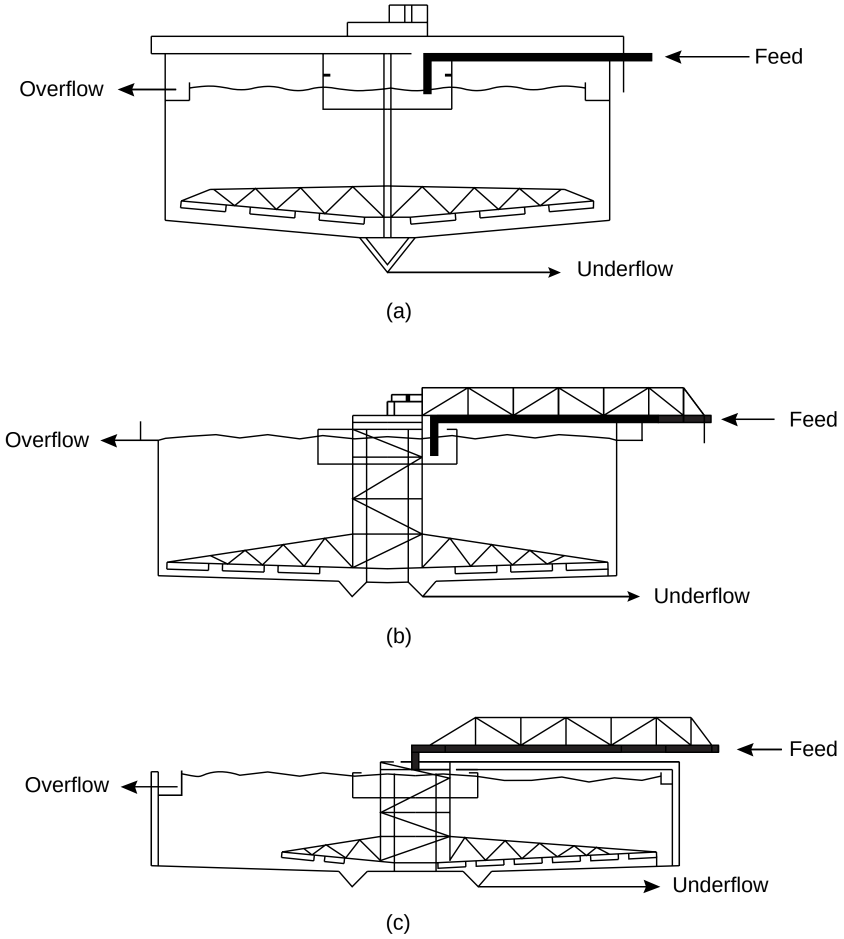


Figure 10.11. Types of thickener and clarifier (*a*) Bridge supported (up to <40 m dia.) (*b*) Centre column supported (<30 m dia.) (*c*) Traction driven (<60 m dia.)

process in the chemical and other process industries. Many types of equipment and filter media are used; designed to meet the needs of particular applications. Descriptions of the filtration equipment used in the process industries and their fields of application can be found in various handbooks: Perry *et al*. (1997), Dickenson (1997), Schweitzer (1997), and in several specialist texts on the subject: Cheremisnoff (1998), Orr (1977). A short discussion of filtration theory and descriptions of the principal types of equipment is given in Volume 2, Chapter 7.

The most commonly used filter medium is woven cloth, but a great variety of other media is also used. The main types are listed in Table 10.2. A comprehensive discussion of the factors to be considered when selecting filter media is given by Purchas (1971) and Mais (1971); see also Purchas and Sutherland (2001). Filter aids are often used to increase the rate of filtration of difficult slurries. They are either applied as a precoat to the filter cloth or added to the slurry, and deposited with the solids, assisting in the formation of a porous cake.

Table 10.2. Filter media

Type	Examples	Minimum size particle trapped (μm)
1. Solid fabrications	Scalloped washers Wire-wound tubes	5
2. Rigid porous media	Ceramics, stoneware	1
	Sintered metal	3
3. Metal	Perforated sheets	100
	Woven wire	5
4. Porous plastics	Pads, sheets	3
	Membranes	0.005
5. Woven fabrics	Natural and synthetic fibre cloths	10
6. Non-woven sheets	Felts, lap	10
	Paper, cellulose	5
7. Cartridges	Yarn-wound spools, graded fibres	2
8. Loose solids	Fibres, asbestos, cellulose	sub-micron

Industrial filters use vacuum, pressure, or centrifugal force to drive the liquid (filtrate) through the deposited cake of solids. Filtration is essentially a discontinuous process. With batch filters, such as plate and frame presses, the equipment has to be shut down to discharge the cake; and even with those filters designed for continuous operation, such as rotating-drum filters, periodic stoppages are necessary to change the filter cloths. Batch filters can be coupled to continuous plant by using several units in parallel, or by providing buffer storage capacity for the feed and product.

The principal factors to be considered when selecting filtration equipment are:

1. The nature of the slurry and the cake formed.
2. The solids concentration in the feed.
3. The throughput required.
4. The nature and physical properties of the liquid: viscosity, flammability, toxicity, corrosiveness.
5. Whether cake washing is required.
6. The cake dryness required.
7. Whether contamination of the solid by a filter aid is acceptable.
8. Whether the valuable product is the solid or the liquid, or both.

The overriding factor will be the filtration characteristics of the slurry; whether it is fast filtering (low specific cake resistance) or slow filtering (high specific cake resistance). The filtration characteristics can be determined by laboratory or pilot plant tests. A guide to filter selection by the slurry characteristics is given in Table 10.3; which is based on a similar selection chart given by Porter *et al*. (1971).

Table 10.3. Guide to filter selection

Slurry characteristics	Fast filtering	Medium filtering	Slow filtering	Dilute	Very dilute
Cake formation rate	cm/s	mm/s	0.02–0.12 mm/s	0.02 mm/s	No cake
Normal concentration	>20%	10–20%	1–10%	<5%	<0.1%
Settling rate	Very fast	Fast	Slow	Slow	—
Leaf test rate, kg/h m^2	>2500	250–2500	25–250	<25	—
Filtrate rate, m^3/h m^2	>10	5–10	0.02–0.05	0.02–5	0.02–5
Filter application					
Continuous vacuum filters					
Multicompartment drum	▬	▬	▬		
Single compartment drum	▬				
Top feed drum	▬				
Scroll discharge drum	▬	▬			
Tilting pan	▬	▬			
Belt	▬	▬			
Disc		▬	▬		
Batch vacuum leaf		▬	▬	▬	▬
Batch nutsche	▬	▬	▬	▬	▬
Batch pressure filters					
Plate and frame		▬	▬	▬	▬
Vertical leaf		▬	▬	▬	▬
Horizontal plate	▬	▬	▬	▬	▬
Cartridge edge					▬

The principal types of industrial scale filter used are described briefly below.

Nutsche (gravity and vacuum operation)

This is the simplest type of batch filter. It consists of a tank with a perforated base, which supports the filter medium.

Plate and frame press (pressure operation) (Figure 10.12)

The oldest and most commonly used batch filter. Versatile equipment, made in a variety of materials, and capable of handling viscous liquids and cakes with a high specific resistance.

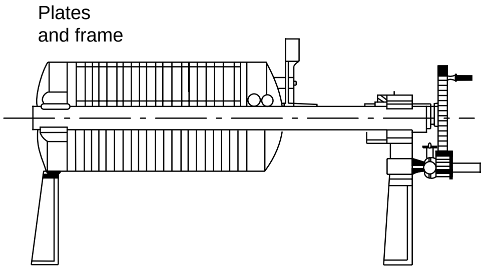


Figure 10.12. Plate and frame filter press

Leaf filters (pressure and vacuum operation)

Various types of leaf filter are used, with the leaves arranged in horizontal or vertical rows. The leaves consist of metal frames over which filter cloths are draped. The cake is removed either mechanically or by sluicing it off with jets of water. Leaf filters are used for similar applications as plate and frame presses, but generally have lower operating costs.

Rotary drum filters (usually vacuum operation) (Figure 10.13)

A drum filter consists essentially of a large hollow drum round which the filter medium is fitted. The drum is partially submerged in a trough of slurry, and the filtrate sucked through the filter medium by vacuum inside the drum. Wash water can be sprayed on to the drum surface and multicompartment drums are used so that the wash water can be kept separate from the filtrate. A variety of methods is used to remove the cake from the drum: knives, strings, air jets and wires. Rotating drum filters are essentially continuous in operation. They can handle large throughputs, and are widely used for free filtering slurries.

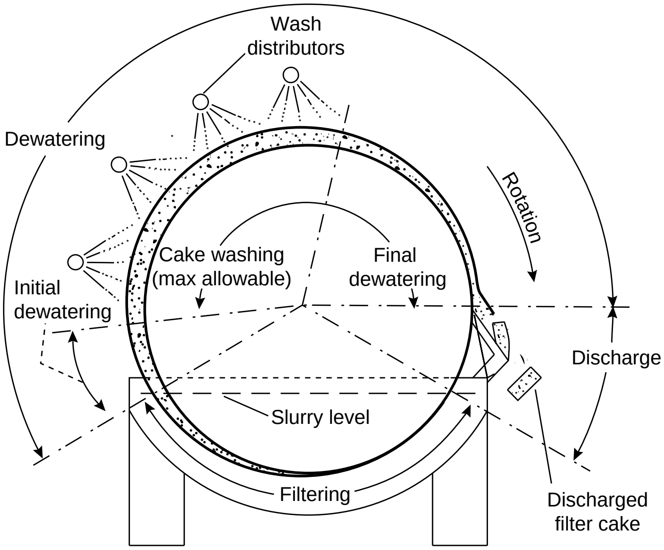


Figure 10.13. Drum filter

Disc filters (pressure and vacuum operation)

Disc filters are similar in principle to rotary filters, but consist of several thin discs mounted on a shaft, in place of the drum. This gives a larger effective filtering area on a given floor area, and vacuum disc filters are used in preference to drum filters where space is restricted. At sizes above approximately 25 m^2 filtration area, disc filters are cheaper; but their applications are more restricted, as they are not as suitable for the application of wash water, or precoating.

Belt filters (vacuum operation) (Figure 10.14)

A belt filter consists of an endless reinforced rubber belt, with drainage hole along its centre, which supports the filter medium. The belt passes over a stationary suction box, into which the filtrate is sucked. Slurry and wash water are sprayed on to the top of the belt.

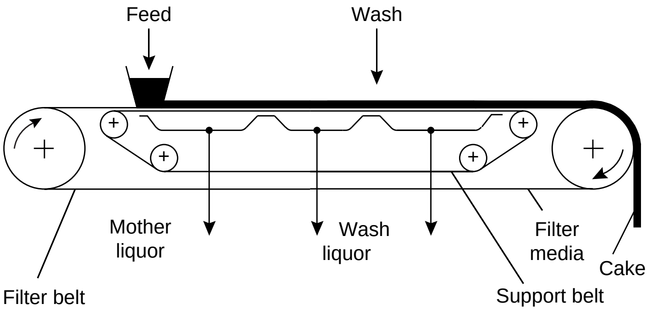


Figure 10.14. Belt filter

Horizontal pan filters (vacuum operation) (Figure 10.15)

This type is similar in operation to a vacuum Nutsche filter. It consists of shallow pans with perforated bases, which support the filter medium. By arranging a series of pans around the circumference of a rotating wheel, the operation of filtering, washing, drying and discharging can be made automatic.

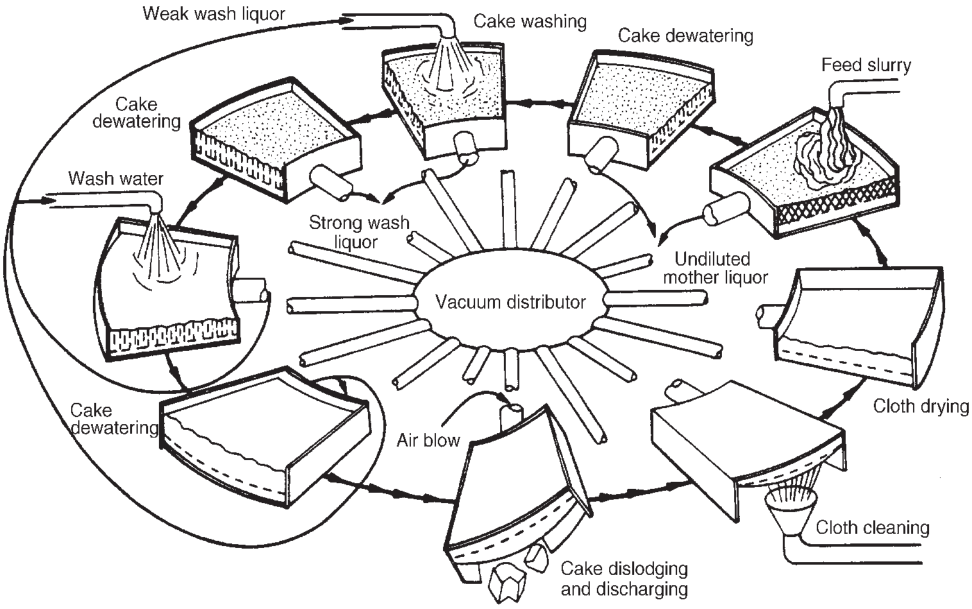


Figure 10.15. Pan filters

Centrifugal filters

Centrifugal filters use centrifugal force to drive the filtrate through the filter cake. The equipment used is described in the next section.

10.4.3. Centrifuges

Centrifuges are classified according to the mechanism used for solids separation:

(a) Sedimentation centrifuges: in which the separation is dependent on a difference in density between the solid and liquid phases (solid heavier).
(b) Filtration centrifuges: which separate the phases by filtration. The walls of the centrifuge basket are porous, and the liquid filters through the deposited cake of solids and is removed.

The choice between a sedimentation or filtration centrifuge for a particular application will depend on the nature of the feed and the product requirements.

The main factors to be considered are summarised in Table 10.4. As a general rule, sedimentation centrifuges are used when it is required to produce a clarified liquid, and filtration centrifuges to produce a pure, dry, solid.

Table 10.4. Selection of sedimentation or filter centrifuge

Factor	Sedimentation	Filtration
Solids size, fine		x
Solids size, >150 μm	x	
Compressible cakes	x	
Open cakes		x
Dry cake required		x
High filtrate clarity	x	
Crystal breakage problems		x
Pressure operation		
High-temperature operation	will depend on the type of centrifuge used	

A variety of centrifugal filter and sedimenter designs is used. The main types are listed in Table 10.5. They can be classified by a number of design and operating features, such as:

1. Mode of operation — batch or continuous.
2. Orientation of the bowl/basket — horizontal or vertical.
3. Position of the suspension and drive — overhung or underhung.
4. Type of bowl — solid, perforated basket, disc bowl.
5. Method of solids cake removal.
6. Method of liquid removal.

Descriptions of the various types of centrifuges and their fields of application can be found in various handbooks, in a book by Leung (1998) and articles by Ambler (1971) and Linley (1984).

The fields of application of each type, classified by the size range of the solid particles separated, are given in Figure 10.16. A similar selection chart is given by Schroeder (1998).

Sedimentation centrifuges

There are four main types of sedimentation centrifuge:

Table 10.5. Centrifuge types (after Sutherland, 1970)

Sedimentation	Filtration-fixed bed
Laboratory	Vertical basket
Bottle	Manual discharge
Ultra	Bag discharge
	Knife discharge
Tubular bowl	Horizontal basket
	Inclined basket
Disc	
Batch bowl	
Nozzle discharge	
Valve discharge	Filtration-moving bed
Opening bowl	
Imperforate basket	Conical bowl
Manual discharge	Wide angle
Skimmer discharge	Vibrating
	Torsional
	Tumbling
Scroll discharge	Scroll discharge
Horizontal	
Cantilevered	Cylindrical bowl
Vertical	Scroll discharge
Screen bowl	Pusher

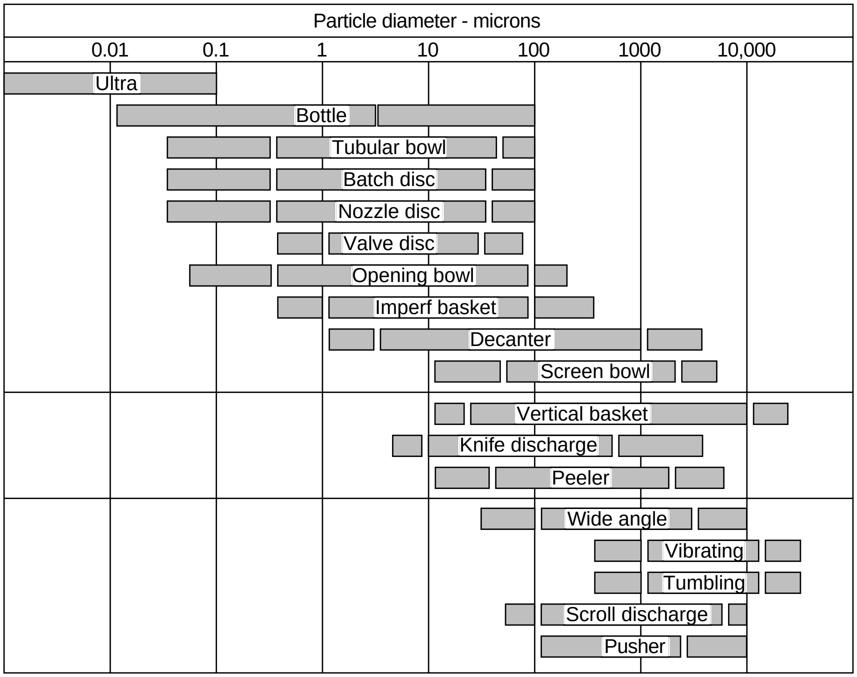


Figure 10.16. Classification of centrifuges by particle size (after Sutherland, 1970)

1. Tubular bowl (Figure 10.17)

High-speed, vertical axis, tubular bowl centrifuges are used for the separation of immiscible liquids, such as water and oil, and for the separation of fine solids. The bowl is driven at speeds of around 15,000 rpm (250 Hz) and the centrifugal force generated exceeds 130,000 N.

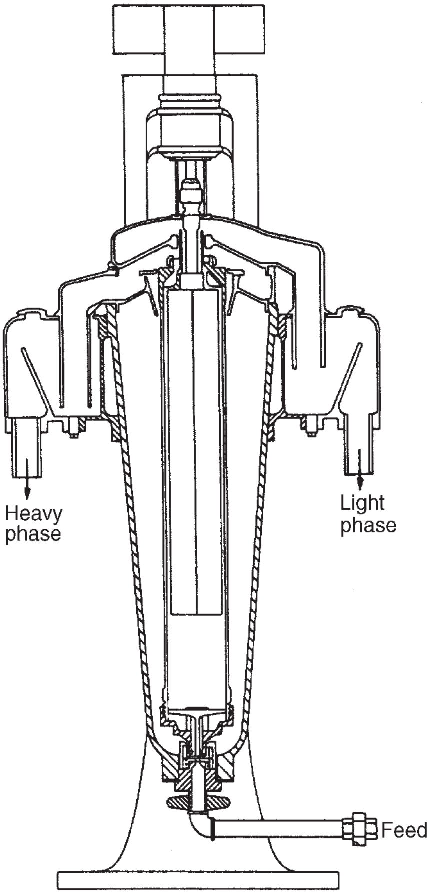


Figure 10.17. Tubular Bowl centrifuge

2. Disc bowl (Figure 10.18)

The conical discs in a disc bowl centrifuge split the liquid flow into a number of very thin layers, which greatly increases the separating efficiency. Disc bowl centrifuges are used for separating liquids and fine solids, and for solids classification.

3. Scroll discharge

In this type of machine the solids deposited on the wall of the bowl are removed by a scroll (a helical screw conveyer) which revolves at a slightly different speed from the

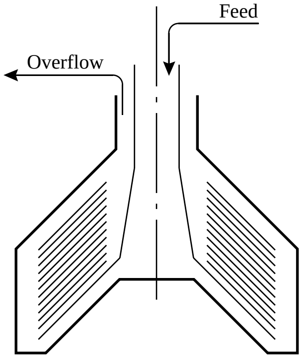


Figure 10.18. Disc bowl centrifuge

bowl. Scroll discharge centrifuges can be designed so that solids can be washed and relatively dry solids be discharged.

4. Solid bowl batch centrifuge

The simplest type; similar to the tubular bowl machine type but with a smaller bowl length to diameter ratio (less than 0.75). The tubular bowl type is rarely used for solids concentrations above 1 per cent by volume. For concentrations between 1 to 15 per cent, any of the other three types can be used. Above 15 per cent, either the scroll discharge type or the batch type may be used, depending on whether continuous or intermittent operation is required.

Sigma theory for sedimentation centrifuges

The basic equations describing sedimentation in a centrifugal field have been developed in Volume 2, Chapter 9. In that discussion the term *sigma* (Σ) is introduced, which can be used to define the performance of a centrifuge independently of the physical properties of the solid-fluid system. The sigma value of a centrifuge, normally expressed in cm^2, is equal to the cross-sectional area of a gravity settling tank having the same clarifying capacity.

This approach to describing centrifuge performance has become known as the "sigma theory". It provides a means for comparing the performance of sedimentation centrifuges and for scaling up from laboratory and pilot scale tests; see Ambler (1952) and Trowbridge (1962).

In the general case, it can be shown that:

$$Q = 2u_g\Sigma \tag{10.1}$$

and (where Stokes' law applies)

$$u_g = \frac{\Delta\rho d_s^2 g}{18\mu} \tag{10.2}$$

Note: The factor of 2 is included in equation 10.1 as d_s is the *cut-off* size, 50 per cent of particles of this size will be removed in passage through the centrifuge.

where Q = volumetric flow of liquid through the centrifuge, m^3/s,
u_g = terminal velocity of the solid particle settling under gravity through the liquid, m/s,
Σ = sigma value of the centrifuge, m^2,
$\Delta\rho$ = density difference between solid and liquid, kg/m^3
d_s = the diameter of the solid particle, *the cut-off* size, m ($\mu m \times 10^{-6}$),
μ = viscosity of the liquid, $Nm^{-2}s$.
g = gravitational acceleration, 9.81 m/s^2,

Morris (1966) gives a method for the selection of the appropriate type of sedimentation centrifuge for a particular application based on the ratio of the liquid overflow to sigma value (Q/Σ). His values for the operating range of each type, and their approximate efficiency rating, are given in Table 10.6. The efficiency term is used to account for the different amounts by which the various designs differ from the theoretical sigma values given by equation 10.1. Sigma values depend solely on the geometrical configuration and speed of the centrifuge. Details of the calculation for various types are given by Ambler (1952). To use Table 10.6, it is necessary to know the feed rate of slurry (and hence the liquid overflow Q), the density of the liquid and solid, the liquid viscosity; and the diameter of the particle for, say, a 98 per cent size removal. The use of Table 10.6 is illustrated in Example 10.1.

Table 10.6. Selection of sedimentation centrifuges

Type	Approximate efficiency (%)	Normal operating range Q, m^3/h at Q/Σ m/s
Tubular bowl	90	0.4 at 5×10^{-8} to 4 at 3.5×10^{-7}
Disc	45	0.1 at 7×10^{-8} to 110 at 4.5×10^{-7}
Solid bowl (scroll discharge)	60	0.7 at 1.5×10^{-6} to 15 at 1.5×10^{-5}
Solid bowl (basket)	75	0.4 at 5×10^{-6} to 4 at 1.5×10^{-4}

A selection guide for sedimentation centrifuges by Lavanchy *et al.* (1964), which includes other types of solid-liquid separators, is shown in Figure 10.19, adapted to SI units.

Example 10.1

A precipitate is to be continuously separated from a slurry. The solids concentration is 5 per cent and the slurry feed rate 5.5 m^3/h. The relevant physical properties at the system operating temperature are:
liquid density 1050 kg/m^3, viscosity 4 cp ($mNm^{-2}s$),
solid density 2300 kg/m^3, "cut-off" particle size 10 $\mu m = 10 \times 10^{-6}$ m.

Solution

$$\text{Overflow rate, } Q = 0.95 \times 5.5 = 5.23 \text{ m}^3/\text{h}$$
$$= \frac{5.13}{3600} = 1.45 \times 10^{-3} \text{ m}^3/\text{s}$$
$$\Delta\rho = 2300 - 1050 = 1250 \text{ kg/m}^3$$

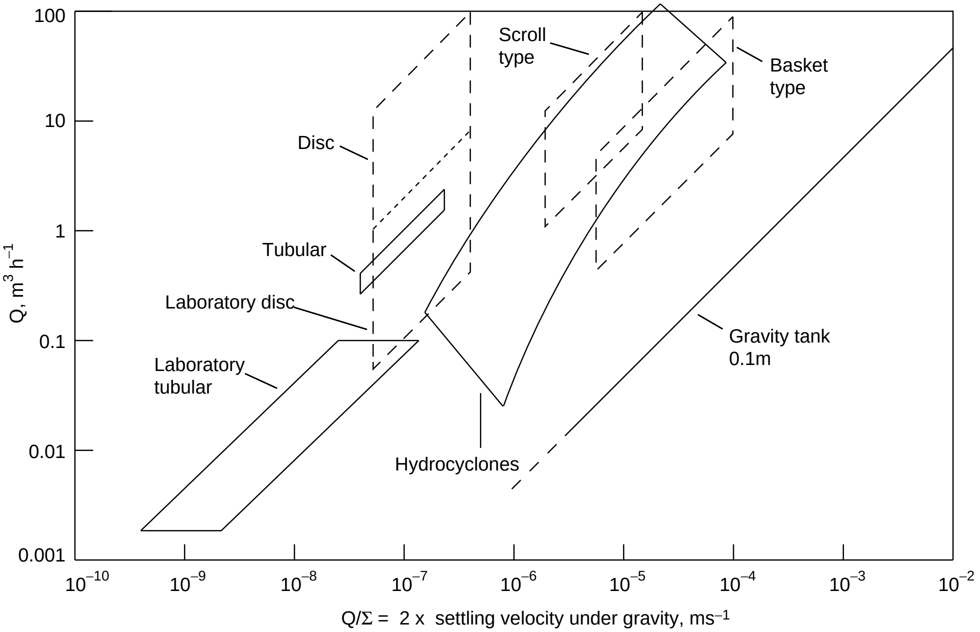


Figure 10.19. Performance of sedimentation equipment (after Lavanchy *et al.*, 1964)

From equations 10.1 and 10.2

$$\frac{Q}{\Sigma} = 2 \times \frac{1250(10 \times 10^{-6})^2}{18 \times 4 \times 10^{-3}} \times 9.81 = 3.4 \times 10^{-5}$$

From Table 10.6 for a Q of 5.23 m^3/h at a Q/Σ of 3.4×10^{-5} a solid bowl basket type should be used.

To obtain an idea of the size of the machine needed the sigma value can be calculated using the efficiency value from Table 10.6.

From equation 10.1:

$$\Sigma = \frac{Q}{eff. \times 2u_g} = \frac{1.45 \times 10^{-3}}{0.75 \times 3.4 \times 10^{-5}}$$

$$= \underline{\underline{56.9 \text{ m}^2}}$$

The sigma value is the equivalent area of a gravity settler that would perform the same separation as the centrifuge.

Filtration centrifuges (centrifugal filters)

It is convenient to classify centrifugal filters into two broad classes, depending on how the solids are removed: fixed bed or moving bed.

In the fixed-bed type, the cake of solids remains on the walls of the bowl until removed manually, or automatically by means of a knife mechanism. It is essentially cyclic in operation. In the moving-bed type, the mass of solids is moved along the bowl by the action of a scroll (similar to the solid-bowl sedimentation type); or by a ram (pusher type); or by a vibration mechanism; or by the bowl angle. Washing and drying zones can be incorporated into the moving bed type.

Bradley (1965) has grouped the various types into the family tree shown in Figure 10.20.

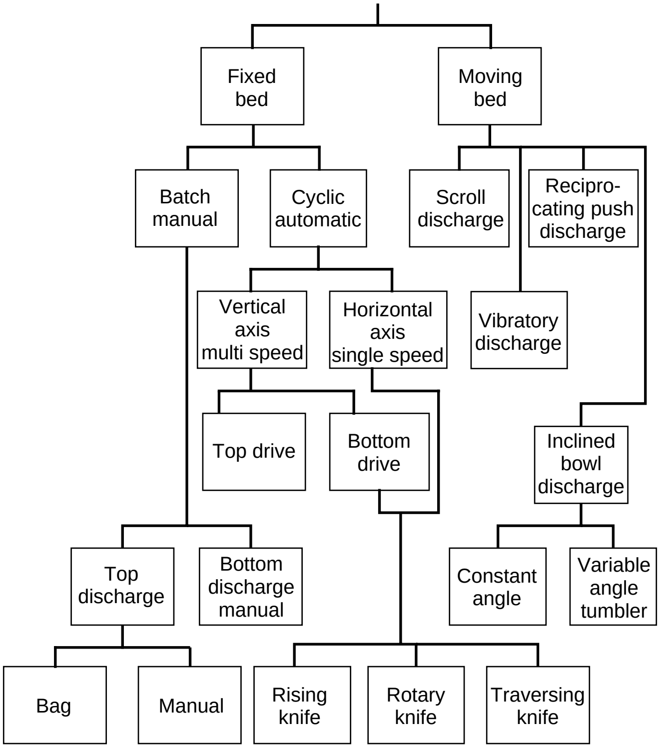
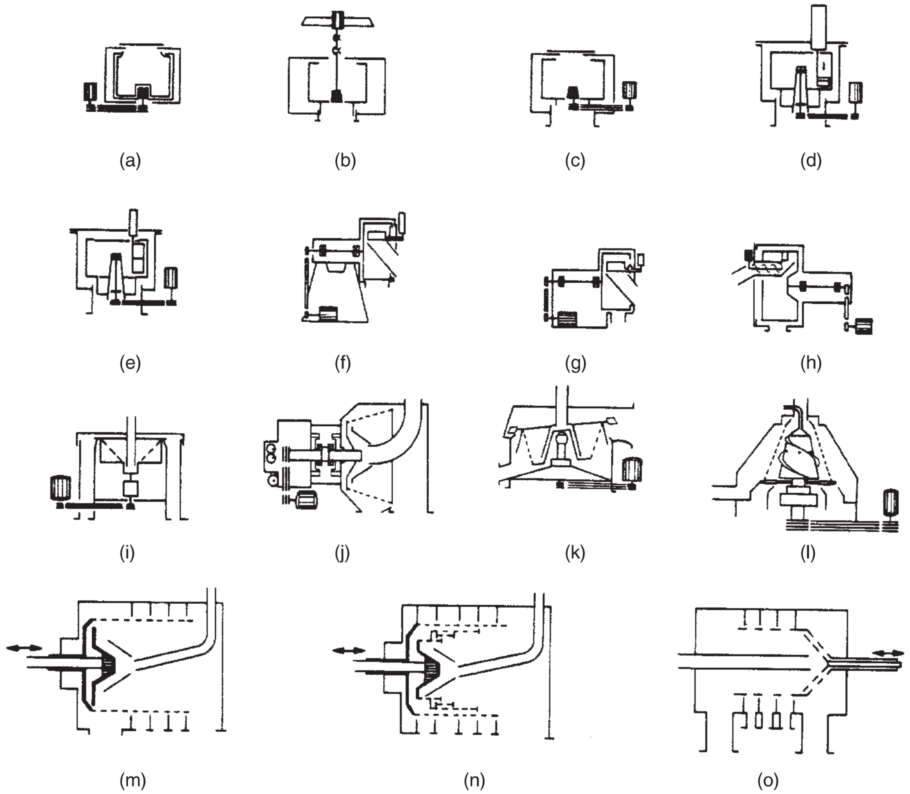


Figure 10.20. Filtration centrifuge family tree (after Bradley, 1965a)

Schematic diagrams of the various types are shown in Figure 10.21. The simplest machines are the basket types (Figures 10.21*a*, *b*, *c*), and these form the basic design from which the other types have been developed (Figures 10.21*d* to *o*).

The various arrangements of knife mechanisms used for automatic removal of the cake are shown in Figures 10.21*d* to *h*. The bottom discharge-type machines (Figures 10.21*d*, *e*) can be designed for variable speed, automatic discharge; and are suitable for use with fragile, or plate or needle-shaped crystals, where it is desirable to avoid breakage or compaction of the bed. They can be loaded and discharged at low speeds, which reduces breakage and compaction of the cake. The single-speed machines (Figures 10.21*f*, *g*, *h*) are used where cakes are thin, and short cycle times are required. They can be designed for high-temperature and pressure operation. When continuous operation is required, the scroll, pusher, or other self-discharge types are used (Figures 10.21*i* to *o*). The scroll discharge centrifuge is a low-cost, flexible machine, capable of a wide range of applications; but is not suitable for handling fragile materials.



(a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k) (l) (m) (n) (o)

Figure 10.21. Schematic diagrams of filtration centrifuge types (Bradley, 1965) (*a*) Bottom drive batch basket with bag (*b*) Top drive bottom discharge batch basket (*c*) Bottom drive bottom discharge batch basket (*d*) Bottom drive automatic basket, rising knife (*e*) Bottom drive automatic basket, rotary knife (*f*) Single-reversing knife rising knife (*g*) Single-speed automatic rotary knife (*h*) Single-speed automatic traversing knife (*i*) Inclined wall self-discharge (*j*) Inclined vibrating wall self-discharge (*k*) Inclined "tumbling" wall self-discharge (*l*) Inclined wall scroll discharge (*m*) Traditional single-stage pusher (*n*) Traditional multi-stage pusher (*o*) Conical pusher with de-watering cone

It is normally used for coarse particles, where some contamination of the filtrate with fines can be tolerated.

The capacity of filtration centrifuges is very dependent on the solids concentration in the feed. For example, at 10 per cent feed slurry concentration 9 kg of liquid will be centrifuged for every 1 kg of solids separated; whereas with a 50 per cent solids concentration the quantity will be less than 1 kg. For dilute slurries it is well worth considering using some form of pre-concentration; such as gravity sedimentation or a hydrocyclone.

10.4.4. Hydrocyclones (liquid-cyclones)

Hydrocyclones are used for solid-liquid separations; as well as for solids classification, and liquid-liquid separation. It is a centrifugal device with a stationary wall, the centrifugal force being generated by the liquid motion. The operating principle is basically the same as that of the gas cyclone described in Section 10.8.3, and in Volume 2, Chapter 8. Hydrocyclones are simple, robust, separating devices, which can be used over the particle size range from 4 to 500 μm. They are often used in groups, as illustrated in Figure 10.24*b*. The design and application of hydrocyclones is discussed fully in books by Abulnaga (2002) and Svarovsky and Thew (1992). Design methods and charts are also given by Zanker (1977), Day *et al.* (1997) and Moir (1985).

The nomographs by Zanker can be used to make a preliminary estimate of the size of cyclone needed. The specialist manufacturers of hydrocyclone equipment should be consulted to determine the best arrangements and design for a particular application.

Zanker's method is outlined below and illustrated in Example 10.2. Figure 10.23 is based on an empirical equation by Bradley (1960):

$$d_{50} = 4.5\left[\frac{D_c^3\mu}{L^{1.2}(\rho_s - \rho_L)}\right] \tag{10.3}$$

where d_{50} = the particle diameter for which the cyclone is 50 per cent efficient, μm,
D_c = diameter of the cyclone chamber, cm,

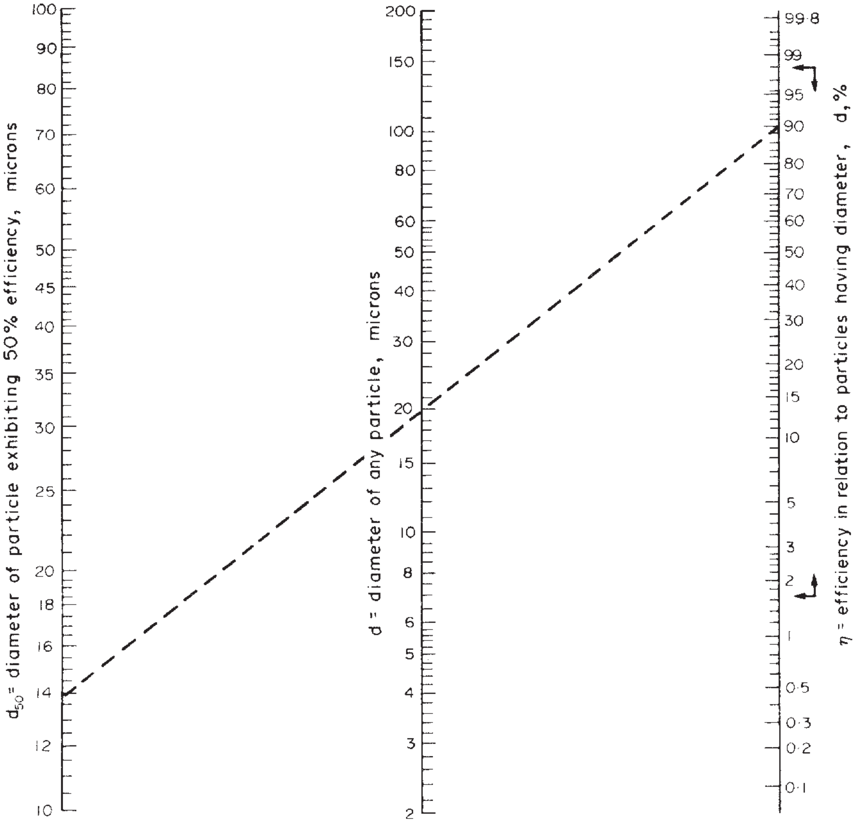


Figure 10.22. Determination of d_{50} from the desired particle separation (Equation 10.3, Zanker, 1977) (Example 10.2)

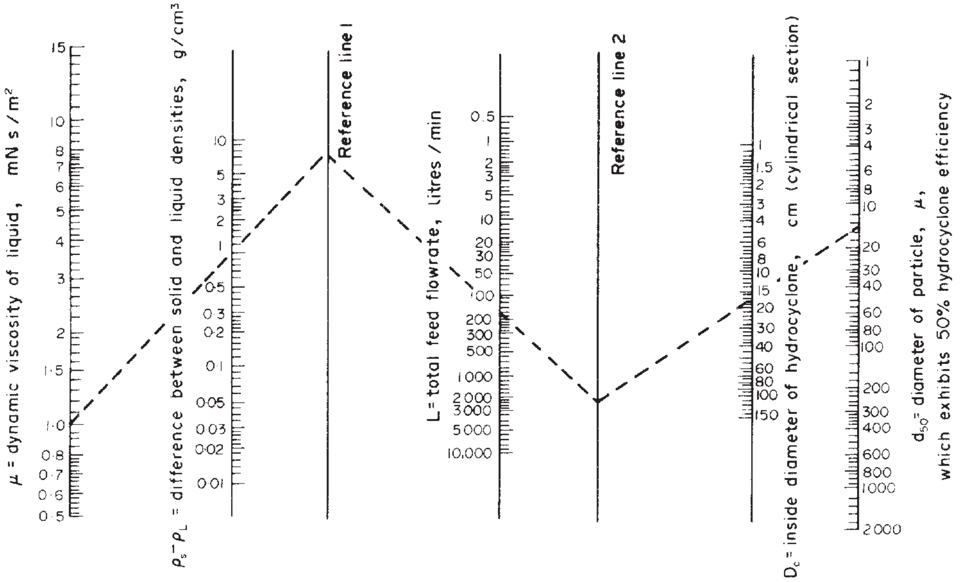
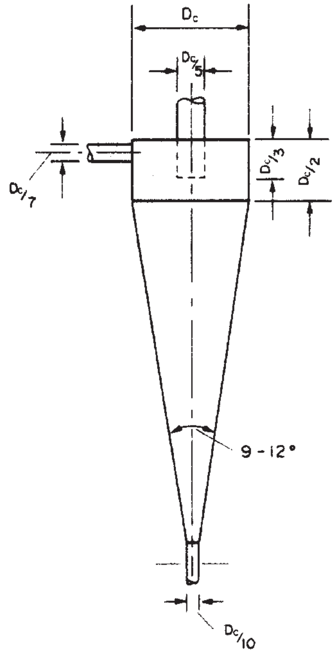
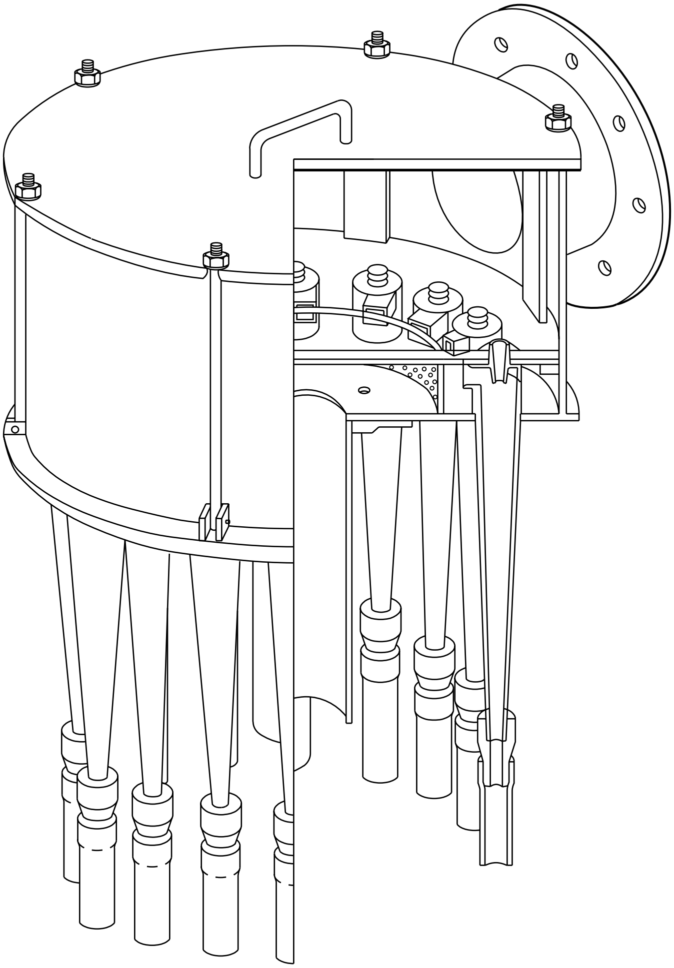


Figure 10.23. Chamber dia. D_c from flow-rate, physical properties, and d_{50} particle size (Equation 10.4, Zanker, 1977) (Example 10.2)



(a)

Figure 10.24. (*a*) Hydrocyclone-typical proportions



(b)

Figure 10.24. (*b*) A "Clog" assembly of 16 × 2 in (50 mm) diameter hydrocyclone. (Courtesy of Richard Mozley Ltd.)

μ = liquid viscosity, centipoise (mN s/m^2),
L = feed flow rate, l/min,
ρ_L = density of the liquid, g/cm^3,
ρ_s = density of the solid, g/cm^3.

The equation gives the chamber diameter required to separate the so-called d_{50} particle diameter, as a function of the slurry flow rate and the liquid and solid physical properties. The d_{50} particle diameter is the diameter of the particle, 50 per cent of which will appear in the overflow, and 50 per cent in the underflow. The separating efficiency for other particles is related to the d_{50} diameter by Figure 10.22, which is based on a formula by Bennett (1936).

$$\eta = 100\left[1 - e^{-(d/d_{50} - 0.115)^3}\right] \qquad (10.4)$$

where η = the efficiency of the cyclone in separating any particle of diameter d, per cent,

d = the selected particle diameter, μm.

The method applies to hydrocyclones with the proportions shown in Figure 10.24.

Example 10.2

Estimate the size of hydrocyclone needed to separate 90 per cent of particles with a diameter greater than 20 μm, from 10 m^3/h of a dilute slurry.

Physical properties: solid density 2000 kg/m^3, liquid density 1000 kg/m^3, viscosity 1 mN s/m^2

Solution

$$\text{Flow-rate} = \frac{10 \times 10^3}{60} = 166.7\,\text{l/min}$$

$$(\rho_s - \rho_L) = 2.0 - 1.0 = 1.0\ \text{g/cm}^3$$

From Figure 10.22, for 90 per cent removal of particles above 20 μm

$$d_{50} = 14\ \mu\text{m}$$

From Figure 10.23, for $\mu = 1$ mN s/m^2, $(\rho_s - \rho_L)$ = 1.0 g/cm^3, L = 167/min

$$D_c = \underline{\underline{16\ \text{cm}}}$$

10.4.5. Pressing (expression)

Pressing, in which the liquid is squeezed (expressed) from a mass of solids by compression, is used for certain specialised applications. Pressing consumes a great deal of energy, and should not be used unless no other separating technique is suitable. However, in some applications dewatering by pressing can be competitive with drying.

Presses are of two basic types: hydraulic batch presses and screw presses. Hydraulic presses are used for extracting fruit juices, and screw presses for dewatering materials; such as paper pulp, rubbish and manure. The equipment used is described in the handbooks; Perry *et al.* (1997).

10.4.6. Solids drying

Drying is the removal of water, or other volatile liquids, by evaporation. Most solid materials require drying at some stage in their production. The choice of suitable drying equipment cannot be separated from the selection of the upstream equipment feeding the drying stage.

Table 10.7. Dryer selection

Mode of operation	Generic type	Feed condition			Specific dryer types	Jacketed	Suitable for heat-sensitive materials	Suitable for vacuum service	Retention or cycle time	Heat transfer method	Capacity	Typical evaporation capacity
		1	2	3								
Batch	Stationary		⟷	⟷	1. Shelf 2. Cabinet 3. Compartment	Yes	Yes	Yes	6.48 h	Radiant and conduction	Limited	0.15–1.0 kg/hm² heat transfer area
			⟷	⟷	Truck	No	Yes	No	6.48 h	Convection	Limited	0.15–1.0
		⟷	⟷		1. Kettle 2. Pan	Yes	No	Yes	3.12 h	Conduction	Limited	1.5–15
			⟷		Rotary shell	Yes	Yes	Yes	4.48 h	Conduction	Limited	0.5–12
			⟷		Rotary internal	Yes	Yes	Yes	4.48 h	Conduction	Limited	0.5–12
			⟷		Double cone	Yes	Yes	Yes	3.12 h	Conduction	Limited	0.5–12
Continuous	Drum	⟷			1. Single drum 2. Double drum 3. Twin drum	No	Yes	Yes	Very short	Conduction	Medium	5–50
	Rotary		⟷		Rotary direct heat	No	No	No	Long	Convection	High	3–110 kg/hm³ dryer volume
			⟷		Rotary, indirect heat	No	No	No	Long	Conduction	Medium	15–200
			⟷		Rotary, steam tube	No	Depends on material	No	Long	Conduction	High	15–200
			⟷		Rotary, direct-indirect heat	No	No	No	Long	Conduction Convection	High	50–150
			⟷		Louver	No	Depends on material	No	Long	Convection	High	5–240
			⟷	⟷	Tunnel belt, screen	No	Yes	No	Long	Convection	Medium	1.5–35
	Conveyor		⟷		Rotary shelf	Yes	Depends on material	No	Medium	Conduction Convection	Medium	0.5–10 kg/hm²
			⟷		Trough	Yes	Depends on material	Yes	Varies	Conduction	Medium	0.5–15
			⟷		Vibrating	Yes	Depends on material	No	Medium	Convection Conduction	Medium	0.5–100
			⟷		Turbo	No	Depends on material	No	Medium	Convection	Medium	1–10
	Suspended particle	⟷			Spray	No	Yes	No	Short	Convection	High	1.5–50 kg/hm³
			⟷		Flash	No	Yes	No	Short	Convection	High	–
			⟷		Fluid bed	No	Yes	No	Short	Convection	Medium	–

⟷ = applicable to feed conditions noted

Key to feed conditions:

1. Solutions, colloidal suspensions and emulsions, pumpable solids suspensions, pastes and sludges.
2. Free-flowing powders, granular, crystalline or fibrous solids that can withstand mechanical handling.
3. Solids incapable of withstanding mechanical handling.

The overriding consideration in the selection of drying equipment is the nature and concentration of the feed. Drying is an energy-intensive process, and the removal of liquid by thermal drying will be more costly than by mechanical separation techniques.

Drying equipment can be classified according to the following design and operating features:

1. Batch or continuous.
2. Physical state of the feed: liquid, slurry, wet solid.
3. Method of conveyance of the solid: belt, rotary, fluidised.
4. Heating system: conduction, convection, radiation.

Except for a few specialised applications, hot air is used as the heating and mass transfer medium in industrial dryers. The air may be directly heated by the products of combustion of the fuel used (oil, gas or coal) or indirectly heated, usually by banks of steam-heated finned tubes. The heated air is usually propelled through the dryer by electrically driven fans.

Table 10.7, adapted from a similar selection guide by Parker (1963a), shows the basic features of the various types of solids dryer used in the process industries; and Table 10.8, by Williams-Gardner (1965), shows typical applications.

Batch dryers are normally used for small-scale production and where the drying cycle is likely to be long. Continuous dryers require less labour, less floor space; and produce a more uniform quality product.

When the feed is solids, it is important to present the material to the dryer in a form that will produce a bed of solids with an open, porous, structure.

For pastes and slurries, some form of pretreatment equipment will normally be needed, such as extrusion or granulation.

The main factors to be considered when selecting a dryer are:

1. Feed condition: solid, liquid, paste, powder, crystals.
2. Feed concentration, the initial liquid content.
3. Product specification: dryness required, physical form.
4. Throughput required.
5. Heat sensitivity of the product.
6. Nature of the vapour: toxicity, flammability.
7. Nature of the solid: flammability (dust explosion hazard), toxicity.

The drying characteristics of the material can be investigated by laboratory and pilot plant tests; which are best carried out in consultation with the equipment vendors.

The theory of drying processes is discussed in Volume 2, Chapter 16. Full descriptions of the various types of dryer and their applications are given in that chapter and in Perry *et al.* (1997) and Walas (1990). Only brief descriptions of the principal types will be given in this section.

The basic types used in the chemical process industries are: tray, band, rotary, fluidised, pneumatic, drum and spray dryers.

Tray dryers (Figure 10.25)

Batch tray dryers are used for drying small quantities of solids, and are used for a wide range of materials.

Table 10.8. Dryer applications

Dryer type	*System*	*Feed form*	*Typical products*
Batch ovens	Forced convection	Paste, granules, extrude cake	Pigment dyestuffs, pharmaceuticals, fibres
	Vacuum	Extrude cake	Pharmaceuticals
„ pan (agitated)	Atmospheric and vacuum	Crystals, granules, powders	Fine chemicals, food products
„ rotary	Vacuum	Crystals, granules solvent recovery	Pharmaceuticals
„ fluid bed	Forced convection	Granular, crystals	Fine chemicals, pharmaceuticals, plastics
„ infra-red	Radiant	Components sheets	Metal products, plastics
Continuous rotary	Convection Direct/indirect Direct Indirect Conduction	Crystals, coarse powders, extrudes, preformed cake lumps, granular paste and fillers, cakes back-mixed with dry product	Chemical ores, food products, clays, pigments, chemicals Carbon black
„ film drum	Conduction	Liquids, suspensions	Foodstuffs, pigment
„ trough	Conduction		Ceramics, adhesives
„ spray	Convection	Liquids, suspensions	Foodstuffs, pharmaceuticals, ceramics, fine chemicals, detergents, organic extracts
„ band	Convection	Preformed solids	Foodstuffs, pigments, chemicals, rubber, clays, ores, textiles
„ fluid bed	Convection	Preformed solids granules, crystals	Ores, coal, clays, chemicals
„ pneumatic	Convection	Preformed pastes, granules, crystals, coarse products	Chemicals, starch, flour, resins, wood-products, food products
„ infra-red	Radiant	Components sheets	Metal products, moulded fibre articles, painted surfaces

The material to be dried is placed in solid bottomed trays over which hot air is blown; or perforated bottom trays through which the air passes.

Batch dryers have high labour requirements, but close control can be maintained over the drying conditions and the product inventory, and they are suitable for drying valuable products.

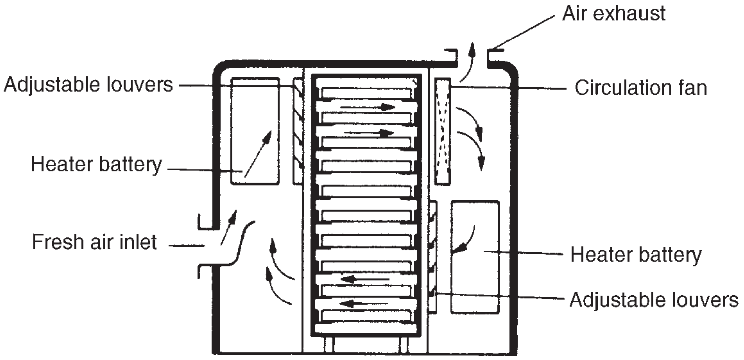


Figure 10.25. Tray dryer

Conveyor dryers (continuous circulation band dryers) (Figure 10.26)

In this type, the solids are fed on to an endless, perforated, conveyor belt, through which hot air is forced. The belt is housed in a long rectangular cabinet, which is divided up into zones, so that the flow pattern and temperature of the drying air can be controlled. The relative movement through the dryer of the solids and drying air can be parallel or, more usually, counter-current.

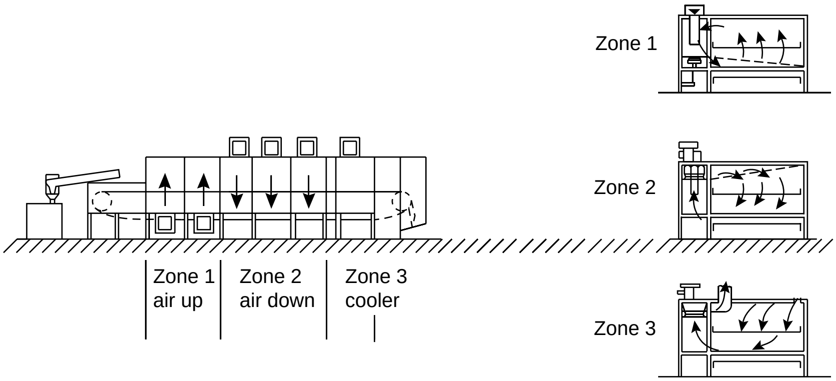


Figure 10.26. Conveyor dryer

This type of dryer is clearly only suitable for materials that form a bed with an open structure. High drying rates can be achieved, with good product-quality control. Thermal efficiencies are high and, with steam heating, steam usage can be as low as 1.5 kg per kg of water evaporated. The disadvantages of this type of dryer are high initial cost and, due to the mechanical belt, high maintenance costs.

Rotary dryer (Figure 10.27)

In rotary dryers the solids are conveyed along the inside of a rotating, inclined, cylinder and are heated and dried by direct contact with hot air gases flowing through the cylinder. In some, the cylinders are indirectly heated.

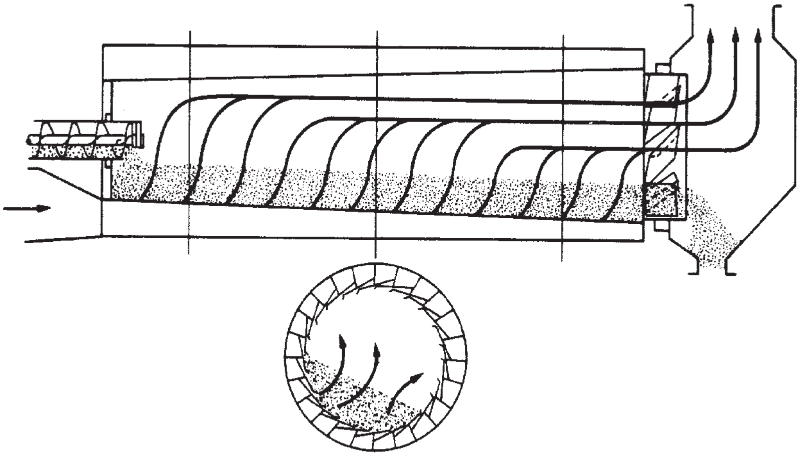


Figure 10.27. Rotary dryer

Rotating dryers are suitable for drying free-flowing granular materials. They are suitable for continuous operation at high throughputs; have a high thermal efficiency and relatively low capital cost and labour costs. Some disadvantages of this type are: a non-uniform residence time, dust generation and high noise levels.

Fluidised bed dryers (Figure 10.28)

In this type of dryer, the drying gas is passed through the bed of solids at a velocity sufficient to keep the bed in a fluidised state; which promotes high heat transfer and drying rates.

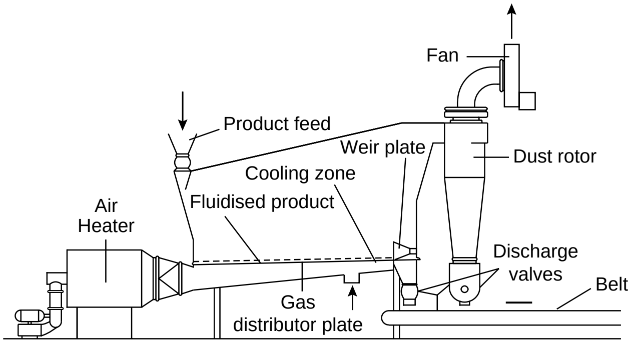


Figure 10.28. Fluidised bed dryer

Fluidised bed dryers are suitable for granular and crystalline materials within the particle size range 1 to 3 mm. They are designed for continuous and batch operation.

The main advantages of fluidised dryers are: rapid and uniform heat transfer; short drying times, with good control of the drying conditions; and low floor area requirements. The power requirements are high compared with other types.

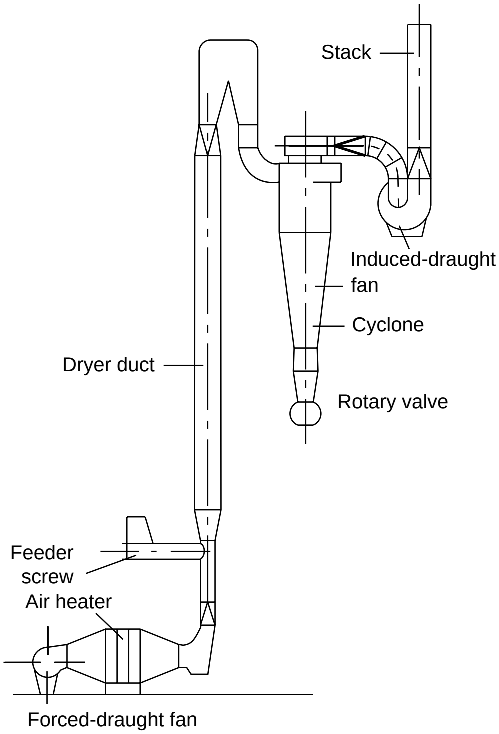


Figure 10.29. Pneumatic dryer

Pneumatic dryers (Figure 10.29)

Pneumatic dryers, also called flash dryers, are similar in their operating principle to spray dryers. The product to be dried is dispersed into an upward-flowing stream of hot gas by a suitable feeder. The equipment acts as a pneumatic conveyor and dryer. Contact times are short, and this limits the size of particle that can be dried. Pneumatic dryers are suitable for materials that are too fine to be dried in a fluidised bed dryer but which are heat sensitive and must be dried rapidly. The thermal efficiency of this type is generally low.

Spray dryers (Figure 10.30)

Spray dryers are normally used for liquid and dilute slurry feeds, but can be designed to handle any material that can be pumped. The material to be dried is atomised in a nozzle, or by a disc-type atomiser, positioned at the top of a vertical cylindrical vessel. Hot air flows up the vessel (in some designs downward) and conveys and dries the droplets. The liquid vaporises rapidly from the droplet surface and open, porous particles are formed. The dried particles are removed in a cyclone separator or bag filter.

The main advantages of spray drying are the short contact time, making it suitable for drying heat-sensitive materials, and good control of the product particle size, bulk density, and form. Because the solids concentration in the feed is low the heating requirements will be high. Spray drying is discussed in a book by Masters (1991).

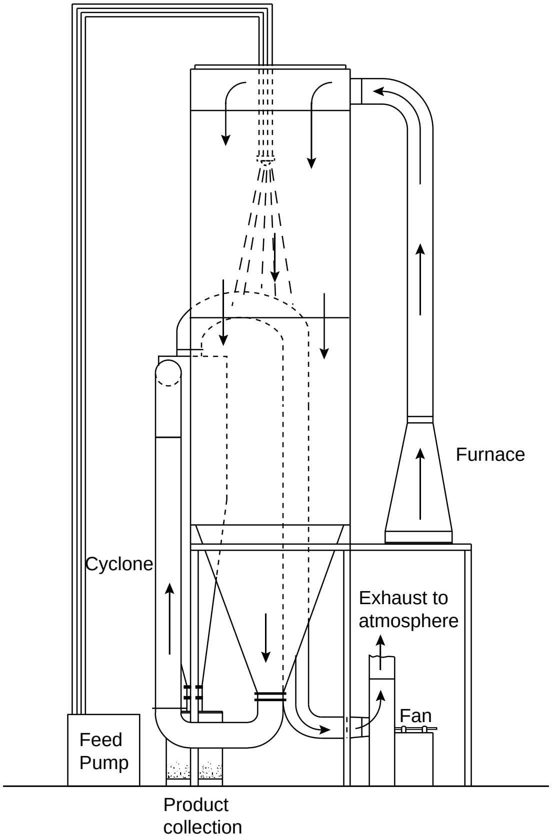


Figure 10.30. Spray dryer

Rotary drum dryers (Figure 10.31)

Drum dryers are used for liquid and dilute slurry feeds. They are an alternative choice to spray dryers when the material to be dried will form a film on a heated surface, and is not heat sensitive.

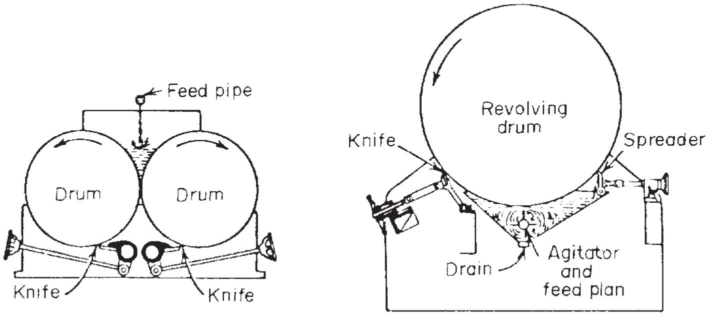


Figure 10.31. Rotary drum dryers

They consist essentially of a revolving, internally heated, drum, on which a film of the solids is deposited and dried. The film is formed either by immersing part of the drum in a trough of the liquid or by spraying, or splashing, the feed on to the drum surface; double drums are also used in which the feed is fed into the "nip" formed between the drums.

The drums are usually heated with steam, and steam economies of 1.3 kg steam per kg of water evaporated are typically achieved.

10.5. SEPARATION OF DISSOLVED SOLIDS

On an industrial scale, evaporation and crystallisation are the main processes used for the recovery of dissolved solids from solutions.

Membrane filtration processes, such as reverse osmosis, and micro and ultra filtration, are used to "filter out" dissolved solids in certain applications; see Table 10.9. These specialised processes will not be discussed in this book. A comprehensive description of the techniques used and their applications is given in Volume 2, Chapter 8; see also: Scott and Hughes (1995), Cheryan (1986), McGregor (1986) and Porter (1997).

Table 10.9. Membrane filtration process

Process	Approximate size range (m)	Applications
Microfiltration	10^{-8} to 10^{-4}	pollen, bacteria, blood cells
Ultrafiltration	10^{-9} to 10^{-8}	proteins and virus
Nanofiltration	5×10^{-9} to 15×10^{-9}	water softening
Reverse osmosis	10^{-10} to 10^{-9}	desalination
Dialysis	10^{-9} to molecules	blood purification
Electrodialysis	10^{-9} to molecules	separation of electrolytes
Pervaporation	10^{-9} to molecules	dehydration of ethanol
Gas permeation	10^{-9} to molecules	hydrogen recovery, dehydration

10.5.1. Evaporators

Evaporation is the removal of a solvent by vaporisation, from solids that are not volatile. It is normally used to produce a concentrated liquid, often prior to crystallisation, but a dry solid product can be obtained with some specialised designs. The general subject of evaporation is covered in Volume 2, Chapter 14. That chapter includes a discussion of heat transfer in evaporators, multiple-effect evaporators, and a description of the principal types of equipment. The selection of the appropriate type of evaporator is discussed by Cole (1984). Evaporation is the subject of a book by Billet (1989).

A great variety of evaporator designs have been developed for specialised applications in particular industries. The designs can be grouped into the following basic types.

Direct-heated evaporators

This type includes solar pans and submerged combustion units. Submerged combustion evaporators can be used for applications where contamination of the solution by the products of combustion is acceptable.

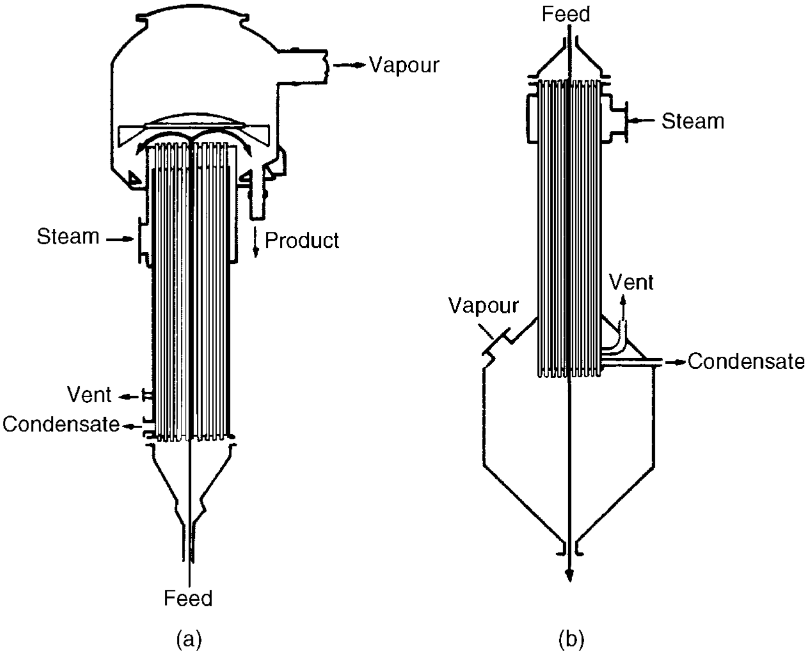


Figure 10.32. Long-tube evaporators (*a*) Rising film (*b*) Falling film

Long-tube evaporators (Figure 10.32)

In this type the liquid flows as a thin film on the walls of a long, vertical, heated, tube. Both falling film and rising film types are used. They are high capacity units; suitable for low viscosity solutions.

Forced-circulation evaporators (Figure 10.33)

In forced circulation evaporators the liquid is pumped through the tubes. They are suitable for use with materials which tend to foul the heat transfer surfaces, and where crystallisation can occur in the evaporator.

Agitated thin-film evaporators (Figure 10.34)

In this design a thin layer of solution is spread on the heating surface by mechanical means. Wiped-film evaporators are used for very viscous materials and for producing solid products. The design and applications of this type of evaporator are discussed by Mutzenburg (1965), Parker (1965) and Fischer (1965).

Short-tube evaporators

Short-tube evaporators, also called callandria evaporators, are used in the sugar industry; see Volume 2.

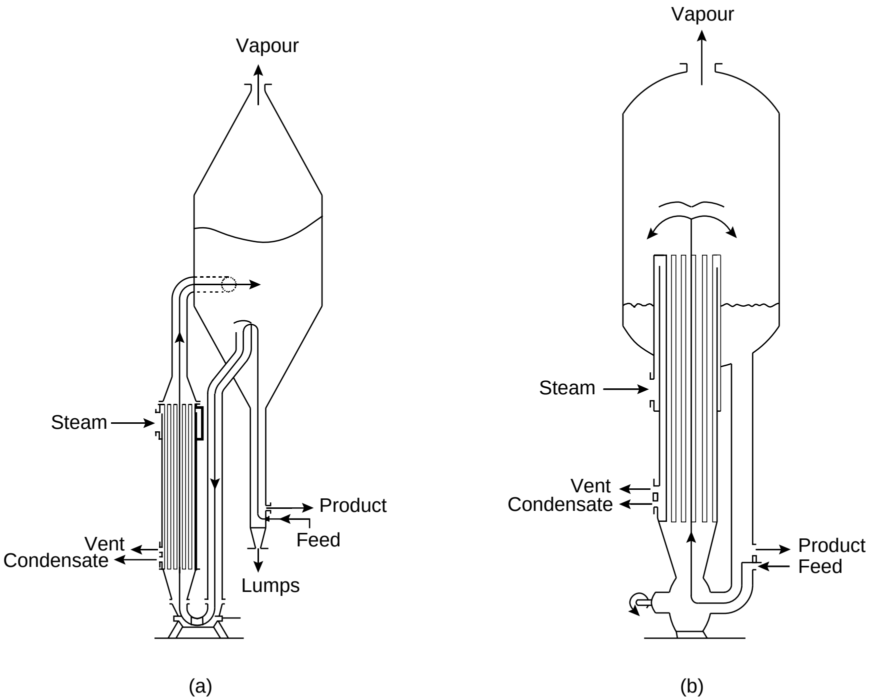


Figure 10.33. Forced-circulation evaporators (*a*) Submerged tube (*b*) Boiling tube

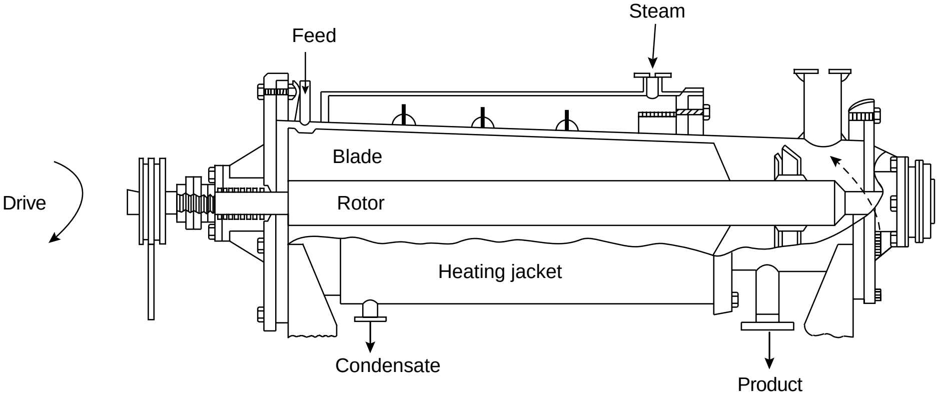


Figure 10.34. Horizontal wiped-film evaporator

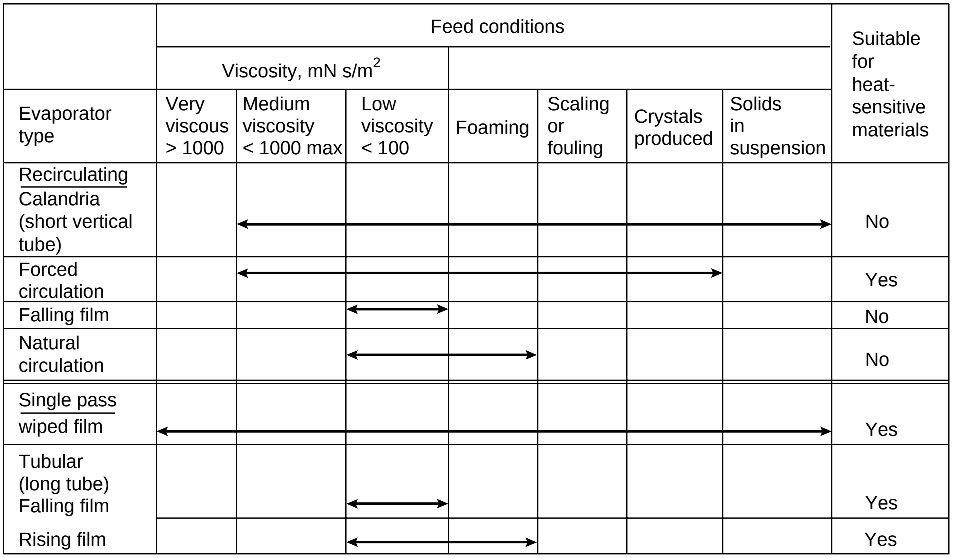
Evaporator selection

The selection of the most suitable evaporator type for a particular application will depend on the following factors:

1. The throughput required.
2. The viscosity of the feed and the increase in viscosity during evaporation.

3. The nature of the product required; solid, slurry, or concentrated solution.
4. The heat sensitivity of the product.
5. Whether the materials are fouling or non-fouling.
6. Whether the solution is likely to foam.
7. Whether direct heating can be used.

A selection guide based on these factors is given in Figure 10.35; see also Parker (1963*b*).



	Feed conditions							Suitable for heat-sensitive materials
	Viscosity, mN s/m^2							
Evaporator type	Very viscous > 1000	Medium viscosity < 1000 max	Low viscosity < 100	Foaming	Scaling or fouling	Crystals produced	Solids in suspension	
Recirculating Calandria (short vertical tube)		←	─	─	─	─	→	No
Forced circulation		←	─	─	─	→		Yes
Falling film			↔					No
Natural circulation			←	→				No
Single pass wiped film	←	─	─	─	─	─	→	Yes
Tubular (long tube) Falling film			↔					Yes
Rising film			←	→				Yes

Figure 10.35. Evaporator selection guide

Auxilliary equipment

Condensers and vacuum pumps will be needed for evaporators operated under vacuum. For aqueous solutions, steam ejectors and jet condensers are normally used. Jet condensers are direct-contact condensers, where the vapour is condensed by contact with jets of cooling water. Indirect, surface condensers, are used where it is necessary to keep the condensed vapour and cooling water effluent separate.

10.5.2. Crystallisation

Crystallisation is used for the production, purification and recovery of solids. Crystalline products have an attractive appearance, are free flowing, and easily handled and packaged. The process is used in a wide range of industries: from the small-scale production of specialised chemicals, such as pharmaceutical products, to the tonnage production of products such as sugar, common salt and fertilisers.

Crystallisation theory is covered in Volume 2, Chapter 15 and in other texts: Mullin (2001) and Jones (2002). Descriptions of the various crystallisers used commercially can be found in these texts and in handbooks: Mersmann (2001), Perry *et al*. (1997) and

Schweitzer (1997). Procedures for the scale-up and design of crystallisers are given by Mersmann (2001), and Mersham (1988), (1984).

Precipitation, which can be considered as a branch of crystallisation, is covered by Sohnel and Garside (1992).

Crystallisation equipment can be classified by the method used to obtain supersaturation of the liquor, and also by the method used to suspend the growing crystals. Supersaturation is obtained by cooling or evaporation. There are four basic types of crystalliser; these are described briefly below.

Tank crystallisers

This is the simplest type of industrial crystallising equipment. Crystallisation is induced by cooling the mother liquor in tanks; which may be agitated and equipped with cooling coils or jackets. Tank crystallisers are operated batchwise, and are generally used for small-scale production.

Scraped-surface crystallisers

This type is similar in principle to the tank type, but the cooling surfaces are continually scraped or agitated to prevent the fouling by deposited crystals and to promote heat transfer. They are suitable for processing high-viscosity liquors. Scraped-surface

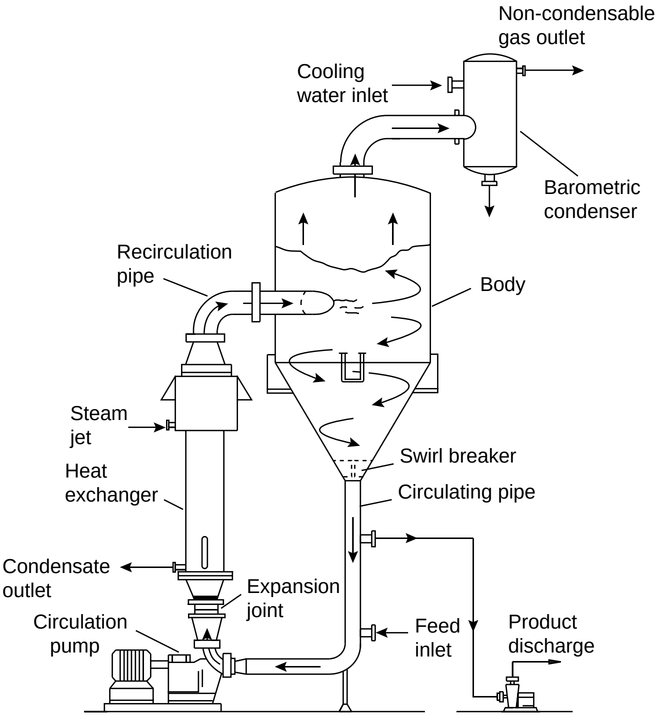


Figure 10.36. Circulating magma crystalliser (evaporative type)

crystallisers can be operated batchwise, with recirculation of the mother liquor, or continuously. A disadvantage of this type is that they tend to produce very small crystals.

Circulating magma crystallisers (Figure 10.36)

In this type both the liquor and growing crystals are circulated through the zone in which supersaturation occurs. Circulating magma crystallisers are probably the most important type of large-scale crystallisers used in the chemical process industry. Designs are available in which supersaturation is achieved by direct cooling, evaporation or evaporative cooling under vacuum.

Circulating liquor crystallisers (Figure 10.37)

In this type only the liquor is circulated through the heating or cooling equipment; the crystals are retained in suspension in the crystallising zone by the up-flow of liquor. Circulating liquor crystallisers produce crystals of regular size. The basic design consists of three components: a vessel in which the crystals are suspended and grow and are removed; a means of producing supersaturation, by cooling or evaporation; and a means of circulating the liquor. The Oslo crystalliser (Figure 10.37) is the archetypical design for this type of crystallising equipment.

Circulating liquor crystallisers and circulating magma crystallisers are used for the large-scale production of a wide range of crystal products.

Typical applications of the main types of crystalliser are summarised in Table 10.10 (see page 440); see also Larson (1978).

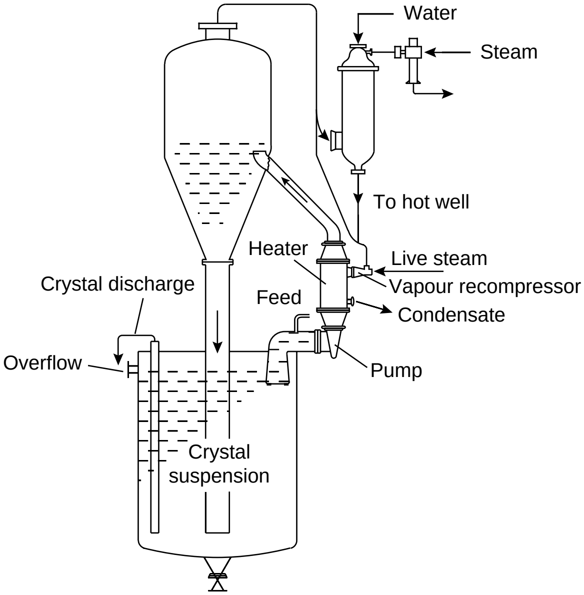


Figure 10.37. Oslo evaporative crystalliser

Table 10.10. Selection of crystallisers

Crystalliser type	Applications	Typical uses
Tank	Batch operation, small-scale production	Fatty acids, vegetable oils, sugars
Scraped surface	Organic compounds, where fouling is a problem, viscous materials	Chlorobenzenes, organic acids, paraffin waxes, naphthalene, urea
Circulating magma	Production of large-sized crystals. High throughputs	Ammonium and other inorganic salts, sodium and potassium chlorides
Circulating liquor	Production of uniform crystals (smaller size than circulating magma). High throughputs.	Gypsum, inorganic salts, sodium and potassium nitrates, silver nitrates

10.6. LIQUID-LIQUID SEPARATION

Separation of two liquid phases, immiscible or partially miscible liquids, is a common requirement in the process industries. For example, in the unit operation of liquid-liquid extraction the liquid contacting step must be followed by a separation stage (Chapter 11, Section 11.16). It is also frequently necessary to separate small quantities of entrained water from process streams. The simplest form of equipment used to separate liquid phases is the gravity settling tank, the decanter. Various proprietary equipment is also used to promote coalescence and improve separation in difficult systems, or where emulsions are likely to form. Centrifugal separators are also used.

10.6.1. Decanters (settlers)

Decanters are used to separate liquids where there is a sufficient difference in density between the liquids for the droplets to settle readily. Decanters are essentially tanks which give sufficient residence time for the droplets of the dispersed phase to rise (or settle) to the interface between the phases and coalesce. In an operating decanter there will be three distinct zones or bands: clear heavy liquid; separating dispersed liquid (the dispersion zone); and clear light liquid.

Decanters are normally designed for continuous operation, but the same design principles will apply to batch operated units. A great variety of vessel shapes is used for decanters, but for most applications a cylindrical vessel will be suitable, and will be the cheapest shape. Typical designs are shown in Figures 10.38 and 10.39. The position of the interface can be controlled, with or without the use of instruments, by use of a syphon take-off for the heavy liquid, Figure 10.38.

The height of the take-off can be determined by making a pressure balance. Neglecting friction loss in the pipes, the pressure exerted by the combined height of the heavy and light liquid in the vessel must be balanced by the height of the heavy liquid in the take-off leg, Figure 10.38.

$$(z_1 - z_3)\rho_1 g + z_3\rho_2 g = z_2\rho_2 g$$

hence

$$z_2 = \frac{(z_1 - z_3)\rho_1}{\rho_2} + z_3 \tag{10.5}$$

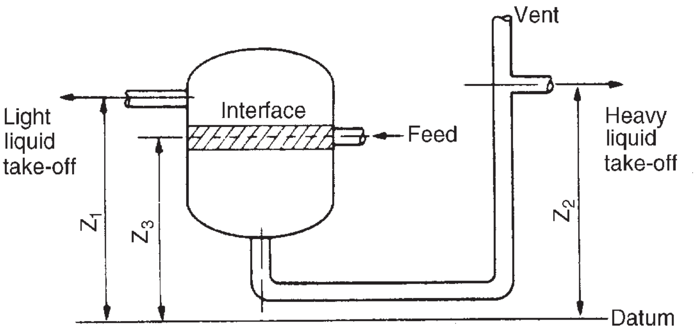


Figure 10.38. Vertical decanter

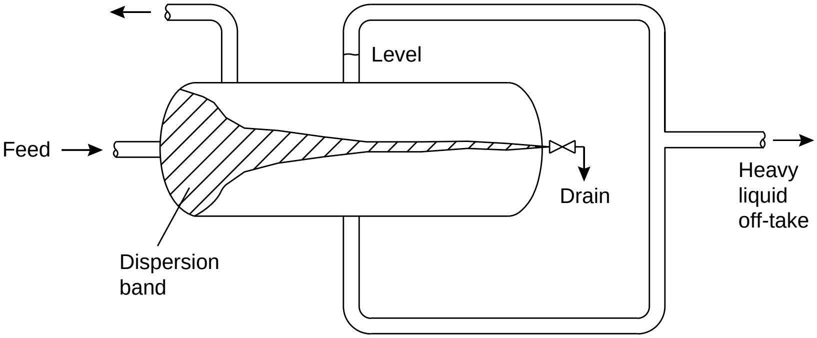


Figure 10.39. Horizontal decanter

where ρ_1 = density of the light liquid, kg/m^3,
ρ_2 = density of the heavy liquid, kg/m^3,
z_1 = height from datum to light liquid overflow, m,
z_2 = height from datum to heavy liquid overflow, m,
z_3 = height from datum to the interface, m.

The height of the liquid interface should be measured accurately when the liquid densities are close, when one component is present only in small quantities, or when the throughput is very small. A typical scheme for the automatic control of the interface, using a level instrument that can detect the position of the interface, is shown in Figure 10.40. Where one phase is present only in small amounts it is often recycled to the decanter feed to give more stable operation.

Decanter design

A rough estimate of the decanter volume required can be made by taking a hold-up time of 5 to 10 min, which is usually sufficient where emulsions are not likely to form. Methods

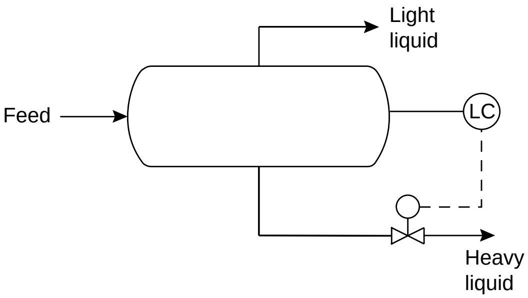


Figure 10.40. Automatic control, level controller detecting interface

for the design of decanters are given by Hooper (1997) and Signales (1975). The general approach taken is outlined below and illustrated by Example 10.3.

The decanter vessel is sized on the basis that the velocity of the continuous phase must be less than settling velocity of the droplets of the dispersed phase. Plug flow is assumed, and the velocity of the continuous phase calculated using the area of the interface:

$$u_c = \frac{L_c}{A_i} < u_d \tag{10.6}$$

where u_d = settling velocity of the dispersed phase droplets, m/s,
u_c = velocity of the continuous phase, m/s,
L_c = continuous phase volumetric flow rate, m^3/s,
A_i = area of the interface, m^2.

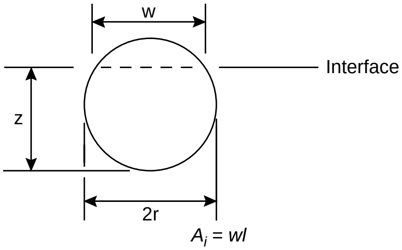
Stokes' law (see Volume 2, Chapter 3) is used to determine the settling velocity of the droplets:

$$u_d = \frac{d_d^2 g(\rho_d - \rho_c)}{18\mu_c} \tag{10.7}$$

where d_d = droplet diameter, m,
u_d = settling (terminal) velocity of the dispersed phase droplets with diameter d, m/s,
ρ_c = density of the continuous phase, kg/m^3,
ρ_d = density of the dispersed phase, kg/m^3,
μ_c = viscosity of the continuous phase, N s/m^2,
g = gravitational acceleration, 9.81 m/s^2.

Equation 10.7 is used to calculate the settling velocity with an assumed droplet size of 150 μm, which is well below the droplet sizes normally found in decanter feeds. If the calculated settling velocity is greater than 4×10^{-3} m/s, then a figure of 4×10^{-3} m/s is used.

For a horizontal, cylindrical, decanter vessel, the interfacial area will depend on the position of the interface.



and

$$w = 2(2rz - z^2)^{1/2}$$

where w = width of the interface, m,
z = height of the interface from the base of the vessel, m,
l = length of the cylinder, m,
r = radius of the cylinder, m.

For a vertical, cylindrical decanter:

$$A_i = \pi r^2$$

The position of the interface should be such that the band of droplets that collect at the interface waiting to coalesce and cross the interface does not extend to the bottom (or top) of the vessel. Ryon *et al*. (1959) and Mizrahi and Barnea (1973) have shown that the depth of the dispersion band is a function of the liquid flow rate and the interfacial area. A value of 10 per cent of the decanter height is usually taken for design purposes. If the performance of the decanter is likely to be critical the design can be investigated using scale models. The model should be scaled to operate at the same Reynolds number as the proposed design, so that the effect of turbulence can be investigated; see Hooper (1975).

Example 10.3

Design a decanter to separate a light oil from water.

The oil is the dispersed phase.

Oil, flow rate 1000 kg/h, density 900 kg/m^3, viscosity 3 mN s/m^2.

Water, flow rate 5000 kg/h, density 1000 kg/m^3, viscosity 1 mN s/m^2.

Solution

Take $d_d = 150\ \mu\text{m}$

$$u_d = \frac{(150 \times 10^{-6})^2\, 9.81(900 - 1000)}{18 \times 1 \times 10^{-3}} \qquad (10.7)$$

$$= -0.0012 \text{ m/s}, -1.2 \text{ mm/s (rising)}$$

As the flow rate is small, use a vertical, cylindrical vessel.

$$L_c = \frac{5000}{1000} \times \frac{1}{3600} = 1.39 \times 10^{-3} \text{ m}^3/\text{s}$$

$$u_c \not> u_d, \text{ and } u_c = \frac{L_c}{A_i}$$

hence
$$A_i = \frac{1.39 \times 10^{-3}}{0.0012} = 1.16 \text{ m}^2$$

$$r = \sqrt{\frac{1.16}{\pi}} = 0.61 \text{ m}$$

$$\text{diameter} = \underline{\underline{1.2 \text{ m}}}$$

Take the height as twice the diameter, a reasonable value for a cylinder:

$$\text{height} = \underline{\underline{2.4 \text{ m}}}$$

Take the dispersion band as 10 per cent of the height = $\underline{\underline{0.24 \text{ m}}}$

Check the residence time of the droplets in the dispersion band

$$= \frac{0.24}{u_d} = \frac{0.24}{0.0012} = 200 \text{ s } (\sim 3 \text{ min})$$

This is satisfactory, a time of 2 to 5 min is normally recommended. Check the size of the water (continuous, heavy phase) droplets that could be entrained with the oil (light phase).

$$\text{Velocity of oil phase} = \frac{1000}{900} \times \frac{1}{3600} \times \frac{1}{1.16}$$
$$= 2.7 \times 10^{-4} \text{ m/s } (0.27 \text{ mm/s})$$

From equation 10.7

$$d_d = \left[\frac{u_d 18 \mu_c}{g(\rho_d - \rho_c)}\right]^{1/2}$$

so the entrained droplet size will

$$= \left[\frac{2.7 \times 10^{-4} \times 18 \times 3 \times 10^{-3}}{9.81(1000 - 900)}\right]^{1/2}$$
$$= \underline{\underline{1.2 \times 10^{-4} \text{ m}}} = 120 \text{ } \mu\text{m}$$

which is satisfactory; below 150 μm.

Piping arrangement

To minimise entrainment by the jet of liquid entering the vessel, the inlet velocity for a decanter should keep below 1 m/s.

$$\text{Flow-rate} = \left[\frac{1000}{900} + \frac{5000}{1000}\right] \frac{1}{3600} = 1.7 \times 10^{-3} \text{ m}^3/\text{s}$$

$$\text{Area of pipe} = \frac{1.7 \times 10^{-3}}{1} = 1.7 \times 10^{-3} \text{ m}^2$$

$$\text{Pipe diameter} = \sqrt{\frac{1.7 \times 10^{-3} \times 4}{\pi}} = 0.047 \text{ m, say } \underline{\underline{50 \text{ mm}}}$$

Take the position of the interface as half-way up the vessel and the light liquid off-take as at 90 per cent of the vessel height, then

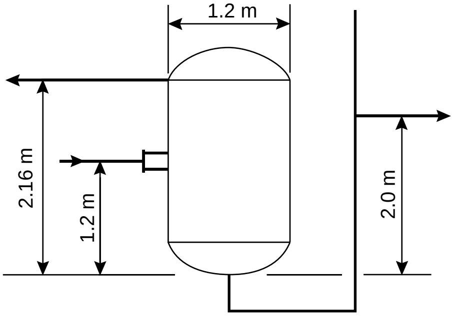
$$z_1 = 0.9 \times 2.4 = 2.16 \text{ m}$$

$$z_3 = 0.5 \times 2.4 = 1.2 \text{ m}$$

$$z_2 = \frac{(2.16 - 1.2)}{1000} \times 900 + 1.2 = \underline{\underline{2.06 \text{ m}}} \quad (10.5)$$

$$\text{say } \underline{\underline{2.0 \text{ m}}}$$

Proposed design



Drain valves should be fitted at the interface so that any tendency for an emulsion to form can be checked; and the emulsion accumulating at the interface drained off periodically as necessary.

10.6.2. Plate separators

Stacks of horizontal, parallel, plates are used in some proprietary decanter designs to increase the interfacial area per unit volume and to reduce turbulence. They, in effect, convert the decanter volume into several smaller separators connected in parallel.

10.6.3. Coalescers

Proprietary equipment, in which the dispersion is forced through some form of coalescing medium, is often used for the coalescence and separation of finely dispersed droplets. A medium is chosen that is preferentially wetted by the dispersed phase; knitted wire or plastic mesh, beds of fibrous material, or special membranes are used. The coalescing medium works by holding up the dispersed droplets long enough for them to form globlets of sufficient size to settle. A typical unit is shown in Figure 10.41; see Redmon (1963). Coalescing filters are suitable for separating small quantities of dispersed liquids from large throughputs.

Electrical coalescers, in which a high voltage field is used to break down the stabilising film surrounding the suspended droplets, are used for desalting crude oils and for similar applications; see Waterman (1965).

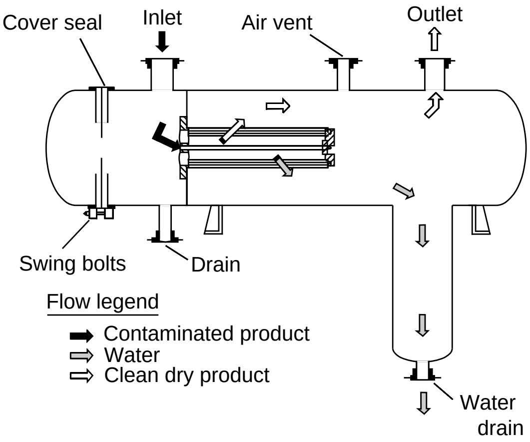


Figure 10.41. Typical coalescer design

10.6.4. Centrifugal separators

Sedimentation centrifuges

For difficult separations, where simple gravity settling is not satisfactory, sedimentation centrifuges should be considered. Centrifuging will give a cleaner separation than that obtainable by gravity settling. Centrifuges can be used where the difference in gravity between the liquids is very small, as low as 100 kg/m^3, and they can handle high throughputs, up to around 100 m^3/h. Also, centrifuging will usually break any emulsion that may form. Bowl or disc centrifuges are normally used (see Section 10.4.3).

Hydrocyclones

Hydrocyclones are used for some liquid-liquid separations, but are not so effective in this application as in separating solids from liquids.

10.7. SEPARATION OF DISSOLVED LIQUIDS

The most commonly used techniques for the separation and purification of miscible liquids are distillation and solvent extraction. In recent years, adsorption, ion exchange and chromatography have become practical alternatives to distillation or solvent extraction in many special applications.

Distillation is probably the most widely used separation technique in the chemical process industries, and is covered in Chapter 11 of this volume, and Chapter 11 of Volume 2. Solvent extraction and the associated technique, leaching (solid-liquid extraction) are covered in Volume 2, Chapters 13 and 10. Adsorption, which can be used for the separation of liquid and gases mixtures, is covered in Chapter 17 of Volume 2. Adsorption is also covered in the books by Suziki (1990) and Crittenden and Thomas (1998).

Ion exchange, the separation of dissolved solids, is covered in Chapter 18 of Volume 2. Through ion exchange is usually associated with water purification the technique has applications in other industries.

Chromatography, which is finding increasing applications in the downstream processing of biochemical products, is covered in Chapter 19 of Volume 2.

In this section, the discussion is restricted to a brief review of solvent-extraction processes.

10.7.1. Solvent extraction and leaching

Solvent extraction (liquid–liquid extraction)

Solvent extraction, also called liquid–liquid extraction, can be used to separate a substance from a solution by extraction into another solvent. It can be used ether to recover a valuable substance from the original solution, or to purify the original solvent by removing an unwanted component. Examples of solvent extraction are: the extraction of uranium and plutonium salts from solution in nitric acid, in the nuclear industry; and the purification of water.

The process depends on the substance being extracted, the solute, having a greater solubility in the solvent used for the extraction than in the original feed solvent. The two solvents must be essentially immiscible.

The solvents are mixed in a contactor, to effect the transfer of solute, and then the phases separated. The depleted feed solvent leaving the extractor is called the raffinate, and the solute rich extraction solvent, the extract. The solute is normally recovered from the extraction solvent, by distillation, and the extraction solvent recycled.

The simplest form of extractor is a mixer-settler, which consist of an agitated tank and a decanter.

The design of extraction columns is discussed in Chapter 11, Section 11.16. See also, Volume 2, Chapter 13, Walas (1990) and Perry *et al.* (1997).

Leaching

Liquids can be extracted from solids by leaching. As the name implies, the soluble liquid contained in a solid is leached out by contacting the solid with a suitable solvent. A principal application of leaching is in the extraction of valuable oils from nuts and seeds; such as, palm oil and rape seed oil.

The equipment used to contact the solids with the solvent is usually a special designs to suit the type of solid being processed, and is to an extent unique to the particular industry. General details of leaching equipment are given in Volume 2, Chapter 10 and in Perry *et al.* (1997).

The leaching is normally done using a number of stages. In this respect, the process is similar to liquid–liquid extraction, and the methods used to determine the number of stages required are similar.

For a detailed discussion of the procedures used to determine the number of stages required for a particular process, see Volume 2, Chapter 10 or Prabhudesai (1997).

10.8. GAS-SOLIDS SEPARATIONS (GAS CLEANING)

The primary need for gas-solid separation processes is for gas cleaning: the removal of dispersed finely divided solids (dust) and liquid mists from gas streams. Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Also, effluent gas streams must be cleaned to comply with air-pollution regulations and for reasons of hygiene, to remove toxic and other hazardous materials; see IChemE (1992).

There is also often a need for clean, filtered, air for process using air as a raw material, and where clean working atmospheres are needed: for instance, in the pharmaceutical and electronics industries.

The particles to be removed may range in size from large molecules, measuring a few hundredths of a micrometre, to the coarse dusts arising from the attrition of catalysts or the fly ash from the combustion of pulverised fuels.

A variety of equipment has been developed for gas cleaning. The principal types used in the process industries are listed in Table 10.11, which is adapted from a selection guide given by Sargent (1971). Table 10.11 shows the general field of application of each type in terms of the particle size separated, the expected separation efficiency, and the throughput. It can be used to make a preliminary selection of the type of equipment likely to be suitable for a particular application. Descriptions of the equipment shown in Table 10.11 can be found in various handbooks: Perry *et al.* (1997), Schweitzer (1997); and in specialist texts: Strauss (1975). Gas cleaning is also covered in Volume 2, Chapter 1.

Gas-cleaning equipment can be classified according to the mechanism employed to separate the particles: gravity settling, impingement, centrifugal force, filtering, washing and electrostatic precipitation.

10.8.1. Gravity settlers (settling chambers)

Settling chambers are the simplest form of industrial gas-cleaning equipment, but have only a limited use; they are suitable for coarse dusts, particles larger than 50 μm. They are essentially long, horizontal, rectangular chambers; through which the gas flows. The solids settle under gravity and are removed from the bottom of the chamber. Horizontal plates or vertical baffles are used in some designs to improve the separation. Settling chambers offer little resistance to the gas flow, and can be designed for operation at high temperature and high pressure, and for use in corrosive atmospheres.

The length of chamber required to settle a given particle size can be estimated from the settling velocity (calculated using Stokes' law) and the gas velocity. A design procedure is given by Jacob and Dhodapkar (1997).

10.8.2. Impingement separators

Impingement separators employ baffles to achieve the separation. The gas stream flows easily round the baffles, whereas the solid particles, due to their higher momentum, tend to continue in their line of flight, strike the baffles and are collected. A variety of baffle

Table 10.11. Gas-cleaning equipment

Type of equipment	Minimum particle size (μm)	Minimum loading (mg/m^3)	Approx. efficiency (%)	Typical gas velocity (m/s)	Maximum capacity (m^3/s)	Gas pressure drop (mm H_2O)	Liquid rate ($m^3/10^3$ m^3 gas)	Space required (relative)
Dry collectors								
Settling chamber	50	12,000	50	1.5–3	none	5	—	Large
Baffle chamber	50	12,000	50	5–10	none	3–12	—	Medium
Louver	20	2500	80	10–20	15	10–50	—	Small
Cyclone	10	2500	85	10–20	25	10–70	—	Medium
Multiple cyclone	5	2500	95	10–20	100	50–150	—	Small
Impingement	10	2500	90	15–30	none	25–50	—	Small
Wet scrubbers								
Gravity spray	10	2500	70	0.5–1	50	25	0.05–0.3	Medium
Centrifugal	5	2500	90	10–20	50	50–150	0.1–1.0	Medium
Impingement	5	2500	95	15–30	50	50–200	0.1–0.7	Medium
Packed	5	250	90	0.5–1	25	25–250	0.7–2.0	Medium
Jet	0.5 to 5 (range)	250	90	10–100	50	none	7–14	Small
Venturi	0.5	250	99	50–200	50	250–750	0.4–1.4	Small
Others								
Fabric filters	0.2	250	99	0.01–0.1	100	50–150	—	Large
Electrostatic precipitators	2	250	99	5–30	1000	5–25	—	Large

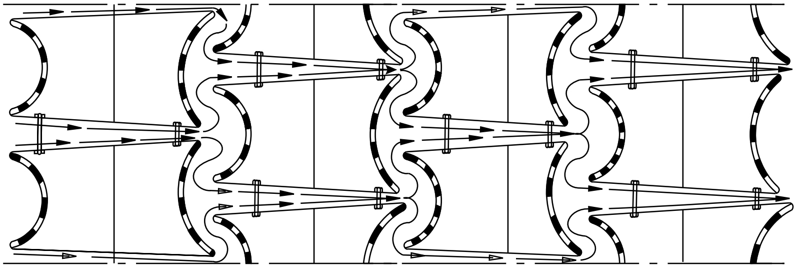


Figure 10.42. Impingement separator (section showing gas flow)

designs is used in commercial equipment; a typical example is shown in Figure 10.42. Impingement separators cause a higher pressure drop than settling chambers, but are capable of separating smaller particle sizes, 10–20 μm.

10.8.3. Centrifugal separators (cyclones)

Cyclones are the principal type of gas-solids separator employing centrifugal force, and are widely used. They are basically simple constructions; can be made from a wide range of materials; and can be designed for high temperature and pressure operation.

Cyclones are suitable for separating particles above about 5 μm diameter; smaller particles, down to about 0.5 μm, can be separated where agglomeration occurs.

The most commonly used design is the reverse-flow cyclone, Figure 10.43; other configurations are used for special purposes. In a reverse-flow cyclone the gas enters the top chamber tangentially and spirals down to the apex of the conical section; it then moves upward in a second, smaller diameter, spiral, and exits at the top through a central vertical pipe. The solids move radially to the walls, slide down the walls, and are collected at the bottom. Design procedures for cyclones are given by Constantinescu (1984). Strauss (1975), Koch and Licht (1977) and Stairmand (1951). The theoretical concepts and experimental work on which the design methods are based on discussed in Volume 2, Chapter 8. Stairmand's method is outlined below and illustrated in Example 10.4.

Cyclone design

Stairmand developed two standard designs for gas-solid cyclones: a high-efficiency cyclone, Figure 10.44*a*, and a high throughput design, Figure 10.44*b*. The performance curves for these designs, obtained experimentally under standard test conditions, are shown in Figures 10.45*a* and 10.45*b*. These curves can be transformed to other cyclone sizes and operating conditions by use of the following scaling equation, for a given separating efficiency:

$$d_2 = d_1\left[\left(\frac{D_{c_2}}{D_{c_1}}\right)^3 \times \frac{Q_1}{Q_2} \times \frac{\Delta\rho_1}{\Delta\rho_2} \times \frac{\mu_2}{\mu_1}\right]^{1/2} \tag{10.8}$$

where d_1 = mean diameter of particle separated at the standard conditions, at the chosen separating efficiency, Figures 10.45*a* or 10.45*b*,

d_2 = mean diameter of the particle separated in the proposed design, at the same separating efficiency,

D_{c_1} = diameter of the standard cyclone = 8 inches (203 mm),

D_{c_2} = diameter of proposed cyclone, mm,

Q_1 = standard flow rate:

for high efficiency design = 223 m^3/h,

for high throughput design = 669 m^3/h,

Q_2 = proposed flow rate, m^3/h,

$\Delta\rho_1$ = solid-fluid density difference in standard conditions = 2000 kg/m^3,

$\Delta\rho_2$ = density difference, proposed design,

μ_1 = test fluid viscosity (air at 1 atm, 20°C)

= 0.018 mN s/m^2,

μ_2 = viscosity, proposed fluid.

A performance curve for the proposed design can be drawn up from Figures 10.45*a* or 10.45*b* by multiplying the grade diameter at, say, each 10 per cent increment of efficiency, by the scaling factor given by equation 10.8; as shown in Figure 10.46 (p. 453).

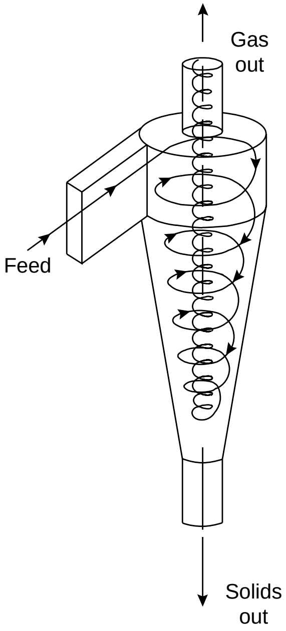
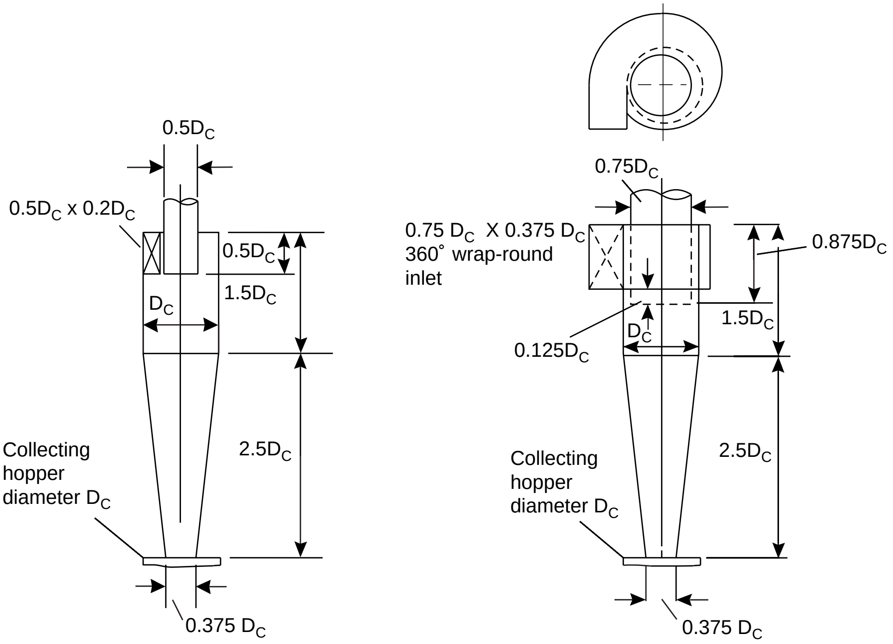
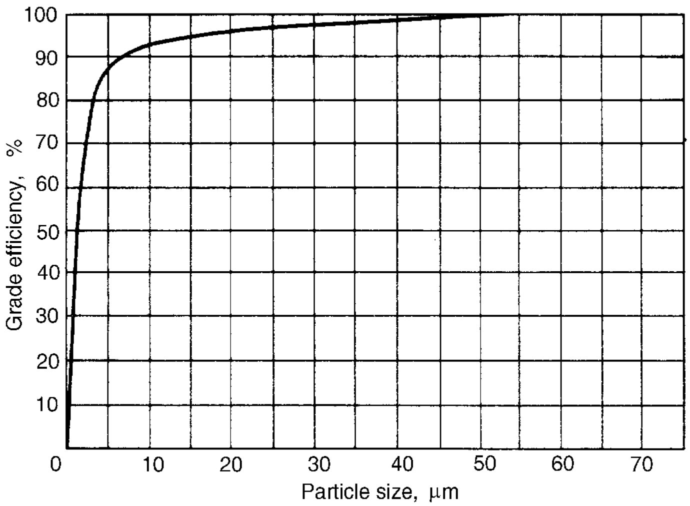


Figure 10.43. Reverse-flow cyclone



(a) (b)

Figure 10.44. Standard cyclone dimension (*a*) High efficiency cyclone (*b*) High gas rate cyclone



(a)

Figure 10.45. Performance curves, standard conditions (*a*) High efficiency cyclone

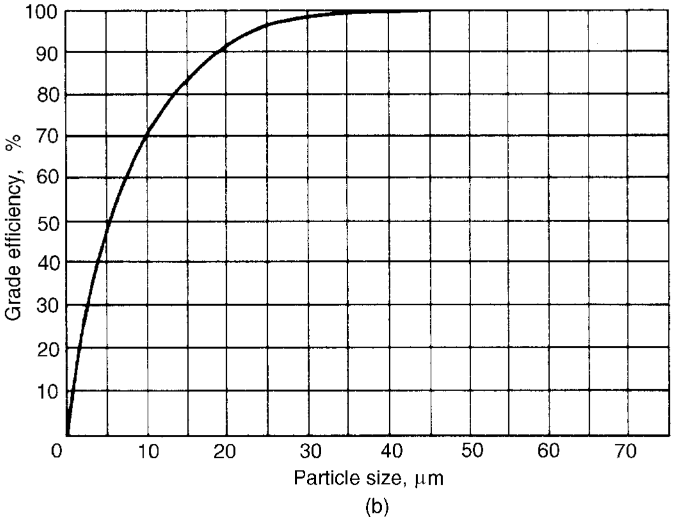


Figure 10.45 (continued). Performance curves, standard conditions (*b*) High gas rate cyclone

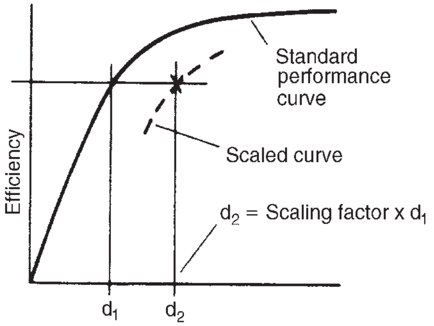


Figure 10.46. Scaled performance curve

An alternative method of using the scaling factor, that does not require redrawing the performance curve, is used in Example 10.4. The cyclone should be designed to give an inlet velocity of between 9 and 27 m/s (30 to 90 ft/s); the optimum inlet velocity has been found to be 15 m/s (50 ft/s).

Pressure drop

The pressure drop in a cyclone will be due to the entry and exit losses, and friction and kinetic energy losses in the cyclone. The empirical equation given by Stairmand (1949) can be used to estimate the pressure drop:

$$\Delta P = \frac{\rho_f}{203}\left\{u_1^2\left[1 + 2\phi^2\left(\frac{2r_t}{r_e} - 1\right)\right] + 2u_2^2\right\} \tag{10.9}$$

where ΔP = cyclone pressure drop, millibars,

ρ_f = gas density, kg/m^3,

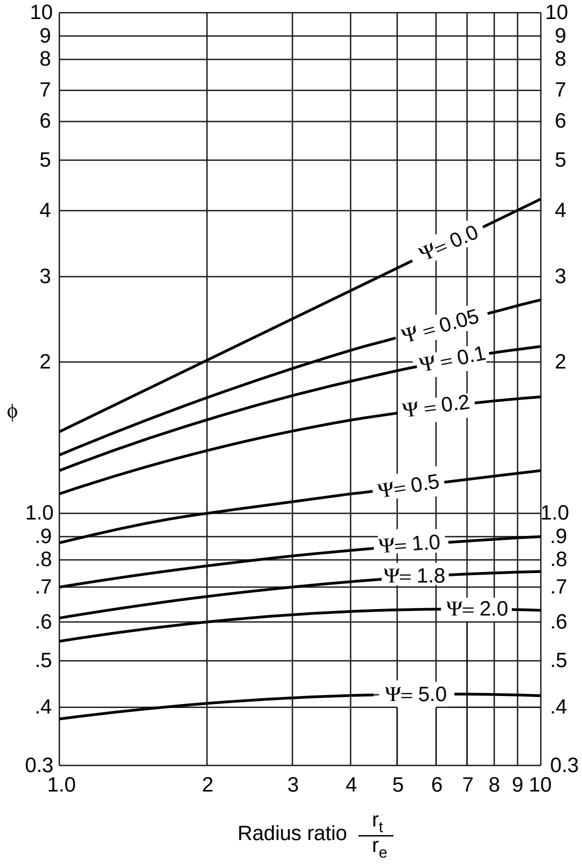


Figure 10.47. Cyclone pressure drop factor

u_1 = inlet duct velocity, m/s,
u_2 = exit duct velocity, m/s,
r_t = radius of circle to which the centre line of the inlet is tangential, m,
r_e = radius of exit pipe, m,
ϕ = factor from Figure 10.47,
ψ = parameter in Figure 10.47, given by:

$$\psi = f_c \frac{A_s}{A_1}$$

f_c = friction factor, taken as 0.005 for gases,
A_s = surface area of cyclone exposed to the spinning fluid, m^2.
For design purposes this can be taken as equal to the surface area of a cylinder with the same diameter as the cylone and length equal to the total height of the cyclone (barrel plus cone).
A_1 = area of inlet duct, m^2.

Stairmand's equation is for the gas flowing alone, containing no solids. The presence of solids will normally increase the pressure drop over that calculated using equation 10.9, depending on the solids loading. Alternative design methods for cyclones, which include procedures for estimating the true pressure drop, are given by Perry *et al*. (1997) and Yang (1999); see also Zenz (2001).

General design procedure

1. Select either the high-efficiency or high-throughput design, depending on the performance required.
2. Obtain an estimate of the particle size distribution of the solids in the stream to be treated.
3. Estimate the number of cyclones needed in parallel.
4. Calculate the cyclone diameter for an inlet velocity of 15 m/s (50 ft/s). Scale the other cyclone dimensions from Figures 10.44*a* or 10.44*b*.
5. Calculate the scale-up factor for the transposition of Figures 10.45*a* or 10.45*b*.
6. Calculate the cyclone performance and overall efficiency (recovery of solids). If unsatisfactory try a smaller diameter.
7. Calculate the cyclone pressure drop and, if required, select a suitable blower.
8. Cost the system and optimise to make the best use of the pressure drop available, or, if a blower is required, to give the lowest operating cost.

Example 10.4

Design a cyclone to recover solids from a process gas stream. The anticipated particle size distribution in the inlet gas is given below. The density of the particles is 2500 kg/m^3, and the gas is essentially nitrogen at 150°C. The stream volumetric flow-rate is 4000 m^3/h, and the operation is at atmospheric pressure. An 80 per cent recovery of the solids is required.

Particle size (μm)	50	40	30	20	10	5	2
Percentage by weight less than	90	75	65	55	30	10	4

Solution

As 30 per cent of the particles are below 10 μm the high-efficiency design will be required to give the specified recovery.

$$\text{Flow-rate} = \frac{4000}{3600} = 1.11\ \text{m}^3/\text{s}$$

$$\text{Area of inlet duct, at 15 m/s} = \frac{1.11}{15} = 0.07\ \text{m}^2$$

From Figure 10.44*a*, duct area $= 0.5\ D_c \times 0.2\ D_c$

$$\text{so, } D_c = 0.84$$

This is clearly too large compared with the standard design diameter of 0.203 m.

Try four cyclones in parallel, $D_c = 0.42$ m.

$$\text{Flow-rate per cyclone} = 1000\ \text{m}^3/\text{h}$$

$$\text{Density of gas at } 150^\circ\text{C} = \frac{28}{22.4} \times \frac{273}{423} = 0.81\ \text{kg/m}^2,$$

negligible compared with the solids density

$$\text{Viscosity of N}_2 \text{ at } 150^\circ\text{C} = 0.023\ \text{cp(mN s/m}^2)$$

From equation 10.8,

$$\text{scaling factor} = \left[\left(\frac{0.42}{0.203}\right)^3 \times \frac{223}{1000} \times \frac{2000}{2500} \times \frac{0.023}{0.018}\right]^{1/2} = \underline{\underline{1.42}}$$

The performance calculations, using this scaling factor and Figure 10.45*a*, are set out in the table below:

Calculated performance of cyclone design, Example 10.4

1 Particle size (μm)	2 Per cent in range	3 Mean particle size ÷ scaling factor	4 Efficiency at scaled size % (Figure 10.46a)	5 Collected $\frac{(2) \times (4)}{100}$	6 Grading at exit (2)–(5)	7 Per cent at exit
>50	10	35	98	9.8	0.2	1.8
50–40	15	32	97	14.6	0.4	3.5
40–30	10	25	96	9.6	0.4	3.5
30–20	10	18	95	9.5	0.5	4.4
20–10	25	11	93	23.3	1.7	15.1
10–5	20	5	86	17.2	2.8	24.8
5–2	6	3	72	4.3	1.7	15.1
2–0	4	1	10	0.4	3.6	31.8
	100		Overall collection efficiency	$\underline{\underline{88.7}}$	11.3	100.0

The collection efficiencies shown in column 4 of the table were read from Figure 10.45*a* at the scaled particle size, column 3. The overall collection efficiency satisfies the specified solids recovery. The proposed design with dimension in the proportions given in Figure 10.44*a* is shown in Figure 10.48.

Pressure-drop calculation

$$\text{Area of inlet duct, } A_1, = 210 \times 80 = 16{,}800\ \text{mm}^2$$

$$\begin{aligned}\text{Cyclone surface area, } A_s &= \pi 420 \times (630 + 1050)\\ &= 2.218 \times 10^6\ \text{mm}^2\end{aligned}$$

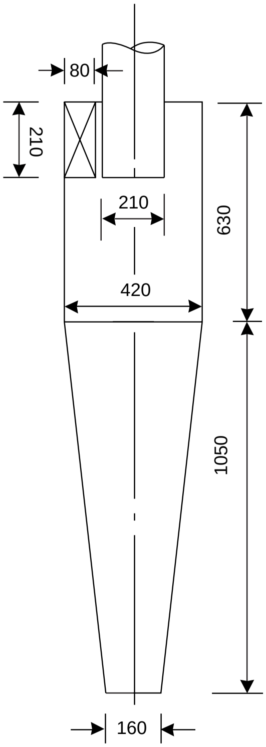


Figure 10.48. Proposed cyclone design, all dimensions mm (Example 10.4)

f_c taken as 0.005

$$\psi = \frac{f_c, A_s}{A_1} = \frac{0.005 \times 2.218 \times 10^6}{16{,}800} = 0.66$$

$$\frac{r_t}{r_e} = \frac{(420 - (80/2))}{210} = 1.81$$

From Figure 10.47, $\phi = 0.9$.

$$u_1 = \frac{1000}{3600} \times \frac{10^6}{16{,}800} = 16.5 \text{ m/s}$$

$$\text{Area of exit pipe} = \frac{\pi \times 210^2}{4} = 34{,}636 \text{ mm}^2$$

$$u_2 = \frac{1000}{3600} \times \frac{10^6}{34{,}636} = 8.0 \text{ m/s}$$

From equation 10.6

$$\Delta P = \frac{0.81}{203}[16.5^2[1 + 2 \times 0.9^2(2 \times 1.81 - 1)] + 2 \times 8.0^2]$$

$$= \underline{\underline{6.4 \text{ millibar}}} \ \ (67 \text{ mm } H_2O)$$

This pressure drop looks reasonable.

10.8.4. Filters

The filters used for gas cleaning separate the solid particles by a combination of impingement and filtration; the pore sizes in the filter media used are too large simply to filter out the particles. The separating action relies on the precoating of the filter medium by the first particles separated; which are separated by impingement on the filter medium fibres. Woven or felted cloths of cotton and various synthetic fibres are commonly used as the filter media. Glass-fibre mats and paper filter elements are also used.

A typical example of this type of separator is the bag filter, which consists of a number of bags supported on a frame and housed in a large rectangular chamber, Figure 10.49. The deposited solids are removed by mechanically vibrating the bag, or by periodically reversing the gas flow. Bag filters can be used to separate small particles, down to around 1 μm, with a high separating efficiency. Commercial units are available to suit most applications and should be selected in consultation with the vendors.

The design and specification of bag filters (baghouses) is covered by Kraus (1979).

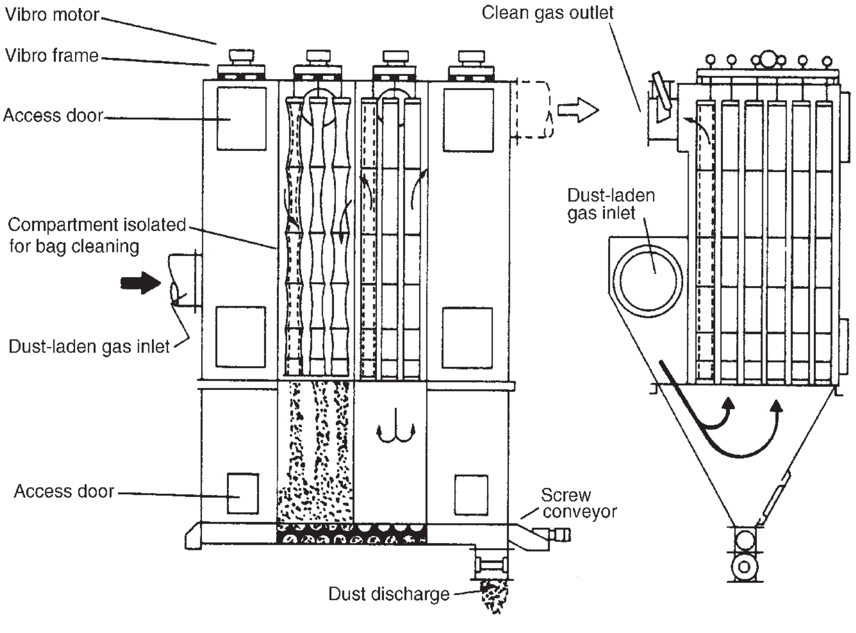


Figure 10.49. Multi-compartment vibro bag filter

Air filters

Dust-free air is required for many process applications. The requirements of air filtration differ from those of process gas filtration mainly in that the quantity of dust to be removed will be lower, typically less than 10 mg/m^3 ($\sim$5 grains per 1000 ft^3); and also in that there is no requirement to recover the material collected.

Three basic types of air filter are used: viscous, dry and continuous. Viscous and dry units are similar in construction, but the filter medium of the viscous type is coated with a viscous material, such as a mineral oil, to retain the dust. The filters are made up from standard, preformed, sections, supported on a frame in a filter housing. The sections are removed periodically for cleaning or replacement. Various designs of continuous filtration equipment are also available, employing either viscous or dry filter elements, but in which the filter is cleaned continuously. A comprehensive description of air-filtration equipment is given by Strauss (1975).

10.8.5. Wet scrubbers (washing)

In wet scrubbing the dust is removed by counter-current washing with a liquid, usually water, and the solids are removed as a slurry. The principal mechanism involved is the impact (impingement) of the dust particles and the water droplets. Particle sizes down to 0.5 μm can be removed in suitably designed scrubbers. In addition to removing solids, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents.

Spray towers, and plate and packed columns are used, as well as a variety of proprietary designs. Spray towers have a low pressure drop but are not suitable for removing very fine particles, below 10 μm. The collecting efficiency can be improved by the use of plates or packing but at the expense of a higher pressure drop.

Venturi and orifice scrubbers are simple forms of wet scrubbers. The turbulence created by the venturi or orifice is used to atomise water sprays and promote contact between the liquid droplets and dust particles. The agglomerated particles of dust and liquid are then collected in a centrifugal separator, usually a cyclone.

10.8.6. Electrostatic precipitators

Electrostatic precipitators are capable of collecting very fine particles, <2 μm, at high efficiencies. However, their capital and operating costs are high, and electrostatic precipitation should only be considered in place of alternative processes, such as filtration, where the gases are hot or corrosive. Electrostatic precipitators are used extensively in the metallurgical, cement and electrical power industries. Their main application is probably in the removal of the fine fly ash formed in the combustion of pulverised coal in powerstation boilers. The basic principle of operation is simple. The gas is ionised in passing between a high-voltage electrode and an earthed (grounded) electrode; the dust particles become charged and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration, or by washing. Wires are normally used for the high-voltage electrode, and plates or tubes for the earthed electrode. A typical design is shown in Figure 10.50. A full description of the construction, design and application of electrostatic precipitators is given by Schneider *et al.* (1975) and Parker (2002).

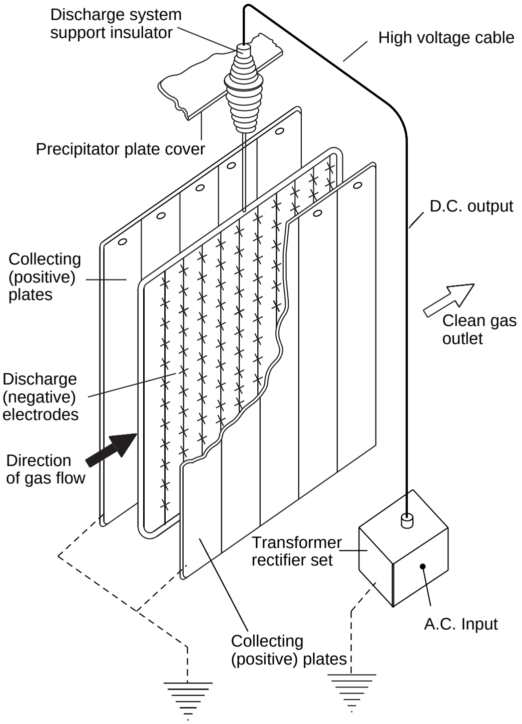


Figure 10.50. Electrostatic precipitator

10.9. GAS–LIQUID SEPARATORS

The separation of liquid droplets and mists from gas or vapour streams is analogous to the separation of solid particles and, with the possible exception of filtration, the same techniques and equipment can be used.

Where the carryover of some fine droplets can be tolerated it is often sufficient to rely on gravity settling in a vertical or horizontal separating vessel (knockout pot).

Knitted mesh demisting pads are frequently used to improve the performance of separating vessels where the droplets are likely to be small, down to 1 μm, and where high separating efficiencies are required. Proprietary demister pads are available in a wide range of materials, metals and plastics; thickness and pad densities. For liquid separators, stainless steel pads around 100 mm thick and with a nominal density of 150 kg/m^3 would generally be used. Use of a mister pad allows a smaller vessel to be used. Separating efficiencies above 99% can be obtained with low pressure drop. The design and specification of demister pads for gas–liquid separators is discussed by Pryce Bailey and Davies (1973).

The design methods for horizontal separators given below are based on a procedure given by Gerunda (1981).

Cyclone separators are also frequently used for gas–liquid separation. They can be designed using the same methods for gas–solids cyclones. The inlet velocity should be kept below 30 m/s to avoid pick-up of liquid form the cyclone surfaces.

10.9.1. Settling velocity

Equation 10.10 can be used to estimate the settling velocity of the liquid droplets, for the design of separating vessels.

$$u_t = 0.07[(\rho_L - \rho_v)/\rho_v)]^{1/2} \tag{10.10}$$

where u_t = settling velocity, m/s,
ρ_L = liquid density, kg/m^3,
ρ_v = vapour density, kg/m^3.

If a demister pad is not used, the value of u_t obtained from equation 10.10 should be multiplied by a factor of 0.15 to provide a margin of safety and to allow for flow surges.

10.9.2. Vertical separators

The layout and typical proportions of a vertical liquid–gas separator are shown in Figure 10.51*a*.

The diameter of the vessel must be large enough to slow the gas down to below the velocity at which the particles will settle out. So the minimum allowable diameter will

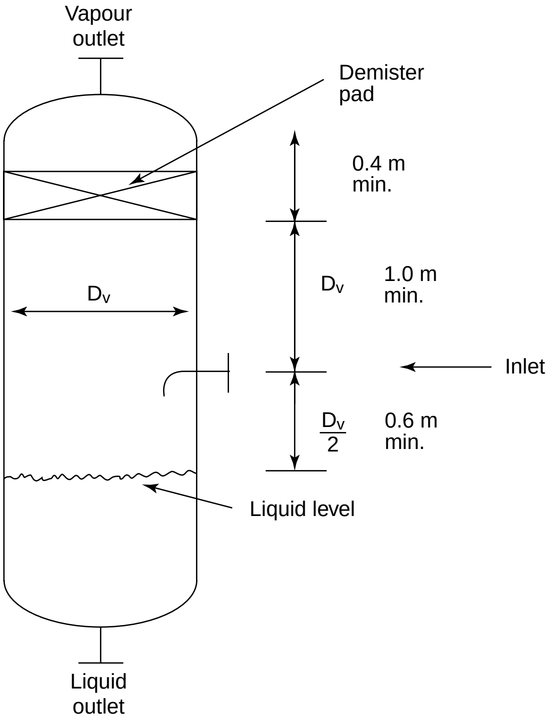


Figure 10.51*a*. Vertical liquid-vapour separator

be given by:

$$D_v = \sqrt{\left(\frac{4V_v}{\pi u_s}\right)} \tag{10.11}$$

where D_v = minimum vessel diameter, m,

V_v = gas, or vapour volumetric flow-rate, m^3/s,

$u_s = u_t$, if a demister pad is used, and 0.15 u_t for a separator without a demister pad; u_t from equation (10.10), m/s.

The height of the vessel outlet above the gas inlet should be sufficient to allow for disengagement of the liquid drops. A height equal to the diameter of the vessel or 1 m, which ever is the greatest, should be used, see Figure 10.51*a*.

The liquid level will depend on the hold-up time necessary for smooth operation and control; typically 10 minutes would be allowed.

Example 10.5

Make a preliminary design for a separator to separate a mixture of steam and water; flow-rates: steam 2000 kg/h, water 1000 kg/h; operating pressure 4 bar.

Solution

From steam tables, at 4 bar: saturation temperature 143.6°C, liquid density 926.4 kg/m^3, vapour density 2.16 kg/m^3.

$$u_t = 0.07[(926.4 - 2.16)/2.16]^{\frac{1}{2}} = 1.45 \text{ m/s} \tag{10.10}$$

As the separation of condensate from steam is unlikely to be critical, a demister pad will not be specified.

So, $u_t = 0.15 \times 1.45 = 0.218$ m/s

$$\text{Vapour volumetric flow-rate} = \frac{2000}{3600 \times 2.16} = 0.257 \text{ m}^3/\text{s}$$

$$D_v = \sqrt{[(4 \times 0.257)/(\pi \times 0.218)]} = 1.23 \text{ m, round to } 1.25 \text{ m (4 ft).} \tag{10.11}$$

$$\text{Liquid volumetric flow-rate} = \frac{1000}{3600 \times 926.14} = 3.0 \times 10^{-4} \text{ m}^3/\text{s}$$

Allow a minimum of 10 minutes hold-up.

$$\text{Volume held in vessel} = 3.0 \times 10^{-4} \times (10 \times 60) = 0.18 \text{ m}^3$$

$$\text{Liquid depth required, } h_v = \frac{\text{volume held-up}}{\text{vessel cross-sectional area}}$$

$$= \frac{0.18}{(\pi \times 1.25^2/4)} = 0.15 \text{ m}$$

Increase to 0.3 m to allow space for positioning the level controller.

10.9.3. Horizontal separators

The layout of a typical horizontal separator is shown in Figure 10.51*b*.

A horizontal separator would be selected when a long liquid hold-up time is required.

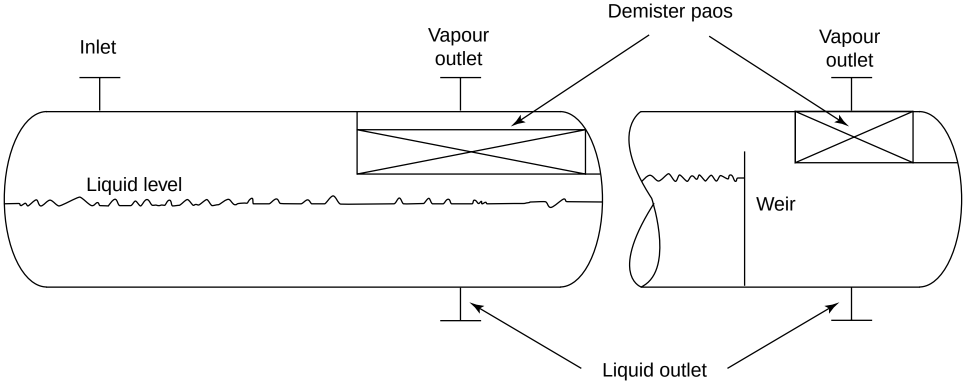


Figure 10.51*b*. Horizontal liquid vapour separator

In the design of a horizontal separator the vessel diameter cannot be determined independently of its length, unlike for a vertical separator. The diameter and length, and the liquid level, must be chosen to give sufficient vapour residence time for the liquid droplets to settle out, and for the required liquid hold-up time to be met.

The most economical length to diameter ratio will depend on the operating pressure (see Chapter 13). As a general guide the following values can be used:

Operating pressure, bar	Length: diameter, L_v/D_v
0–20	3
20–35	4
>35	5

The relationship between the area for vapour flow, A_v, and the height above the liquid level, h_v, can been found from tables giving the dimensions of the segments of circles; see Perry and Green (1984), or from Figure 11.32 and 11.33 in Chapter 11.

For preliminary designs, set the liquid height at half the vessel diameter,

$$h_v = D_v/2 \text{ and } f_v = 0.5,$$

where f_v is the fraction of the total cross-sectional area occupied by the vapour.

The design procedure for horizontal separators is illustrated in the following example, example 10.6.

Example 10.6

Design a horizontal separator to separate 10,000 kg/h of liquid, density 962.0 kg/m^3, from 12,500 kg/h of vapour, density 23.6 kg/m^3. The vessel operating pressure will be 21 bar.

Solution

$$u_t = 0.07[(962.0 - 23.6)/23.6]^{1/2} = 0.44 \text{ m/s}$$

Try a separator without a demister pad.

$$u_a = 0.15 \times 0.44 = 0.066 \text{ m/s}$$

$$\text{Vapour volumetric flow-rate} = \frac{12{,}500}{3600 \times 23.6} = 0.147 \text{ m}^3/\text{s}$$

Take $h_v = 0.5D_v$ and $L_v/D_v = 4$

$$\text{Cross-sectional area for vapour flow} = \frac{\pi D_v^2}{4} \times 0.5 = 0.393Dv^2$$

$$\text{Vapour velocity, } u_v = \frac{0.147}{0.393Dv^2} = 0.374D_v^{-2}$$

Vapour residence time required for the droplets to settle to liquid surface

$$= h_v/u_a = 0.5D_v/0.66 = 7.58D_v$$

Actual residence time = vessel length/vapour velocity

$$= L_v/u_v = \frac{4D_v}{0.374 \text{ Dv}^{-2}} = 10.70D_v^3$$

For satisfactory separation required residence time = actual.

So, $7.58D_v = 10.70D_v^3$

$D_v = 0.84$ m, say 0.92 m (3 ft, standard pipe size)

Liquid hold-up time,

$$\text{liquid volumetric flow-rate} = \frac{10{,}000}{3600 \times 962.0} = 0.00289 \text{ m}^3/\text{s}$$

$$\text{liquid cross-sectional area} = \frac{\pi \times 0.92^2}{4} \times 0.5 = 0.332 \text{ m}^2$$

Length, $L_v = 4 \times 0.92 = 3.7$ m

Hold-up volume $= 0.332 \times 3.7 = 1.23$ m^3

Hold-up time = liquid volume/liquid flow-rate

$= 1.23/0.00289 = 426$ s = 7 minutes.

This is unsatisfactory, 10 minutes minimum required.

Need to increase the liquid volume. This is best done by increasing the vessel diameter. If the liquid height is kept at half the vessel diameter, the diameter must be increased by a factor of roughly $(10/7)^{0.5} = 1.2$.

New $D_v = 0.92 \times 1.2 = 1.1$ m

Check liquid residence time,

$$\text{new liquid volume} = \frac{\pi \times 1.1^2}{4} \times 0.5 \times (4 \times 1.1) = 2.09\ \text{m}^3$$

$$\text{new residence time} = 2.09/0.00289 = 723\ \text{s} = 12\ \text{minutes, satisfactory}$$

Increasing the vessel diameter will have also changed the vapour velocity and the height above the liquid surface. The liquid separation will still be satisfactory as the velocity, and hence the residence time, is inversely proportional to the diameter squared, whereas the distance the droplets have to fall is directly proportional to the diameter.

In practice, the distance travelled by the vapour will be less than the vessel length, L_v, as the vapour inlet and outlet nozzles will be set in from the ends. This could be allowed for in the design but will make little difference.

10.10. CRUSHING AND GRINDING (COMMINUTION) EQUIPMENT

Crushing is the first step in the process of size reduction; reducing large lumps to manageable sized pieces. For some processes crushing is sufficient, but for chemical processes it is usually followed by grinding to produce a fine-sized powder. Though many articles have been published on comminution, and Marshall (1974) mentions over 4000, the subject remains essentially empirical. The designer must rely on experience, and the advice of the equipment manufacturers, when selecting and sizing crushing and grinding equipment; and to estimate the power requirements. Several models have been proposed for the calculation of the energy consumed in size reduction; some of which are discussed in Volume 2, Chapter 2. For a fuller treatment of the subject the reader should refer to the book by Lowrison (1974) and Prasher (1987).

Table 10.12. Selection of comminution equipment (after Lowrison, 1974)

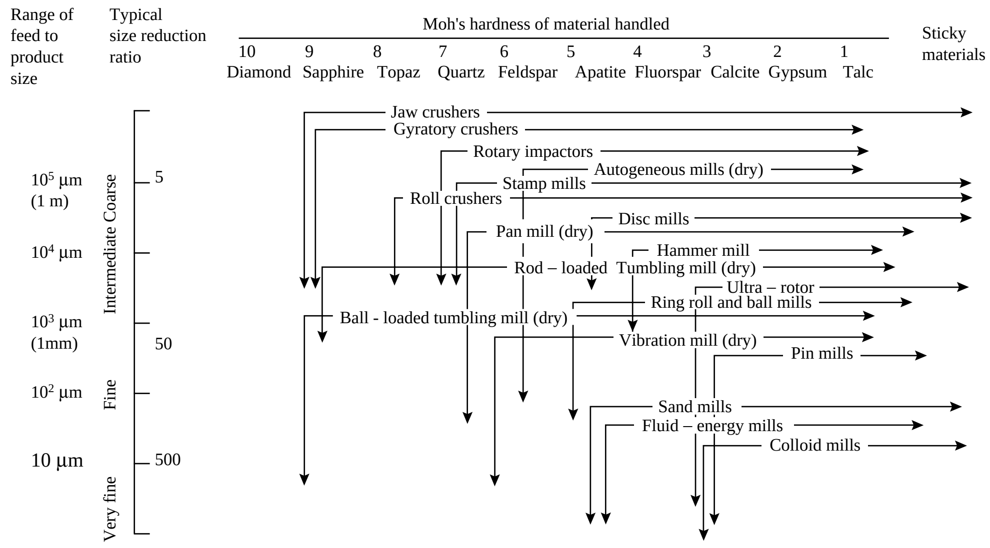


Table 10.13. Selection of comminution equipment for various materials (after Marshall, 1974) Note: Moh's scale of hardness is given in Table 10.12

Material class no	Material classification	Typical materials in class	Suitable equipment for product size classes			Remarks
			Down to 5 mesh	Between 5 and 300 mesh	Less than 300 mesh	
1	Hard and tough	Mica Scrap and powdered metals	Jaw crushers Gyratory crushers Cone crushers Autogeneous mills	Ball, pebble, rod and cone mills Tube mills Vibration mills	Ball, pebble and cone mills Tube mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 5–10, but includes other tough materials of lower hardness
2	Hard, abrasive and brittle	Coke, quartz, granite	Jaw crushers Gyratory and cone crushers Roll crushers	Ball, pebble, rod and cone mills Vibration mills Roller mills	Ball, pebble and cone mills Tube mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 5–10 High wear rate/contamination in high-speed machinery Use machines with abrasion resistant linings
3	Intermediate hard, and friable	Barytes, fluorspar, limestone	Jaw crushers Gyratory crushers Roll crushers Edge runner mills Impact breakers Autogeneous mills Cone crushers	Ball, pebble, rod and cone mills Tube mills Ring roll mills Ring ball mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills	Ball, pebble and cone mills Tube mills Perl mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 3–5

4	Fibrous, low abrasion and possibly tough	Wood, asbestos	Cone crushers Roll crushers Edge runner mills Autogeneous mills Impact breakers	Ball, pebble, rod and cone mills Tube mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills Rotary cutters and dicers	Ball, pebble and cone mills Tube mills Sand mills Perl mills Vibration and vibro-energy mills Colloid mills	Wide range of hardness Low-temperature, liquid nitrogen, useful to embrittle soft but tough materials
5	Soft and friable	Sulphur, gypsum rock salt	Cone crushers Roll crushers Edge runner mills Impact breakers Autogeneous mills	Ball, pebble and cone mills Tube mills Ring roll mills Ring ball mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills	Ball, pebble and cone mills Tube mills Sand mills Perl mills Vibration and vibro-energy mills Colloid mills Fluid-energy mills Peg and disc mills	Moh's hardness 1–3
6	Sticky	Clays, certain organic pigments	Roll crushers Impact breakers Edge runner mills	Ball, pebble, rod and cone mills* Tube mills* Peg and disc mills Cage mills Ring roll mills	Ball, pebble and cone mills* Tube mills* Sand mills Perl mills Vibration and vibro-energy mills Colloid mills	Wide range of Moh's hardness although mainly less than 3 Tends to clog *Wet grinding employed except for certain exceptional cases

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*All ball, pebble, rod and cone mills, edge runner mills, tube mills, vibration mills and some ring ball mills may be used wet or dry except where stated. The perl mills, sand mills and colloid mills may be used for wet milling only.

The main factors to be considered when selecting equipment for crushing and grinding are:

1. The size of the feed.
2. The size reduction ratio.
3. The required particle size distribution of the product.
4. The throughput.
5. The properties of the material: hardness, abrasiveness, stickiness, density, toxicity, flammability.
6. Whether wet grinding is permissible.

The selection guides given by Lowrison (1974) and Marshall (1974), which are reproduced in Tables 10.12 (see p. 465) and 10.13, can be used to make a preliminary selection based on particle size and material hardness. Descriptions of most of the equipment listed in these tables are given in Volume 2, Chapter 2; or can be found in the literature; Perry *et al*. (1997), Hiorns (1970), Lowrison (1974). The most commonly used equipment for coarse size reduction are jaw crushers and rotary crushers; and for grinding, ball mills or their variants: pebble, roll and tube mills.

10.11. MIXING EQUIPMENT

The preparation of mixtures of solids, liquids and gases is an essential part of most production processes in the chemical and allied industries; covering all processing stages, from the preparation of reagents through to the final blending of products. The equipment used depends on the nature of the materials and the degree of mixing required. Mixing is often associated with other operations, such as reaction and heat transfer. Liquid and solids mixing operations are frequently carried out as batch processes.

In this section, mixing processes will be considered under three separate headings: gases, liquids and solids.

10.11.1. Gas mixing

Specialised equipment is seldom needed for mixing gases, which because of their low viscosities mix easily. The mixing given by turbulent flow in a length of pipe is usually sufficient for most purposes. Turbulence promoters, such as orifices or baffles, can be used to increase the rate of mixing. The piping arrangements used for inline mixing are discussed in the section on liquid mixing.

10.11.2. Liquid mixing

The following factors must be taken into account when choosing equipment for mixing liquids:

1. Batch of continuous operation.
2. Nature of the process: miscible liquids, preparation of solutions, or dispersion of immiscible liquids.
3. Degree of mixing required.
4. Physical properties of the liquids, particularly the viscosity.
5. Whether the mixing is associated with other operations: reaction, heat transfer.

For the continuous mixing of low viscosity fluids inline mixers can be used. For other mixing operations stirred vessels or proprietary mixing equipment will be required.

Inline mixing

Static devices which promote turbulent mixing in pipelines provide an inexpensive way of continuously mixing fluids. Some typical designs are shown in Figures 10.52*a*, *b*, *c*. A simple mixing tee, Figure 10.52*a*, followed by a length of pipe equal to 10 to 20 pipe diameters, is suitable for mixing low viscosity fluids ($\leq$50 mN s/m^2) providing the flow is turbulent, and the densities and flow-rates of the fluids are similar.

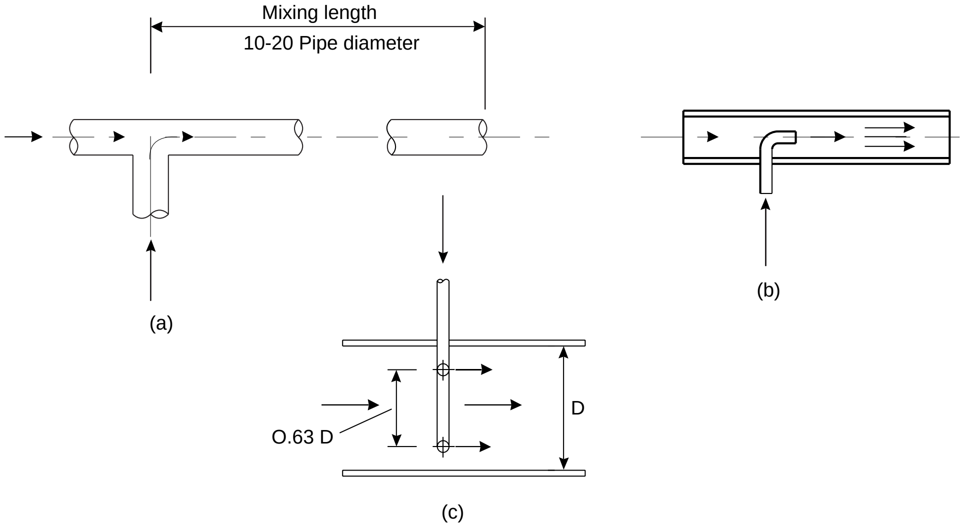

Figure 10.52. Inline mixers (*a*) Tee (*b*) Injection (*c*) Annular

With injection mixers (Figures 10.52*b*,*c*), in which the one fluid is introduced into the flowing stream of the other through a concentric pipe or an annular array of jets, mixing will take place by entrainment and turbulent diffusion. Such devices should be used where one flow is much lower than the other, and will give a satisfactory blend in about 80 pipe diameters. The inclusion of baffles or other flow restrictions will reduce the mixing length required.

The static inline mixer shown in Figure 10.53 is effective in both laminar and turbulent flow, and can be used to mix viscous mixtures. The division and rotation of the fluid at each element causes rapid radical mixing; see Rosenzweig (1977) and Baker (1991). The

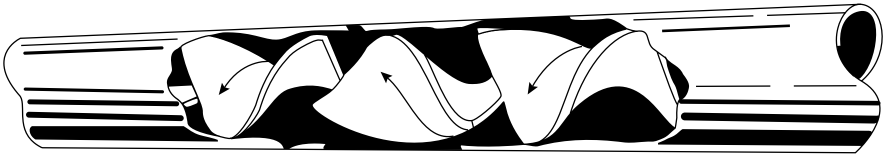

Figure 10.53. Static mixer (Kenics Corporation)

dispersion and mixing of liquids in pipes is discussed by Zughi *et al.* (2003) and Lee and Brodkey (1964).

Centrifugal pumps are effective inline mixers for blending and dispersing liquids. Various proprietary motor-driven inline mixers are also used for special applications; see Perry *et al.* (1997).

Stirred tanks

Mixing vessels fitted with some form of agitator are the most commonly used type of equipment for blending liquids and preparing solutions.

Liquid mixing in stirred tanks is covered in Volume 1, Chapter 7, and in several textbooks; Uhl and Gray (1967), Harnby *et al.* (1997) and Tatterson (1991), (1993).

A typical arrangement of the agitator and baffles in a stirred tank, and the flow pattern generated, is shown in Figure 10.54. Mixing occurs through the bulk flow of the liquid and, on a microscopic scale, by the motion of the turbulent eddies created by the agitator. Bulk flow is the predominant mixing mechanism required for the blending of miscible liquids and for solids suspension. Turbulent mixing is important in operations involving mass and heat transfer; which can be considered as shear controlled processes.

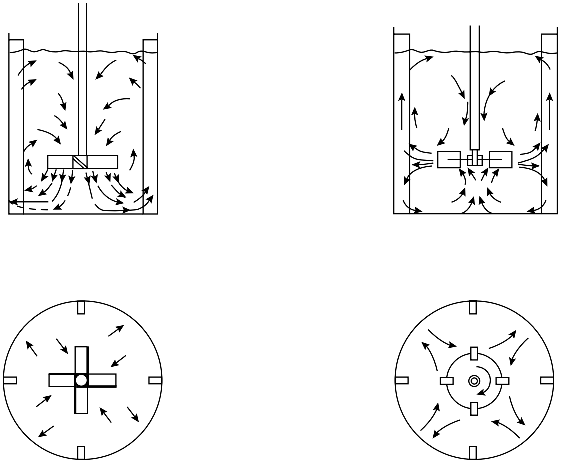

Figure 10.54. Agitator arrangements and flow patterns

The most suitable agitator for a particular application will depend on the type of mixing required, the capacity of the vessel, and the fluid properties, mainly the viscosity.

The three basic types of impeller which are used at high Reynolds numbers (low viscosity) are shown in Figures 10.55*a*, *b*, *c*. They can be classified according to the predominant direction of flow leaving the impeller. The flat-bladed (Rushton) turbines are essentially radial-flow devices, suitable for processes controlled by turbulent mixing (shear controlled processes). The propeller and pitched-bladed turbines are essentially axial-flow devices, suitable for bulk fluid mixing.

Paddle, anchor and helical ribbon agitators (Figures 10.56*a*, *b*, *c*), and other special shapes, are used for more viscous fluids.

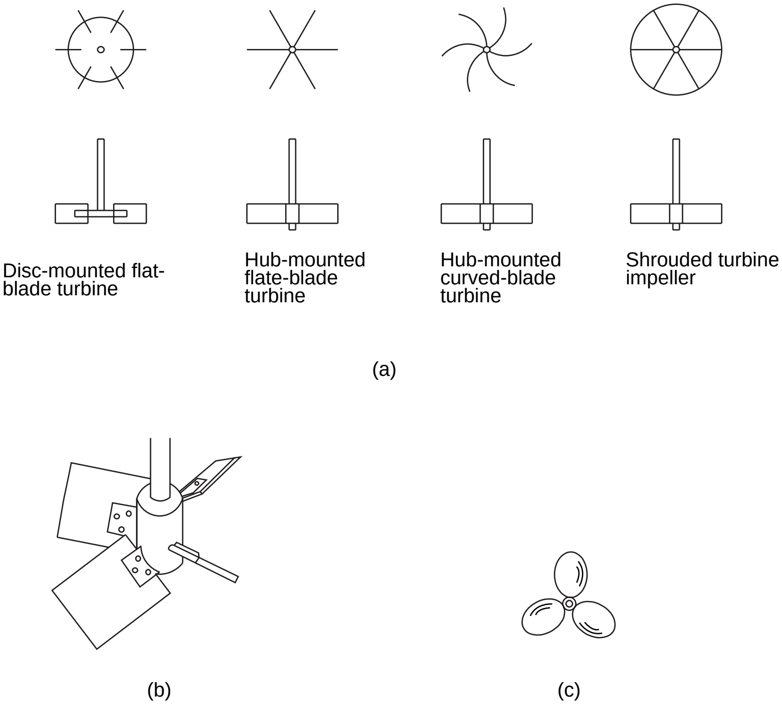

Figure 10.55. Basic impeller types (*a*) Turbine impeller (*b*) Pitched bladed turbine (*c*) Marine propeller

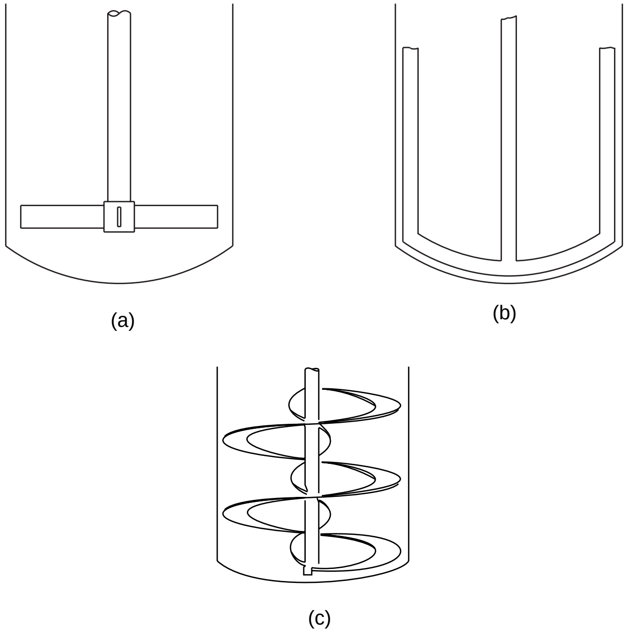

Figure 10.56. Low-speed agitators (*a*) Paddle (*b*) Anchor (*c*) Helical ribbon

The selection chart given in Figure 10.57, which has been adapted from a similar chart given by Penney (1970), can be used to make a preliminary selection of the agitator type, based on the liquid viscosity and tank volume.

For turbine agitators, impeller to tank diameter ratios of up to about 0.6 are used, with the depth of liquid equal to the tank diameter. Baffles are normally used, to improve the mixing and reduce problems from vortex formation. Anchor agitators are used with close clearance between the blades and vessel wall, anchor to tank diameter ratios of

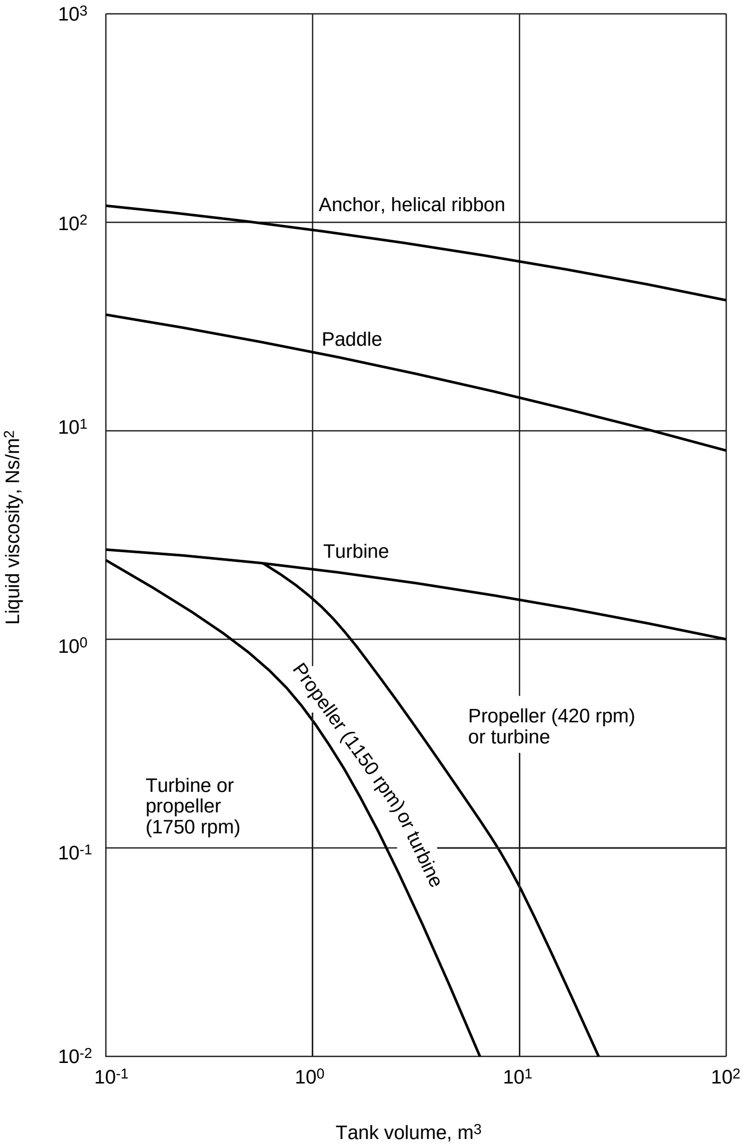

Figure 10.57. Agitator selection guide

0.95 or higher. The selection of agitators for dispersing gases in liquids is discussed by Hicks (1976).

Agitator power consumption

The shaft power required to drive an agitator can be estimated using the following generalised dimensionless equation, the derivation of which is given in Volume 2, Chapter 13.

$$N_p = K Re^b Fr^c \tag{10.11}$$

where N_p = power number = $\dfrac{P}{D^5 N^3 \rho}$,

Re = Reynolds number = $\dfrac{D^2 N \rho}{\mu}$,

Fr = Froude number = $\dfrac{DN^2}{g}$,

P = shaft power, W,

K = a constant, dependent on the agitator type, size, and the agitator-tank geometry,

ρ = fluid density, kg/m^3,

μ = fluid viscosity, Ns/m^2,

N = agitator speed, s^{-1} (revolutions per second) (rps),

D = agitator diameter, m,

g = gravitational acceleration, 9.81 m/s^2.

Values for the constant K and the indices b and c for various types of agitator, tank-agitator geometries, and dimensions, can be found in the literature; Rushton *et al.* (1950). A useful review of the published correlations for agitator power consumption and heat transfer in agitated vessels is given by Wilkinson and Edwards (1972); they include correlations for non-Newtonian fluids. Typical power curves for propeller and turbine agitators are given in Figures 10.58 and 10.59. In the laminar flow region the index "b" $= 1$; and at high Reynolds number the power number is independent of the Froude number; index "c" $= 0$.

An estimate of the power requirements for various applications can be obtained from Table 10.14.

Table 10.14. Power requirements—baffled agitated tanks

Agitation	Applications	Power, kW/m^3
Mild	Blending, mixing	0.04–0.10
	Homogeneous reactions	0.01–0.03
Medium	Heat transfer	0.03–1.0
	Liquid-liquid mixing	1.0–1.5
Severe	Slurry suspension	1.5–2.0
	Gas absorption,	1.5–2.0
	Emulsions	1.5–2.0
Violent	Fine slurry suspension	>2.0

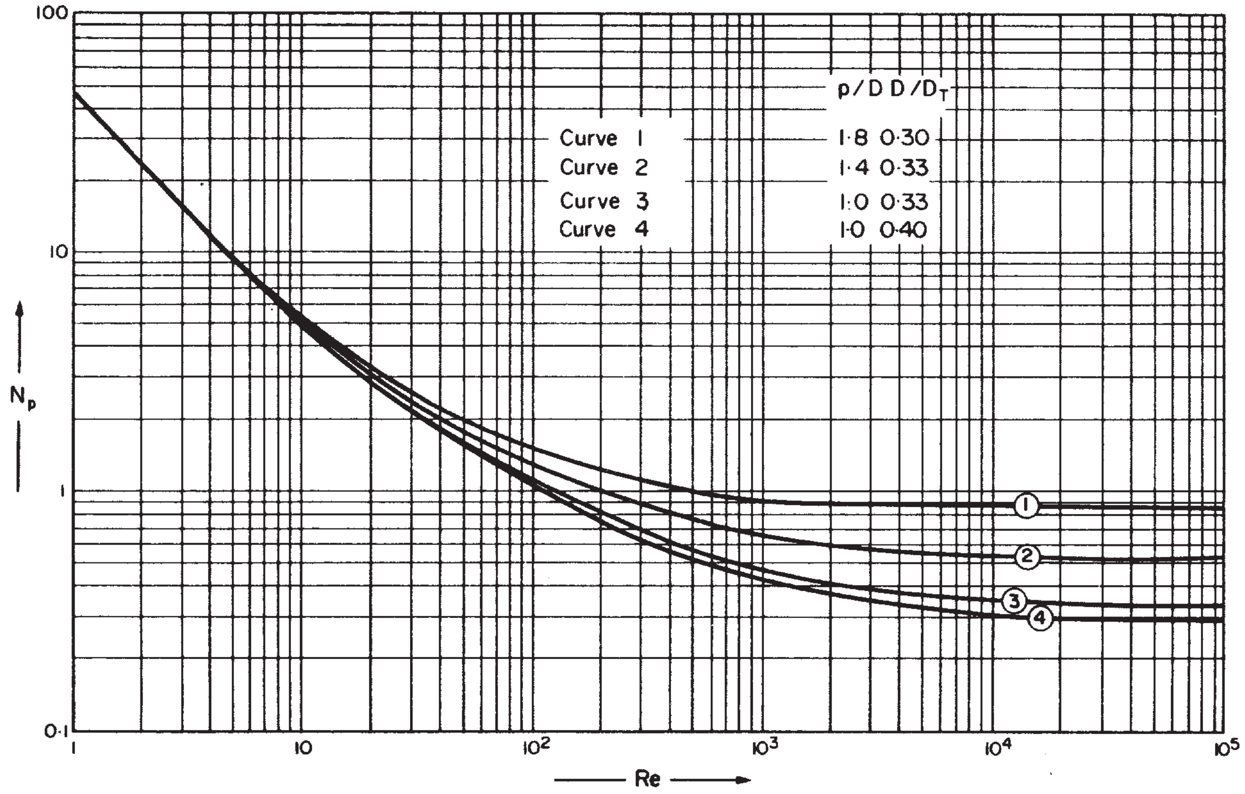

Figure 10.58. Power correlation for single three-bladed propellers baffled, (from Uhl and Gray (1967) with permission). p = blade pitch, D = impeller diameter, D_T = tank diameter

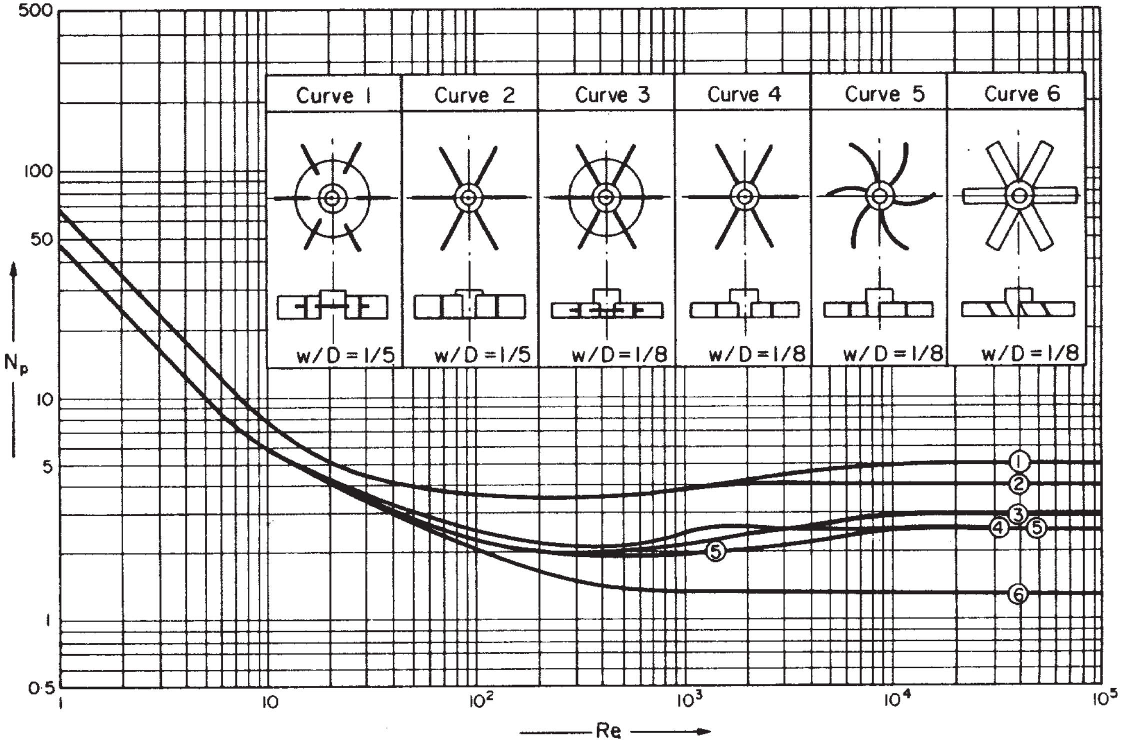

Figure 10.59. Power correlations for baffled turbine impellers, for tank with 4 baffles (From Uhl and Gray (1967) with permission). w = impeller width, D = impeller diameter

Side-entering agitators

Side-entering agitators are used for blending low viscosity liquids in large tanks, where it is impractical to use conventional agitators supported from the top of the tank; see Oldshue *et al*. (1956).

Where they are used with flammable liquids, particular care must be taken in the design and maintenance of the shaft seals, as any leakage may cause a fire.

For blending flammable liquids, the use of liquid jets should be considered as an "intrinsically" safer option; see Fossett and Prosser (1949).

10.11.3. Solids and pastes

A great variety of specialised equipment has been developed for mixing dry solids and pastes (wet solids). The principal types of equipment and their fields of application are given in Table 10.15. Descriptions of the equipment can be found in the literature; Perry *et al*. (1997), Reid (1979). Cone blenders are used for free-flowing solids. Ribbon blenders can be used for dry solids and for blending liquids with solids. Z-blade mixers and pan mixers are used for kneading heavy pastes and doughs. Most solid and paste mixers are designed for batch operation.

A selection chart for solids mixing equipment is given by Jones (1985).

Table 10.15. Solids and paste mixers

Type of equipment	Mixing action	Applications	Examples
Rotating: cone, double cone, drum	Tumbling action	Blending dry, free-flowing powders, granules, crystals	Pharmaceuticals, food, chemicals
Air blast fluidisation	Air blast lifts and mixes particles	Dry powders and granules	Milk powder; detergents, chemicals
Horizontal trough mixer, with ribbon blades, paddles or beaters	Rotating element produces contra-flow movement of materials	Dry and moist powders	Chemicals, food, pigments, tablet granulation
Z-blade mixers	Shearing and kneading by the specially shaped blades	Mixing heavy pastes, creams and doughs	Bakery industry, rubber doughs, plastic dispersions
Pan mixers	Vertical, rotating paddles, often with planetary motion	Mixing, whipping and kneading of materials ranging from low viscosity pastes to stiff doughs	Food, pharmaceuticals and chemicals, printing inks and ceramics
Cylinder mixers, single and double	Shearing and kneading action	Compounding of rubbers and plastics	Rubbers, plastics, and pigment dispersion

10.12. TRANSPORT AND STORAGE OF MATERIALS

In this section the principal means used for the transport and storage of process materials: gases, liquids and solids are discussed briefly. Further details and full descriptions of the equipment used can be found in various handbooks. Pumps and compressors are also discussed in Chapters 3 and 5 of this volume, and in Volume 1, Chapter 8.

10.12.1. Gases

The type of equipment best suited for the pumping of gases in pipelines depends on the flow-rate, the differential pressure required, and the operating pressure.

In general, fans are used where the pressure drop is small, <35 cm H_2O (0.03 bar); axial flow compressors for high flow-rates and moderate differential pressures; centrifugal compressors for high flow-rates and, by staging, high differential pressures. Reciprocating compressors can be used over a wide range of pressures and capacities, but are normally only specified in preference to centrifugal compressors where high pressures are required at relatively low flow-rates.

Reciprocating, centrifugal and axial flow compressors are the principal types used in the chemical process industries, and the range of application of each type is shown in Figure 10.60 which has been adapted from a similar diagram by Dimoplon (1978). A more comprehensive selection guide is given in Table 10.16. Diagrammatic sketches of the compressors listed are given in Figure 10.61.

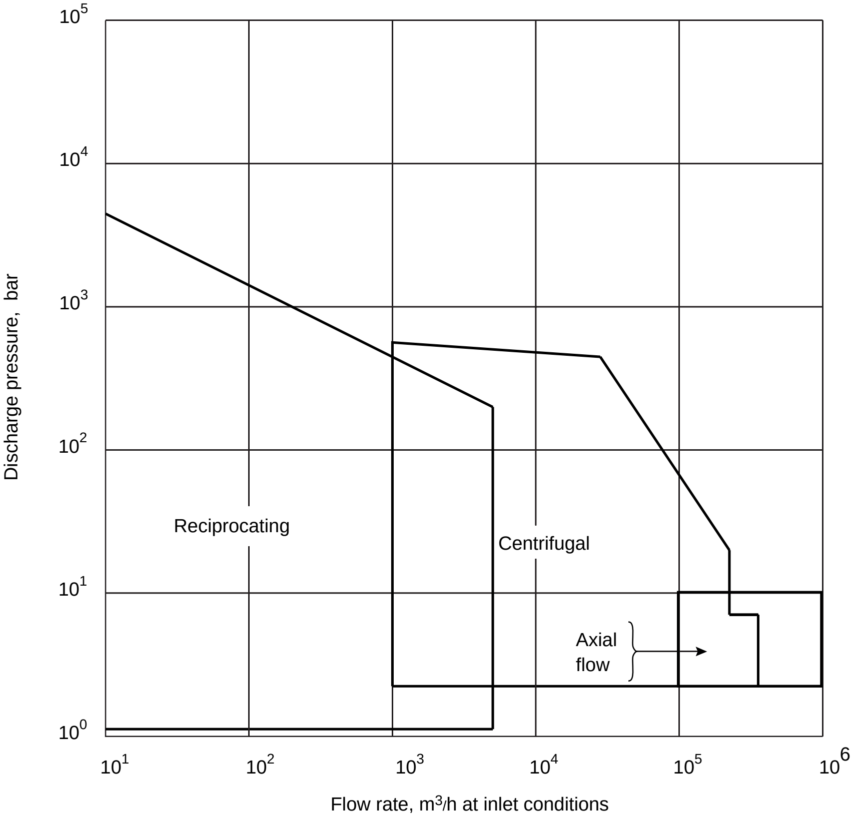

Figure 10.60. Compressor operating ranges

Table 10.16. Operating range of compressors and blowers (after Begg, 1966)

Type of compressor	Normal maximum speed (rpm)	Normal maximum capacity (m^3/h)	Normal maximum pressure (differential) (bar)	
			Single stage	Multiple stage
Displacement				
1. Reciprocating	300	85,000	3.5	5000
2. Sliding vane	300	3400	3.5	8
3. Liquid ring	200	2550	0.7	1.7
4. Rootes	250	4250	0.35	1.7
5. Screw	10,000	12,750	3.5	17
Dynamic				
6. Centrifugal fan	1000	170,000		0.2
7. Turbo blower	3000	8500	0.35	1.7
8. Turbo compressor	10,000	136,000	3.5	100
9. Axial flow fan	1000	170,000	0.35	2.0
10. Axial flow blower	3000	170,000	3.5	10

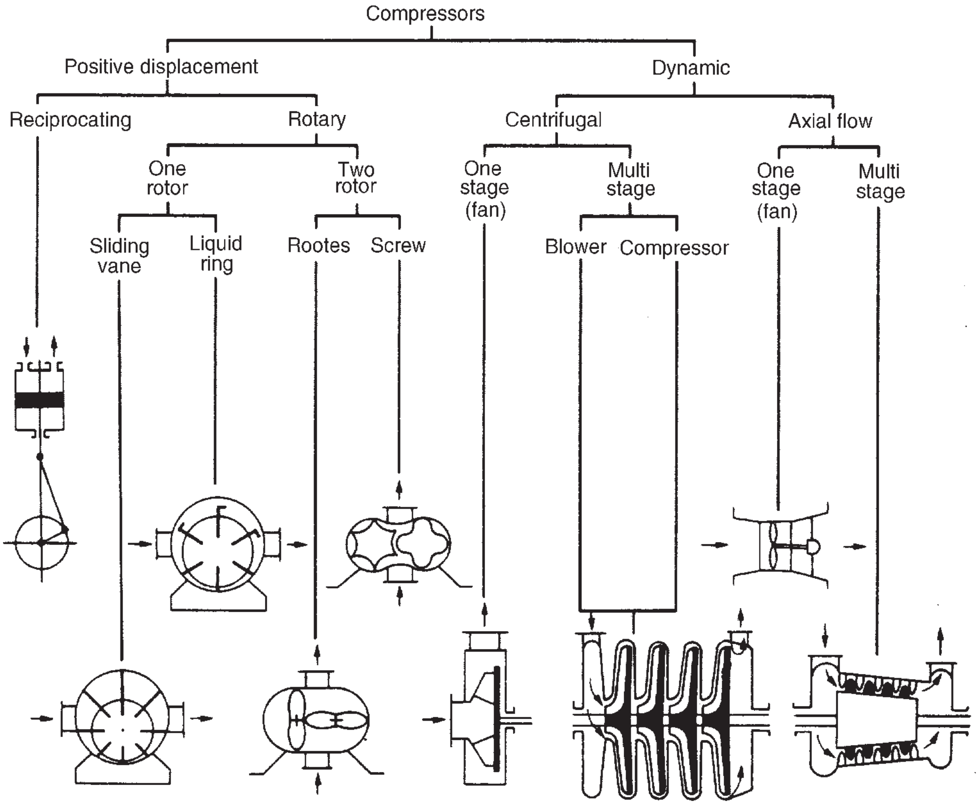

Figure 10.61. Type of compressor (Begg, 1966)

Several textbooks are available on compressor design, selection and operation: Bloch *et al*. (1982), Brown (1990) and Aungier (1999), (2003).

Vacuum production

The production of vacuum (sub-atmospheric pressure) is required for many chemical engineering processes; for example, vacuum distillation, drying and filtration. The type of vacuum pump needed will depend on the degree of vacuum required, the capacity of the system and the rate of air inleakage.

Reciprocating and rotary positive displacement pumps are commonly used where moderately low vacuum is required, about 10 mmHg (0.013 bar), at moderate to high flow rates; such as in vacuum filtration.

Steam-jet ejectors are versatile and economic vacuum pumps and are frequently used, particularly in vacuum distillation. They can handle high vapour flow rates and, by using several ejectors in series, can produce low pressures, down to about 0.1 mmHg (0.13 mbar).

The operating principle of steam-jet ejectors is explained in Volume 1, Chapter 8. Their specification, sizing and operation are covered in a comprehensive series of papers by Power (1964). Diffusion pumps are used where very low pressures are required (hard vacuum) for processes such as molecular distillation.

For a general reference on the design and application of vacuum system see Ryan and Roper (1986).

Storage

Gases are stored at low pressure in gas holders similar to those used for town gas, which are a familiar sight in any town. The liquid sealed type are most commonly used. These consist of a number of telescopic sections (lifts) which rise and fall as gas is added to or withdrawn from the holder. The dry sealed type is used where the gas must be kept dry. In this type the gas is contained by a piston moving in a large vertical cylindrical vessel. Water seal holders are intrinsically safer for use with flammable gases than the dry seal type; as any leakage through the piston seal may form an explosive mixture in the closed space between the piston and the vessel roof. Details of the construction of gas holders can be found in text books on Gas Engineering; Meade (1921), Smith (1945).

Gases are stored at high pressures where this is a process requirement and to reduce the storage volume. For some gases the volume can be further reduced by liquefying the gas by pressure or refrigeration. Cylindrical and spherical vessels (Horton spheres) are used. The design of pressure vessels is discussed in Chapter 13.

10.12.2. Liquids

The selection of pumps for liquids is discussed in Chapter 5. Descriptions of most of the types of pumps used in the chemical process industries are given in Volume 1, Chapter 8. Several textbooks and handbooks have also been published on this subject: Garay (1997), Karassik (2001) and Parmley (2000).

The principal types used and their operating pressures and capacity ranges are summarised in Table 10.17 and Figure 10.63. Centrifugal pumps will normally be the first

Table 10.17. Normal operating range of pumps

Type	Capacity range (m^3/h)	Typical head (m of water)
Centrifugal	$0.25-10^3$	10–50 300 (multistage)
Reciprocating	0.5–500	50–200
Diaphragm	0.05–50	5–60
Rotary gear and similar	0.05–500	60–200
Rotary sliding vane or similar	0.25–500	7–70

choice for pumping process fluids, the other types only being used for special applications; such as the use of reciprocating and gear pumps for metering.

Pump shaft power

The power required for pumping an incompressible fluid is given by:

$$\text{Power} = \frac{\Delta P Q_p}{\eta_p} \times 100 \tag{10.12}$$

where ΔP = pressure differential across the pump, N/m^2,
Q_p = flow rate, m^3/s,
η_p = pump efficiency, per cent.

See also, Chapter 5, Section 5.4.3.

The efficiency of centrifugal pumps depends on their size. The values given in Figure 10.62 can be used to estimate the power and energy requirements for preliminary design purpose. The efficiency of reciprocating pumps is usually around 90 per cent.

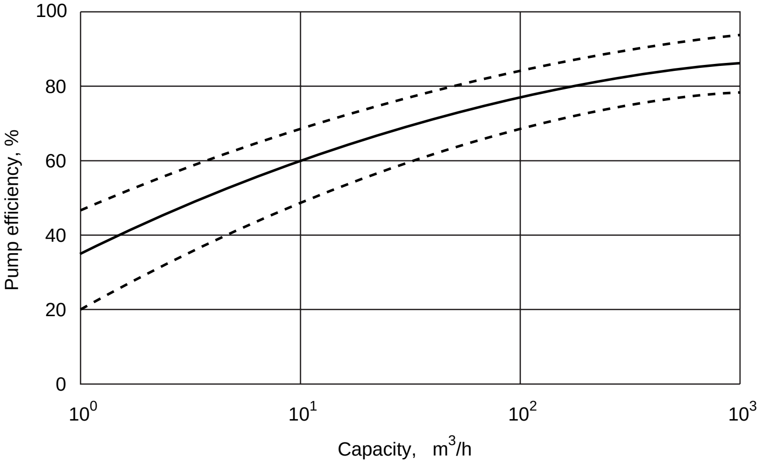

Figure 10.62. Efficiencies of centrifugal pumps

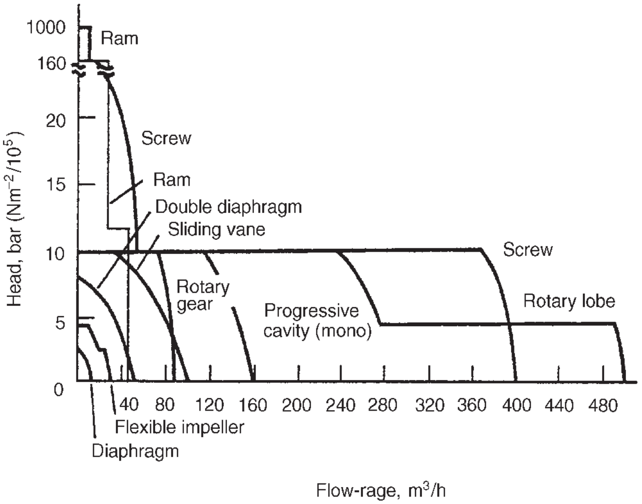

Figure 10.63. Selection of positive displacement pumps (adapted from Marshall (1985)). Descriptions of the types mentioned are given in Volume 1, Chapter 8

Storage

Liquids are usually stored in bulk in vertical cylindrical steel tanks. Fixed and floating-roof tanks are used. In a floating-roof tank a movable piston floats on the surface of the liquid and is sealed to the tank walls. Floating-roof tanks are used to eliminate evaporation losses and, for flammable liquids, to obviate the need for inert gas blanketing to prevent an explosive mixture forming above the liquid, as would be the situation with a fixed-roof tank.

Horizontal cylindrical tanks and rectangular tanks are also used for storing liquids, usually for relatively small quantities.

The design of fixed roof, vertical tanks is discussed in Chapter 13, Section 13.16.

10.12.3. Solids

The movement and storage of solids is usually more expensive than the movement of liquids and gases, which can be easily pumped down a pipeline. The best equipment to use will depend on a number of factors:

1. The throughput.
2. Length of travel.
3. Change in elevation.
4. Nature of the solids: size, bulk density, angle of repose, abrasiveness, corrosiveness, wet or dry.

Belt conveyors are the most commonly used type of equipment for the continuous transport of solids. They can carry a wide range of materials economically over long and short distances; both horizontally or at an appreciable angle, depending on the angle of repose of the solids. A belt conveyor consists of an endless belt of a flexible material, supported on rollers (idlers), and passing over larger rollers at each end, one of which is driven. The belt material is usually fabric-reinforced rubber or plastics; segmental metal belts are also used. Belts can be specified to withstand abrasive and corrosive materials; see BS 490.

Screw conveyors, also called worm conveyors, are used for materials that are free flowing. The basic principle of the screw conveyor has been known since the time of Archimedes. The modern conveyor consists of a helical screw rotating in a U-shaped trough. They can be used horizontally or, with some loss of capacity, at an incline to lift materials. Screw conveyors are less efficient than belt conveyors, due to the friction between the solids and the flights of the screw and the trough, but are cheaper and easier to maintain. They are used to convey solids over short distances, and when some elevation (lift) is required. They can also be used for delivering a metered flow of solids.

The most widely used equipment where a vertical lift is required is the bucket elevator. This consists of buckets fitted to an endless chain or belt, which passes over a driven roller or sprocket at the top end. Bucket elevators can handle a wide range of solids, from heavy lumps to fine powders, and are suitable for use with wet solids and slurries.

The mechanical conveying of solids is the subject of a book by Colijn (1985).

Pneumatic and hydraulic conveying, in which the solid particles are transported along a pipeline in suspension in a fluid, are discussed in Volume 1, Chapter 5, and in a book by Mills (2003); see also Mills *et al.* (2004).

Storage

The simplest way to store solids is to pile them on the ground in the open air. This is satisfactory for the long-term storage of materials that do not deteriorate on exposure to the elements; for example, the seasonal stock piling of coal at collieries and power stations. For large stockpiles, permanent facilities are usually installed for distributing and reclaiming the material; travelling gantry cranes, grabs and drag scrapers feeding belt conveyors are used. For small, temporary, storages mechanical shovels and trunks can be used. Where the cost of recovery from the stockpile is large compared with the value of the stock held, storage in silos or bunkers should be considered.

Overhead bunkers, also called bins or hoppers, are normally used for the short-term storage of materials that must be readily available for the process. They are arranged so that the material can be withdrawn at a steady rate from the base of the bunker on to a suitable conveyor. Bunkers must be carefully designed to ensure the free flow of material within the bunker, to avoid packing and bridging. Jenike (1967) and Jenike and Johnson (1970), has studied the flow of solids in containers and developed design methods. All aspects of the design of bins and hoppers, including feeding and discharge systems, are covered in a book by Reisner (1971).

See also the British Material Handling Board's code of practice on the design of silos and bunkers, BMHB (1992).

The storage and transport of wet solids are covered by Heywood (1991).

10.13. REACTORS

The reactor is the heart of a chemical process. It is the only place in the process where raw materials are converted into products, and reactor design is a vital step in the overall design of the process.

Numerous texts have been published on reactor design, and a selection is given in the bibliography at the end of this chapter. The volumes by Rase (1977), (1990) cover the practical aspects of reactor design and include case studies of industrial reactors. The design of electrochemical reactors is covered by Rousar *et al*. (1985) and Scott (1991).

The treatment of reactor design in this section will be restricted to a discussion of the selection of the appropriate reactor type for a particular process, and an outline of the steps to be followed in the design of a reactor.

The design of an industrial chemical reactor must satisfy the following requirements:

1. The chemical factors: the kinetics of the reaction. The design must provide sufficient residence time for the desired reaction to proceed to the required degree of conversion.
2. The mass transfer factors: with heterogeneous reactions the reaction rate may be controlled by the rates of diffusion of the reacting species; rather than the chemical kinetics.
3. The heat transfer factors: the removal, or addition, of the heat of reaction.
4. The safety factors: the confinement of hazardous reactants and products, and the control of the reaction and the process conditions.

The need to satisfy these interrelated, and often contradictory factors, makes reactor design a complex and difficult task. However, in many instances one of the factors will predominate and will determine the choice of reactor type and the design method.

10.13.1. Principal types of reactor

The following characteristics are normally used to classify reactor designs:

1. Mode of operation: batch or continuous.
2. Phases present: homogeneous or heterogeneous.
3. Reactor geometry: flow pattern and manner of contacting the phases
    - (i) stirred tank reactor;
    - (ii) tubular reactor;
    - (iii) packed bed, fixed and moving;
    - (iv) fluidised bed.

Batch or continuous processing

In a batch process all the reagents are added at the commencement; the reaction proceeds, the compositions changing with time, and the reaction is stopped and the product withdrawn when the required conversion has been reached. Batch processes are suitable for small-scale production and for processes where a range of different products, or grades, is to be produced in the same equipment; for instance, pigments, dyestuffs and polymers.

In continuous processes the reactants are fed to the reactor and the products withdrawn continuously; the reactor operates under steady-state conditions. Continuous production will normally give lower production costs than batch production, but lacks the flexibility of batch production. Continuous reactors will usually be selected for large-scale production. Processes that do not fit the definition of batch or continuous are often referred to as semi-continuous or semi-batch. In a semi-batch reactor some of the reactants may be added, or some of the products withdrawn, as the reaction proceeds. A semi-continuous process can be one which is interrupted periodically for some purpose; for instance, for the regeneration of catalyst.

Homogeneous and heterogeneous reactions

Homogeneous reactions are those in which the reactants, products, and any catalyst used form one continuous phase: gaseous or liquid.

Homogeneous gas phase reactors will always be operated continuously; whereas liquid phase reactors may be batch or continuous. Tubular (pipe-line) reactors are normally used for homogeneous gas-phase reactions; for example, in the thermal cracking of petroleum crude oil fractions to ethylene, and the thermal decomposition of dichloroethane to vinyl chloride. Both tubular and stirred tank reactors are used for homogeneous liquid-phase reactions.

In a heterogeneous reaction two or more phases exist, and the overriding problem in the reactor design is to promote mass transfer between the phases. The possible combination of phases are:

1. Liquid-liquid: immiscible liquid phases; reactions such as the nitration of toluene or benzene with mixed acids, and emulsion polymerisations.
2. Liquid-solid: with one, or more, liquid phases in contact with a solid. The solid may be a reactant or catalyst.
3. Liquid-solid-gas: where the solid is normally a catalyst; such as in the hydrogeneration of amines, using a slurry of platinum on activated carbon as a catalyst.
4. Gas-solid: where the solid may take part in the reaction or act as a catalyst. The reduction of iron ores in blast furnaces and the combustion of solid fuels are examples where the solid is a reactant.
5. Gas-liquid: where the liquid may take part in the reaction or act as a catalyst.

Reactor geometry (type)

The reactors used for established processes are usually complex designs which have been developed (have evolved) over a period of years to suit the requirements of the process, and are unique designs. However, it is convenient to classify reactor designs into the following broad categories.

Stirred tank reactors

Stirred tank (agitated) reactors consist of a tank fitted with a mechanical agitator and a cooling jacket or coils. They are operated as batch reactors or continuously. Several reactors may be used in series.

The stirred tank reactor can be considered the basic chemical reactor; modelling on a large scale the conventional laboratory flask. Tank sizes range from a few litres to several thousand litres. They are used for homogeneous and heterogeneous liquid-liquid and liquid-gas reactions; and for reactions that involve finely suspended solids, which are held in suspension by the agitation. As the degree of agitation is under the designer's control, stirred tank reactors are particularly suitable for reactions where good mass transfer or heat transfer is required.

When operated as a continuous process the composition in the reactor is constant and the same as the product stream, and, except for very rapid reactions, this will limit the conversion that can be obtained in one stage.

The power requirements for agitation will depend on the degree of agitation required and will range from about 0.2 kW/m^3 for moderate mixing to 2 kW/m^3 for intense mixing.

Tubular reactor

Tubular reactors are generally used for gaseous reactions, but are also suitable for some liquid-phase reactions.

If high heat-transfer rates are required, small-diameter tubes are used to increase the surface area to volume ratio. Several tubes may be arranged in parallel, connected to a manifold or fitted into a tube sheet in a similar arrangement to a shell and tube heat exchanger. For high-temperature reactions the tubes may be arranged in a furnace.

The pressure-drop and heat-transfer coefficients in empty tube reactors can be calculated using the methods for flow in pipes given in Volume 1.

Packed bed reactors

There are two basic types of packed-bed reactor: those in which the solid is a reactant, and those in which the solid is a catalyst. Many examples of the first type can be found in the extractive metallurgical industries.

In the chemical process industries the designer will normally be concerned with the second type: catalytic reactors. Industrial packed-bed catalytic reactors range in size from small tubes, a few centimetres diameter, to large diameter packed beds. Packed-bed reactors are used for gas and gas-liquid reactions. Heat-transfer rates in large diameter packed beds are poor and where high heat-transfer rates are required fluidised beds should be considered.

Fluidised bed reactors

The essential features of a fluidised bed reactor is that the solids are held in suspension by the upward flow of the reacting fluid; this promotes high mass and heat-transfer rates and good mixing. Heat-transfer coefficients in the order of 200 $W/m^{2\circ}C$ to jackets and internal coils are typically obtained. The solids may be a catalyst; a reactant in fluidised combustion processes; or an inert powder, added to promote heat transfer.

Though the principal advantage of a fluidised bed over a fixed bed is the higher heat-transfer rate, fluidised beds are also useful where it is necessary to transport large quantities of solids as part of the reaction processes, such as where catalysts are transferred to another vessel for regeneration.

Fluidisation can only be used with relatively small sized particles, $<300\ \mu m$ with gases.

A great deal of research and development work has been done on fluidised bed reactors in recent years, but the design and scale up of large diameter reactors is still an uncertain process and design methods are largely empirical.

The principles of fluidisation processes are covered in Volume 2, Chapter 6. The design of fluidised bed reactors is discussed by Rase (1977).

10.13.2. Design procedure

A general procedure for reactor design is outlined below:

1. Collect together all the kinetic and thermodynamic data on the desired reaction and the side reactions. It is unlikely that much useful information will be gleaned from a literature search, as little is published in the open literature on commercially attractive processes. The kinetic data required for reactor design will normally be obtained from laboratory and pilot plant studies. Values will be needed for the rate of reaction over a range of operating conditions: pressure, temperature, flow-rate and catalyst concentration. The design of experimental reactors and scale-up is discussed by Rase (1977).
2. Collect the physical property data required for the design; either from the literature, by estimation or, if necessary, by laboratory measurements.
3. Identify the predominant rate-controlling mechanism: kinetic, mass or heat transfer. Choose a suitable reactor type, based on experience with similar reactions, or from the laboratory and pilot plant work.
4. Make an initial selection of the reactor conditions to give the desired conversion and yield.
5. Size the reactor and estimate its performance.
   Exact analytical solutions of the design relationships are rarely possible; semi-empirical methods based on the analysis of idealised reactors will normally have to be used.
6. Select suitable materials of construction.
7. Make a preliminary mechanical design for the reactor: the vessel design, heat-transfer surfaces, internals and general arrangement.
8. Cost the proposed design, capital and operating, and repeat steps 4 to 8, as necessary, to optimise the design.

In choosing the reactor conditions, particularly the conversion, and optimising the design, the interaction of the reactor design with the other process operations must not be overlooked. The degree of conversion of raw materials in the reactor will determine the size, and cost, of any equipment needed to separate and recycle unreacted materials. In these circumstances the reactor and associated equipment must be optimised as a unit.

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10.15. NOMENCLATURE

		Dimensions in **MLT**
A_i	Area of interface	$\mathbf{L}^2$
A_s	Surface area of cyclone	$\mathbf{L}^2$
A_v	Area for vapour flow	$\mathbf{L}^2$
A_1	Area of cyclone inlet duct	$\mathbf{L}^2$
b	Index in equation 10.11	—
c	Index in equation 10.11	—
D	Agitator diameter	$\mathbf{L}$
D_c	Cyclone diameter	$\mathbf{L}$
D_{c_1}	Diameter of standard cyclone	$\mathbf{L}$
D_{c_2}	Diameter of proposed cyclone design	$\mathbf{L}$
D_T	Tank diameter	$\mathbf{L}$
D_v	minimum vessel diameter for separator	$\mathbf{L}$
d	Particle diameter	$\mathbf{L}$
d_s	Diameter of solid particle removed in a centrifuge	$\mathbf{L}$
d_1	Mean diameter of particles separated in cyclone under standard conditions	$\mathbf{L}$
d_2	Mean diameter of particles separated in proposed cyclone design	$\mathbf{L}$
d_{50}	Particle diameter for which cyclone is 50 per cent efficient	$\mathbf{L}$
f_c	Friction factor for cyclones	—
f_v	fraction of cross-sectional area occupied by vapour.	—
h_v	height above liquid level	$\mathbf{L}$
K	Constant in equation 10.11	—
L	Cyclone feed volumetric flow-rate	$\mathbf{L}^3\mathbf{T}^{-1}$
L_c	Continuous phase volumetric flow-rate	$\mathbf{L}^3\mathrm{T}^{-1}$
L_v	length of separator	$\mathbf{LT}^{-1}$
l	Length of decanter vessel	$\mathbf{L}$
N	Agitator speed	$\mathbf{T}^{-1}$
P	Agitator shaft power	$\mathbf{ML}^2\mathbf{T}^{-3}$
ΔP	Press differential (pressure drop)	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
p	Agitator blade pitch	$\mathbf{L}$
Q	Volumetric flow-rate of liquid through a centrifuge	$\mathbf{L}^3\mathbf{T}^{-1}$
Q_p	Volumetric liquid flow through a pump	$\mathbf{L}^3\mathbf{T}^{-1}$
Q_1	Standard flow-rate in cyclone	$\mathbf{L}^3\mathbf{T}^{-1}$
Q_2	Proposed flow-rate in cyclone	$\mathbf{L}^3\mathbf{T}^{-1}$
r	Radius of decanter vessel	$\mathbf{L}$
r_e	Radius of cyclone exit pipe	$\mathbf{L}$
r_t	Radius of circle to which centre line of cyclone inlet duct is tangential	$\mathbf{L}$
u_c	Velocity of continuous phase in a decanter	$\mathbf{LT}^{-1}$
u_d	Settling (terminal) velocity of dispersed phase in a decanter	$\mathbf{LT}^{-1}$
u_g	Terminal velocity of solid particles settling under gravity	$\mathbf{LT}^{-1}$
u_s	velocity in a separator	$\mathbf{LT}^{-1}$
u_t	settling velocity	$\mathbf{LT}^{-1}$
$\hat{u}_v$	Maximum allowable vapour velocity in a separating vessel	$\mathbf{LT}^{-1}$
u_1	Velocity in cyclone inlet duct	$\mathbf{LT}^{-1}$
u_2	Velocity in cyclone exit duct	$\mathbf{LT}^{-1}$
V_v	Gas, or vapour volumetric flow-rate	$\mathbf{L}^3\mathbf{T}^{-1}$
w	Width of interface in a decanter	$\mathbf{L}$
z_1	Height to light liquid overflow from a decanter	$\mathbf{L}$
z_2	Height to heavy liquid overflow from a decanter	$\mathbf{L}$
z_3	Height to the interface in a decanter	$\mathbf{L}$
η	Separating efficiency of a centrifuge	—
η_p	Pump efficiency	—
μ	Liquid viscosity	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$
μ_c	Viscosity of continuous phase	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$
μ_1	Cyclone test fluid viscosity	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$

μ_2	Viscosity of fluid in proposed cyclone design	$\mathbf{ML^{-1}T^{-1}}$
ρ	Liquid density	$\mathbf{ML^{-3}}$
ρ_f	Gas density	$\mathbf{ML^{-3}}$
ρ_{L}	Liquid density	$\mathbf{ML^{-3}}$
ρ_s	Density of solid	$\mathbf{ML^{-3}}$
ρ_v	Vapour density	$\mathbf{ML^{-3}}$
ρ_1	Light liquid density in a decanter	$\mathbf{ML^{-3}}$
ρ_2	Heavy liquid density in a decanter	$\mathbf{ML^{-3}}$
$\Delta\rho$	Difference in density between solid and liquid	$\mathbf{ML^{-3}}$
$\Delta\rho_1$	Density difference under standard conditions in standard cyclone	$\mathbf{ML^{-3}}$
$\Delta\rho_2$	Density difference in proposed cyclone design	$\mathbf{ML^{-3}}$
Σ	Sigma value for centrifuges, defined by equation 10.1	$\mathbf{L^{2}}$
ϕ	Factor in Figure 10.48	—
ψ	Parameter in Figure 10.47	—

10.16. PROBLEMS

10.1. The product from a crystalliser is to be separated from the liquor using a centrifuge. The concentration of the crystals is 6.5 per cent and the slurry feed rate to the centrifuge will be 5.0 $\mathrm{m^3/h}$. The density of the liquor is 995 $\mathrm{kg/m^3}$ and that of the crystals 1500 $\mathrm{kg/m^3}$. The viscosity of the liquor is 0.7 $\mathrm{mN\ m^{-2}s}$. The cut-off crystal size required is 5 μm.
Select a suitable type of centrifuge to use for this duty.

10.2. Dissolved solids in the tar from the bottom of a distillation column are precipitated by quenching the hot tar in oil. The solids are then separated from the oil and burnt. The density of the solids is 1100 $\mathrm{kg/m^3}$. The density of the liquid phase after addition of the tar is 860 $\mathrm{kg/m^3}$ and its viscosity, at the temperature of the mixture, 1.7 $\mathrm{mN\ m^{-2}s}$. The solid content of the oil and tar mixture is 10 per cent and the flow-rate of the liquid phase leaving the separator will be 1000 kg/h. The cut-off particle size required is 0.1 mm.
List the types of separator that could be considered for separating the solids from the liquid. Bearing mind the nature of the process, what type of separator would you recommend for this duty?

10.3. The solids from a dilute slurry are to be separated using hydrocyclones. The density of the solids is 2900 $\mathrm{kg/m^3}$, and liquid is water. A recovery of 95 per cent of particles greater than 100 μm is required. The minimum operating temperature will be 10 °C and the maximum 30 °C.

Design a hydrocyclone system to handle 1200 1/m of this slurry.

10.4. A fluidised bed is used in the production of aniline by the hydrogenation of nitrobenzene. Single-stage cyclones, followed by candle filters, are used to remove fines from the gases leaving the fluidised bed.

The reactor operates at a temperature 270 °C and a pressure of 2.5 bara. The reactor diameter is 10 m. Hydrogen is used in large excess in the reaction, and for the purposes of this exercise the properties of the gas may be taken as those of hydrogen at the reactor conditions. The density of the catalyst particles is 1800 $\mathrm{kg/m^3}$.

The estimated particle size distribution of the fines is:

Particle size, μm	50	40	30	20	10	5	2
Percentage by weight less than	100	70	40	20	10	5	2

A 70 per cent recovery of the solids is required in the cyclones.

For a gas flow rate of 100,000 m^3/h, at the reactor conditions, determine how many cyclones operating in parallel are need and design a suitable cyclone. Estimate the size distribution of the particles entering the filters.

10.5. In a process for the production of acrylic fibres by the emulsion polymerisation of acrylonitrile, the unreacted monomer is recovered from water by distillation. Acrylonitrile forms an azeotrope with water and the overhead product from the column contain around 5 mol per cent water. The overheads are condensed and the recovered acrylonitrile separated from the water in a decanter. The decanter operating temperature will be 20 °C.
Size a suitable decanter for a feed-rate of 3000 kg/h.

10.6. In the production of aniline by the hydrogenation of nitrobenzene, the reactor products are separated from unreacted hydrogen in a condenser. The condensate, which is mainly water and aniline, together with a small amount of unreacted nitrobenzene and cyclo-hexylamine, is fed to a decanter to separate the water and aniline. The separation will not be complete, as aniline is slightly soluble in water, and water in aniline. A typical material balance for the decanter is given below:

Basis 100 kg feed

	feed	aqueous stream	organic stream
water	23.8	21.4	2.4
aniline	72.2	1.1	71.1
nitrobenzene	3.2	trace	3.2
cyclo-hexylamine	0.8	0.8	trace
total	100	23.3	76.7

Design a decanter for this duty, for a feed-rate of 3500 kg/h. Concentrate on the separation of the water and aniline. The densities of water–aniline solutions are given in Appendix G, problem C.8. The decanter will operate at a maximum temperature of 30 °C.

10.7. Water droplets are to be separated from air in a simple separation drum. The flow-rate of the air is 1000 m^3/h, at stp, and it contains 75 kg of water. The drum will operate at 1.1 bara pressure and 20 °C.
Size a suitable liquid–vapour separator.

10.8. The vapours from a chlorine vaporiser will contain some liquid droplets. The vaporiser consists of a vertical, cylindrical, vessel with a submerged bundle for heating. A vapour rate of 2500 kg/h is required and the vaporiser will operate at 6 bara.
Size the vessel to restrict the carryover of liquid droplets. The liquid hold-up time need not be considered, as the liquid level will be a function of the thermal design.

CHAPTER 4

Flow-sheeting

4.1. INTRODUCTION

This chapter covers the preparation and presentation of the process flow-sheet. The flow-sheet is the key document in process design. It shows the arrangement of the equipment selected to carry out the process; the stream connections; stream flow-rates and compositions; and the operating conditions. It is a diagrammatic model of the process.

The flow-sheet will be used by the specialist design groups as the basis for their designs. This will include piping, instrumentation, equipment design and plant layout. It will also be used by operating personnel for the preparation of operating manuals and operator training. During plant start-up and subsequent operation, the flow-sheet forms a basis for comparison of operating performance with design.

The flow-sheet is drawn up from material balances made over the complete process and each individual unit. Energy balances are also made to determine the energy flows and the service requirements.

Manual flow-sheeting calculations can be tedious and time consuming when the process is large or complex, and computer-aided flow-sheeting programs are being increasingly used to facilitate this stage of process design. Their use enables the designer to consider different processes, and more alterative processing schemes, in his search for the best process and optimum process conditions. Some of the proprietary flow-sheeting programs available are discussed in this chapter. A simple linear flow-sheeting program is presented in detail and listed in the appendices.

In this chapter the calculation procedures used in flow-sheeting have for convenience been divided into manual calculation procedures and computer-aided procedures.

The next step in process design after the flow-sheet is the preparation of Piping and Instrumentation diagrams (abbreviated to P & I diagrams) often also called the Engineering Flow-sheet or Mechanical Flow-sheet. The P & I diagrams, as the name implies, show the engineering details of the process, and are based on the process flow-sheet. The preparation and presentation of P & I diagrams is discussed in Chapter 5. The abbreviation PFD (for Process Flow Diagram) is often used for process flow-sheets, and PID for Piping and Instrumentation Diagrams.

4.2. FLOW-SHEET PRESENTATION

As the process flow-sheet is the definitive document on the process, the presentation must be clear, comprehensive, accurate and complete. The various types of flow-sheet are discussed below.

4.2.1. Block diagrams

A block diagram is the simplest form of presentation. Each block can represent a single piece of equipment or a complete stage in the process. Block diagrams were used to illustrate the examples in Chapters 2 and 3. They are useful for showing simple processes. With complex processes, their use is limited to showing the overall process, broken down into its principal stages; as in Example 2.13 (Vinyl Chloride). In that example each block represented the equipment for a complete reaction stage: the reactor, separators and distillation columns.

Block diagrams are useful for representing a process in a simplified form in reports and textbooks, but have only a limited use as engineering documents.

The stream flow-rates and compositions can be shown on the diagram adjacent to the stream lines, when only a small amount of information is to be shown, or tabulated separately.

The blocks can be of any shape, but it is usually convenient to use a mixture of squares and circles, drawn with a template.

4.2.2. Pictorial representation

On the detailed flow-sheets used for design and operation, the equipment is normally drawn in a stylised pictorial form. For tender documents or company brochures, actual scale drawings of the equipment are sometimes used, but it is more usual to use a simplified representation. The symbols given in British Standard, BS 1553 (1977) “Graphical Symbols for General Engineering” Part 1, “Piping Systems and Plant” are recommended; though most design offices use their own standard symbols. A selection of symbols from BS 1553 is given in Appendix A. The American National Standards Institute (ANSI) has also published a set of symbols for use on flow-sheets. Austin (1979) has compared the British Standard, ANSI, and some proprietary flow-sheet symbols.

In Europe, the German standards organisation has published a set of guide rules and symbols for flow-sheet presentation, DIN 28004 (1988). This is available in an English translation from the British Standards Institution.

4.2.3. Presentation of stream flow-rates

The data on the flow-rate of each individual component, on the total stream flow-rate, and the percentage composition, can be shown on the flow-sheet in various ways. The simplest method, suitable for simple processes with few equipment pieces, is to tabulate the data in blocks alongside the process stream lines, as shown in Figure 4.1. Only a limited amount of information can be shown in this way, and it is difficult to make neat alterations or to add additional data.

A better method for the presentation of data on flow-sheets is shown in Figure 4.2. In this method each stream line is numbered and the data tabulated at the bottom of the sheet. Alterations and additions can be easily made. This is the method generally used by professional design offices. A typical commercial flow-sheet is shown in Figure 4.3. Guide rules for the layout of this type of flow-sheet presentation are given in Section 4.2.5.

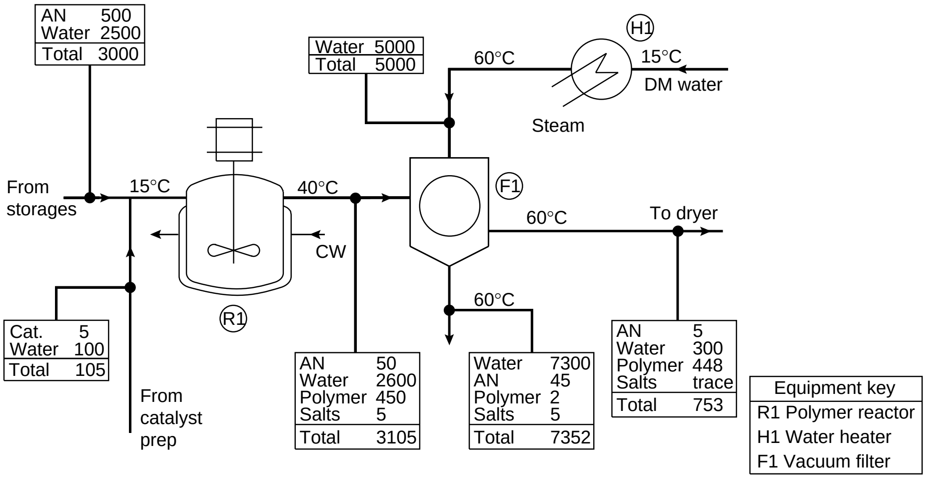


Figure 4.1. Flow-sheet: polymer production

4.2.4. Information to be included

The amount of information shown on a flow-sheet will depend on the custom and practice of the particular design office. The list given below has therefore been divided into essential items and optional items. The essential items must always be shown, the optional items add to the usefulness of the flow-sheet but are not always included.

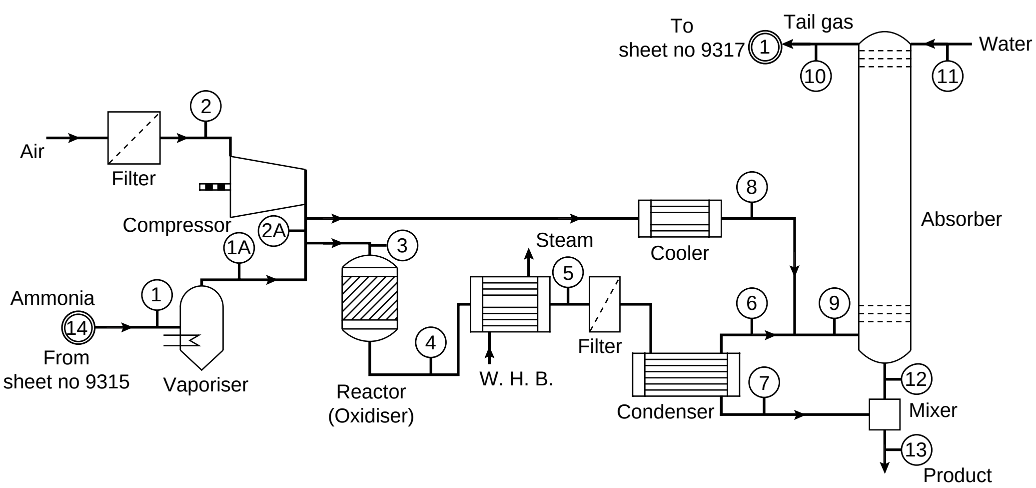
Essential information

1. Stream composition, either:
    (i) the flow-rate of each individual component, kg/h, which is preferred, or
    (ii) the stream composition as a weight fraction.
2. Total stream flow-rate, kg/h.
3. Stream temperature, degrees Celsius preferred.
4. Nominal operating pressure (the required operating pressure).

Optional information

1. Molar percentages composition.
2. Physical property data, mean values for the stream, such as:
    (i) density, kg/m^3,
    (ii) viscosity, mN s/m^2.
3. Stream name, a brief, one or two-word, description of the nature of the stream, for example "ACETONE COLUMN BOTTOMS".
4. Stream enthalpy, kJ/h.

The stream physical properties are best estimated by the process engineer responsible for the flow-sheet. If they are then shown on the flow-sheet, they are available for use by the specialist design groups responsible for the subsequent detailed design. It is best that each group use the same estimates, rather than each decide its own values.

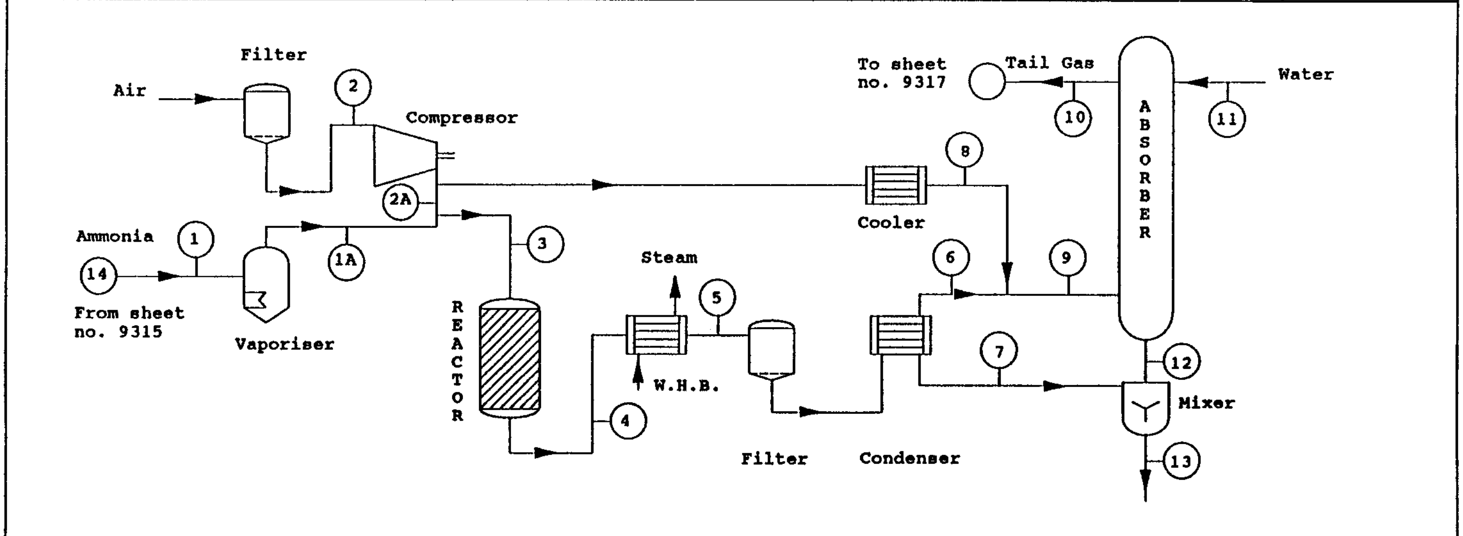


Flows kg/h Pressures nominal

Line no.	1	1A	2	2A	3	4	5	6	7	8	9	10	11	12	13		
Stream	Ammonia	Ammonia	Filtered	Oxidiser	Oxidiser	Oxidiser	W.H.B.	Condenser	Condenser	Secondary	Absorber	Tail(2)	Water	Absorber	Product		C & R Construction Inc
Component	feed	vapour	air	air	feed	outlet	outlet	gas	acid	air	feed	gas	feed	acid	acid		
NH_3	731.0	731.0	—	—	731.0	Nil	—	—	—	—	—	—	—	—	—		Nitric acid 60 per cent
O_2	—	—	3036.9	2628.2	2628.2	935.7	$(935.7)^{(1)}$	275.2	Trace	408.7	683.9	371.5	—	Trace	Trace		100,000 t/y
N_2	—	—	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	Trace	1346.1	10,014.7	10,014.7	—	Trace	Trace		Client BOP Chemicals
NO	—	—	—	—	—	1238.4	$(1238.4)^{(1)}$	202.5	—	—	202.5	21.9	—	Trace	Trace		SLIGO
NO_2		—	—	—	—	—	Trace	$(?)^{(1)}$	967.2	—	—	967.2	$(\text{Trace})^{(1)}$	—	Trace	Trace	Sheet no. 9316
HNO_3		—	—	—	—	—	Nil	Nil	—	850.6	—	—	—	—	1704.0	2554.6	
H_2O		—	—	Trace	—	—	1161.0	1161.0	29.4	1010.1	—	29.4	26.3	1376.9	1136.0	2146.0	
Total	731.0	731.0	13,027.7	11,272.9	12,003.9	12,003.9	12,003.9	10,143.1	1860.7	1754.8	11,897.7	10,434.4	1376.9	2840.0	4700.6		
Press bar	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1		Dwg by Date
Temp. °C	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43		Checked 25/7/1980

Figure 4.2. Flow-sheet: simplified nitric acid process (Example 4.2)
(1) See example

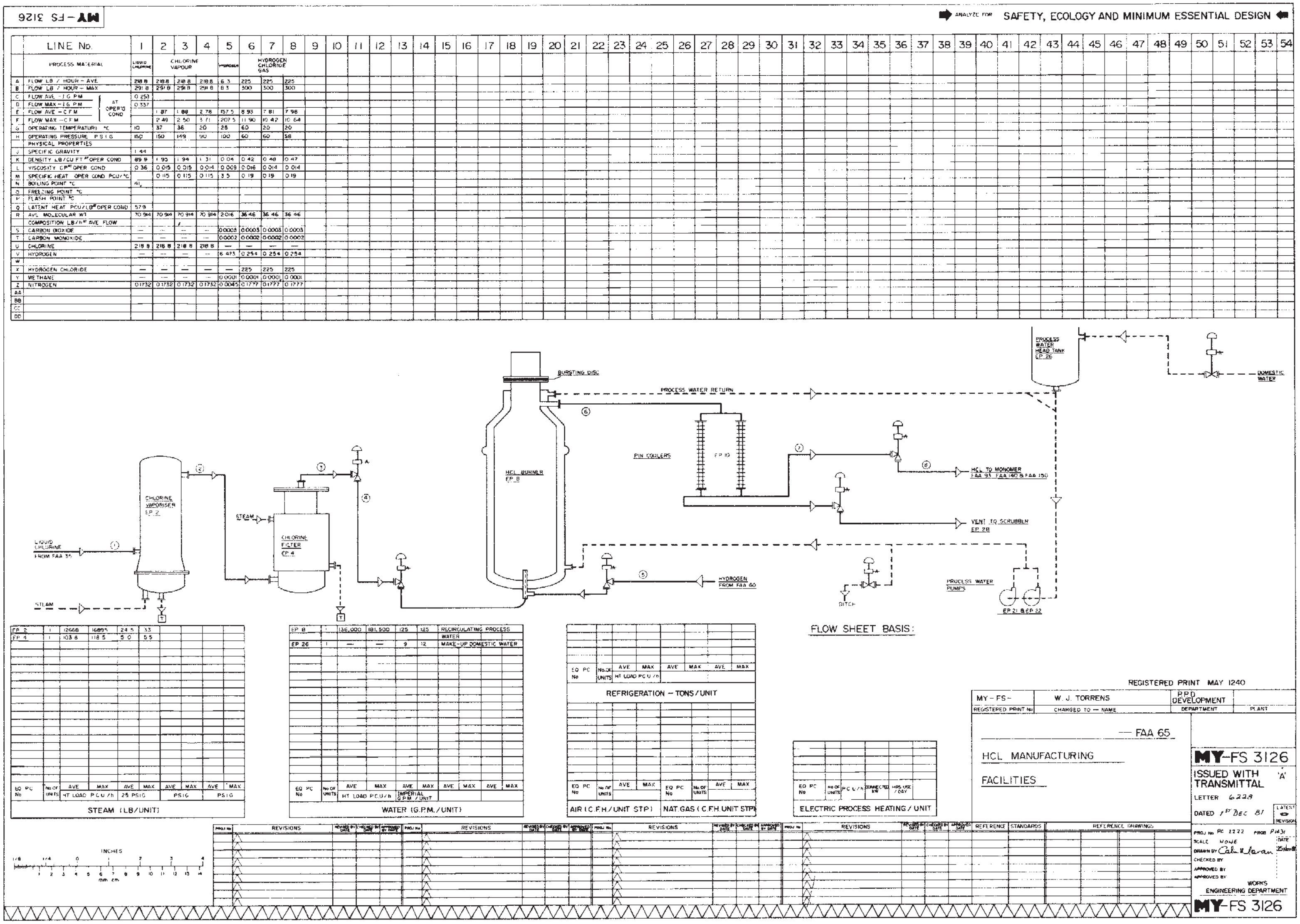
C & R Construction Inc.	Title : Nitric Acid 60 per cent	Dwg by : GRM	DATE :
	Client : BOP Chemicals SILGO	Chk by : RKS	14/12/1992



Flows (kg/h) Pressures nominal

Line No.	1	1A	2	2A	3	4	5	6	7	8	9	10	11	12	13
Stream	Ammonia	Ammonia	Filtered	Oxidiser	Oxidiser	Oxidiser	W.H.B.	Condenser	Condenser	Condenser	Absorber	Tail (2)	Water	Absorber	Product
Component	Feed	Vapour	Air	Air	Feed	Outlet	Outlet	Gas	Acid	Air	Feed	Gas	Feed	Acid	Acid
NH3	731.0	731.0	--	--	731.0	NIL	--	--	--	--	--	--	--	--	--
O2	--	--	3036.9	2628.2	2628.2	935.7	935.7	275.2	TRACE	408.7	683.9	371.5	--	TRACE	TRACE
N2	--	--	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	TRACE	1346.1	10014.7	10014.7	--	TRACE	TRACE
NO	--	--	--	--	--	1238.4	1238.4	202.5	--	--	202.5	21.9	--	TRACE	TRACE
NO2	--	--	--	--	--	TRACE	(?)	967.2	--	--	967.2	TRACE	--	TRACE	TRACE
HNO3	--	--	--	--	--	NIL	NIL	--	850.6	--	--	--	--	1704.0	2554.6
H2O	--	--	TRACE	TRACE	--	1161.0	1161.0	29.4	1010.1	--	29.4	26.3	1376.9	1136.0	2146.0
Total	731.0	731.0	13027.7	11272.9	12003.9	12003.9	12003.9	10143.1	1860.7	1754.8	11897.7	10434.4	1376.9	2840.0	4700.6
Press (Bar)	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1
Temp (°C)	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43

Figure 4.2*a*. Flow-sheet drawn using FLOSHEET



4.2.5. Layout

The sequence of the main equipment items shown symbolically on the flow-sheet follows that of the proposed plant layout. Some licence must be exercised in the placing of ancillary items, such as heat exchangers and pumps, or the layout will be too congested. But the aim should be to show the flow of material from stage to stage as it will occur, and to give a general impression of the layout of the actual process plant.

The equipment should be drawn approximately to scale. Again, some licence is allowed for the sake of clarity, but the principal equipment items should be drawn roughly in the correct proportion. Ancillary items can be drawn out of proportion. For a complex process, with many process units, several sheets may be needed, and the continuation of the process streams from one sheet to another must be clearly shown. One method of indicating a line continuation is shown in Figure 4.2; those lines which are continued over to another are indicated by a double concentric circle round the line number and the continuation sheet number written below.

The table of stream flows and other data can be placed above or below the equipment layout. Normal practice is to place it below. The components should be listed down the left-hand side of the table, as in Figure 4.2. For a long table it is good practice to repeat the list at the right-hand side, so the components can be traced across from either side.

The stream line numbers should follow consecutively from left to right of the layout, as far as is practicable; so that when reading the flow-sheet it is easy to locate a particular line and the associated column containing the data.

All the process stream lines shown on the flow-sheet should be numbered and the data for the stream given. There is always a temptation to leave out the data on a process stream if it is clearly just formed by the addition of two other streams, as at a junction, or if the composition is unchanged when flowing through a process unit, such as a heat exchanger; this should be avoided. What may be clear to the process designer is not necessarily clear to the others who will use the flow-sheet. Complete, unambiguous information on all streams should be given, even if this involves some repetition. The purpose of the flow-sheet is to show the function of each process unit; even to show when it has no function.

4.2.6. Precision of data

The total stream and individual component flows do not normally need to be shown to a high precision on the process flow-sheet; at most one decimal place is all that is usually justified by the accuracy of the flow-sheet calculations, and is sufficient. The flows should, however, balance to within the precision shown. If a stream or component flow is so small that it is less than the precision used for the larger flows, it can be shown to a greater number of places, if its accuracy justifies this and the information is required. Imprecise small flows are best shown as “TRACE”. If the composition of a trace component is specified as a process constraint, as, say, for an effluent stream or product quality specification, it can be shown in parts per million, ppm.

A trace quantity should not be shown as zero, or the space in the tabulation left blank, unless the process designer *is sure* that it has no significance. Trace quantities can be important. Only a trace of an impurity is needed to poison a catalyst, and trace quantities can determine the selection of the materials of construction; see Chapter 7. If the space in the data table is left blank opposite a particular component the quantity may be assumed to be zero by the specialist design groups who take their information from the flow-sheet.

4.2.7. Basis of the calculation

It is good practice to show on the flow-sheet the basis used for the flow-sheet calculations. This would include: the operating hours per year; the reaction and physical yields; and the datum temperature used for energy balances. It is also helpful to include a list of the principal assumptions used in the calculations. This alerts the user to any limitations that may have to be placed on the flow-sheet information.

4.2.8. Batch processes

Flow-sheets drawn up for batch processes normally show the quantities required to produce one batch. If a batch process forms part of an otherwise continuous process, it can be shown on the same flow-sheet, providing a clear break is made when tabulating the data between the continuous and batch sections; the change from kg/h to kg/batch. A continuous process may include batch make-up of minor reagents, such as the catalyst for a polymerisation process.

4.2.9. Services (utilities)

To avoid cluttering up the flow-sheet, it is not normal practice to show the service headers and lines on the process flow-sheet. The service connections required on each piece of equipment should be shown and labelled. The service requirements for each piece of equipment can be tabulated on the flow-sheet.

4.2.10. Equipment identification

Each piece of equipment shown on the flow-sheet must be identified with a code number and name. The identification number (usually a letter and some digits) will normally be that assigned to a particular piece of equipment as part of the general project control procedures, and will be used to identify it in all the project documents.

If the flow-sheet is not part of the documentation for a project, then a simple, but consistent, identification code should be devised. The easiest code is to use an initial letter to identify the type of equipment, followed by digits to identify the particular piece. For example, H — heat exchangers, C — columns, R — reactors. The key to the code should be shown on the flow-sheet.

4.2.11. Computer aided drafting

Most design offices now use computer aided drafting programs for the preparation of flow-sheets and other process drawings. When used for drawing flow-sheets, and piping and instrumentation diagrams (see Chapter 5), standard symbols representing the process equipment, instruments and control systems are held in files and called up as required.

To illustrate the use of a commercial computer aided design program, Figure 4.2 has been redrawn using the program FLOSHEET and is shown as Figure 4.2*a*. FLOSHEET is a versatile flow-sheet drafting program. It is used by many chemical engineering departments in the UK; see Preece (1986) and Preece and Stephens (1989).

FLOSHEET is part of a suite of programs called PROCEDE which has been developed for the efficient handling of all the information needed in process design. It aims to cover the complete process environment, using graphical user interfaces to facilitate the transfer of information, Preece *et al*. (1991). The equipment specification sheets given in Appendix G are from the PROCEDE package.

4.3. MANUAL FLOW-SHEET CALCULATIONS

This section is a general discussion of the techniques used for the preparation of flow-sheets from manual calculations. The stream flows and compositions are calculated from material balances; combined with the design equations that arise from the process and equipment design constraints.

As discussed in Chapter 1, there will be two kinds of design constraints:

External constraints: not directly under the control of the designer, and which cannot normally be relaxed. Examples of this kind of constraint are:

(i) Product specifications, possibly set by customer requirements.
(ii) Major safety considerations, such as flammability limits.
(iii) Effluent specifications, set by government agencies.

Internal constraints: determined by the nature of the process and the equipment functions. These would include:

(i) The process stoichiometry, reactor conversions and yields.
(ii) Chemical equilibria.
(iii) Physical equilibria, involved in liquid-liquid and gas/vapour-liquid separations.
(iv) Azeotropes and other fixed compositions.
(v) Energy-balance constraints. Where the energy and material balance interact, as for example in flash distillation.
(vi) Any general limitations on equipment design.

The flow-sheet is usually drawn up at an early stage in the development of the project. A preliminary flow-sheet will help clarify the designer's concept of the process; and serve as basis for discussions with other members of the design team.

The extent to which the flow-sheet can be drawn up before any work is done on the detailed design of the equipment will depend on the complexity of the process and the information available. If the design is largely a duplication of an existing process, though possibly for a different capacity, the equipment performance will be known and the stream flows and compositions can be readily calculated. For new processes, and for major modifications of existing processes, it will only be possible to calculate some of the flows independently of the equipment design considerations; other stream flows and compositions will be dependent on the equipment design and performance. To draw up the flow-sheet the designer must use his judgement in deciding which flows can be calculated directly; which are only weakly dependent on the equipment design; and which are determined by the equipment design.

By weakly dependent is meant those streams associated with equipment whose performance can be assumed, or approximated, without introducing significant errors in the flow-sheet. The detailed design of these items can be carried out later, to match the performance then specified by the flow-sheet. These will be items which in the designer's estimation do not introduce any serious cost penalty if not designed for their optimum performance. For example, in a phase separator, such as a decanter, if equilibrium between the phases is assumed the outlet stream compositions can be often calculated directly, independent of the separator design. The separator would be designed later, to give sufficient residence time for the streams to approach the equilibrium condition assumed in the flow-sheet calculation.

Strong interaction will occur where the stream flows and compositions are principally determined by the equipment design and performance. For example, the optimum conversion in a reactor system with recycle of the unreacted reagents will be determined by the performance of the separation stage, and reactor material balance cannot be made without considering the design of the separation equipment. To determine the stream flows and compositions it would be necessary to set up a mathematical model of the reactor-separator system, including costing.

To handle the manual calculations arising from complex processes, with strong interactions between the material balance calculations and the equipment design, and where physical recycle streams are present, it will be necessary to sub-divide the process into manageable sub-systems. With judgement, the designer can isolate those systems with strong interactions, or recycle, and calculate the flows sequentially, from sub-system to sub-system, making approximations as and where required. Each sub-system can be considered separately, if necessary, and the calculations repeatedly revised till a satisfactory flow-sheet for the complete process is obtained. To attempt to model a complex process without subdivision and approximation would involve too many variables and design equations to be handled manually. Computer flow-sheeting programs should be used if available.

When sub-dividing the process and approximating equipment performance to produce a flow-sheet, the designer must appreciate that the resulting design for the complete process, as defined by the flow-sheet, will be an approximation to the optimum design. He must continually be aware of, and check, the effect of his approximations on the performance of the complete process.

4.3.1. Basis for the flow-sheet calculations

Time basis

No plant will operate continuously without shut-down. Planned shut-down periods will be necessary for maintenance, inspection, equipment cleaning, and the renewal of catalysts and column packing. The frequency of shut-downs, and the consequent loss of production time, will depend on the nature of the process. For most chemical and petrochemical processes the plant attainment will typically be between 90 to 95 per cent of the total hours in a year (8760). Unless the process is known to require longer shut-down periods, a value of 8000 hours per year can be used for flow-sheet preparation.

Scaling factor

It is usually easiest to carry out the sequence of flow-sheet calculations in the same order as the process steps; starting with the raw-material feeds and progressing stage by stage, where possible, through the process to the final product flow. The required production rate will usually be specified in terms of the product, not the raw-material feeds, so it will be necessary to select an arbitrary basis for the calculations, say 100 kmol/h of the principal raw material. The actual flows required can then be calculated by multiplying each flow by a scaling factor determined from the actual production rate required.

$$\text{Scaling factor} = \frac{\text{mols product per hour specified}}{\begin{array}{c}\text{mols product produced per 100 kmol}\\ \text{of the principal raw material}\end{array}}$$

4.3.2. Flow-sheet calculations on individual units

Some examples of how design constraints can be used to determine stream flows and compositions are given below.

1. Reactors

(i) Reactor yield and conversion specified.

The reactor performance may be specified independently of the detailed design of the reactor. The conditions for the optimum, or near optimum, performance may be known from the operation of existing plant or from pilot plant studies.

For processes that are well established, estimates of the reactor performance can often be obtained from the general and patent literature; for example, the production of nitric and sulphuric acids.

If the yields and conversions are known, the stream flows and compositions can be calculated from a material balance; see Example 2.13.

(ii) Chemical equilibrium.

With fast reactions, the reaction products can often be assumed to have reached equilibrium. The product compositions can then be calculated from the equilibrium data for the reaction, at the chosen reactor temperature and pressure; see Example 4.1.

2. Equilibrium stage

In a separation or mixing unit, the anticipated equipment performance may be such that it is reasonable to consider the outlet streams as being in equilibrium; the approach to equilibrium being in practice close enough that no significant inaccuracy is introduced by assuming that equilibrium is reached. The stream compositions can then be calculated from the phase equilibrium data for the components. This approximation can often be made for single-stage gas-liquid and liquid-liquid separators, such as quench towers, partial condensers and decanters. It is particularly useful if one component is essentially non-condensable and can be used as a tie substance (see Section 2.11). Some examples of the use of this process constraint are given in Examples 4.2 and 4.4.

3. Fixed stream compositions

If the composition (or flow-rate) of one stream is fixed by "internal" or "external" constraints, this may fix the composition and flows of other process streams. In Chapter 1, the relationship between the process variables, the design variables and design equations was discussed. If sufficient design variables are fixed by external constraints, or by the designer, then the other stream flows round a unit will be uniquely determined. For example, if the composition of one product stream from a distillation column is fixed by a product specification, or if an azeotrope is formed, then the other stream composition can be calculated directly from the feed compositions; see Section 2.10. The feed composition would be fixed by the outlet composition of the preceding unit.

4. Combined heat and material balances

It is often possible to make a material balance round a unit independently of the heat balance. The process temperatures may be set by other process considerations, and the energy balance can then be made separately to determine the energy requirements to maintain the specified temperatures. For other processes the energy input will determine the process stream flows and compositions, and the two balances must be made simultaneously; for instance, in flash distillation or partial condensation; see also Example 4.1.

Example 4.1

An example illustrating the calculation of stream composition from reaction equilibria, and also an example of a combined heat and material balance.

In the production of hydrogen by the steam reforming of hydrocarbons, the classic water-gas reaction is used to convert CO in the gases leaving the reforming furnace to hydrogen, in a shift converter.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H^\circ_{298} - 41{,}197 \text{ kJ/kmol}$$

In this example the exit gas stream composition from a converter will be determined for a given inlet gas composition and steam ratio; by assuming that in the outlet stream the gases reach chemical equilibrium. In practice the reaction is carried out over a catalyst, and the assumption that the outlet composition approaches the equilibrium composition is valid. Equilibrium constants for the reaction are readily available in the literature.

A typical gases composition obtained by steam reforming methane is:

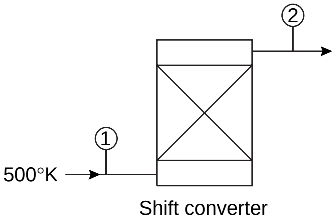
$$CO_2 \ 8.5, \quad CO \ 11.0, \quad H_2 \ 76.5 \text{ mol per cent dry gas}$$

If this is fed to a shift converter at 500°K, with a steam ratio of 3 mol H_2O to 1 mol CO, estimate the outlet composition and temperature.

Solution

Basis: 100 mol/h dry feed gas.

$$H_2O \text{ in feed stream} = 3.0 \times 11.0 = 33 \text{ mol.}$$



Let fractional conversion of CO to H_2 be C. Then mols of CO reacted = $11.0 \times C$. From the stoichiometric equation and feed composition, the exit gas composition will be:

$$CO = 11.0(1 - C)$$

$$CO_2 = 8.5 + 11.0 \times C$$

$$H_2O = 33 - 11.0 \times C$$

$$H_2 = 76.5 + 11.0 \times C$$

At equilibrium $$K_p = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}}$$

The temperature is high enough for the gases to be considered ideal, so the equilibrium constant is written in terms of partial pressure rather than fugacity, and the constant will not be affected by pressure. Mol fraction can be substituted for partial pressure. As the total mols in and out is constant, the equilibrium relationship can be written directly in mols of the components.

$$K_p = \frac{11(1 - C)(33 - 11C)}{(8.5 + 11C)(76.5 + 11C)}$$

Expanding and rearranging

$$(K_p 121 - 121)C^2 + (K_p 935 + 484)C + (K_p 650 - 363) = 0 \tag{1}$$

K_p is a function of temperature.

For illustration, take T out = $700°K$, at which $K_p = 1.11 \times 10^{-1}$

$$-107.6C^2 + 587.8C - 290.85 = 0$$

$$C = 0.57$$

The reaction is exothermic and the operation can be taken as adiabatic, as no cooling is provided and the heat losses will be small.

The gas exit temperature will be a function of the conversion. The exit temperature must satisfy the adiabatic heat balance and the equilibrium relationship.

A heat balance was carried over a range of values for the conversion C, using the program Energy 1, Chapter 3. The value for which the program gives zero heat input or output required (adiabatic) is the value that satisfies the conditions above. For a datum temperature of 25°C:

Data for energy-balance program

	Component	Stream (mol)		C_p° (kJ/kmol)			
		1	2	*a*	*b*	*c*	*d*
1	CO_2	8.5	$8.5 + 11C$	19.80	7.34 E-2	−5.6 E-5	17.15 E-9
2	CO	11.0	$11(1 - C)$	30.87	−1.29 E-2	27.9 E-6	−12.72 E-9
3	H_2O	33.0	$33 - 11C$	32.24	19.24 E-4	10.56 E-6	−3.60 E-9
4	H_2	76.5	$76.5 + 11C$	27.14	9.29 E-3	−13.81 E-6	7.65 E-9

Results

Outlet temp. (K)	K_p	C	Mols converted	Outlet composition, mol				Heat required Q
				CO	CO_2	H_2O	H_2	
550	1.86×10^{-2}	0.88	9.68	1.32	18.18	23.32	86.18	−175,268
600	3.69×10^{-2}	0.79	8.69	2.31	17.19	24.31	85.19	76,462
650	6.61×10^{-2}	0.68	7.48	3.52	15.98	25.52	83.98	337,638

The values for the equilibrium constant K_p were taken from *Technical Data on Fuel*, Spiers.

The outlet temperature at which $Q = 0$ was found by plotting temperature versus Q to be 580 K.

At 580 K, $K_p = 2.82 \times 10^{-2}$.

From equation (1)

$$-117.6C^2 + 510.4 + -344.7 = 0,$$

$$C = 0.83$$

Outlet gas composition

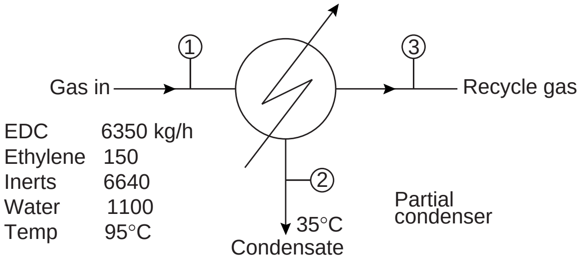
$$\begin{aligned} CO_2 &= 8.5 + 11 \times 0.83 &&= 17.6 \\ CO &= 11(1 - 0.83) &&= 1.9 \\ H_2O &= 33.0 - 11 \times 0.83 &&= 23.9 \\ H_2 &= 76.5 + 11 \times 0.83 &&= \underline{85.6} \\ & && \quad 129.0 \text{ mol} \end{aligned}$$

In this example the outlet exit gas composition has been calculated for an arbitrarily chosen steam: CO ratio of 3. In practice the calculation would be repeated for different steam ratios, and inlet temperatures, to optimise the design of the converter system. Two converters in series are normally used, with gas cooling between the stages. For large units a waste-heat boiler could be incorporated between the stages. The first stage conversion is normally around 80 per cent.

Example 4.2

This example illustrates the use of phase equilibrium relationships (vapour-liquid) in material balance calculations.

In the production of dichloroethane (EDC) by oxyhydrochlorination of ethylene, the products from the reaction are quenched by direct contact with dilute HCl in a quench tower. The gaseous stream from this quench tower is fed to a condenser and the uncondensed vapours recycled to the reactor. A typical composition for this stream is shown in the diagram below; operating pressure 4 bar. Calculate the outlet stream compositions leaving the condenser.



The EDC flow includes some organic impurities and a trace of HCl. The inerts are mainly N_2, CO, O_2 — non-condensable.

Solution

In order to calculate the outlet stream composition it is reasonable, for a condenser, to assume that the gas and liquid streams are in equilibrium at the outlet liquid temperature of 35°C.

The vapour pressures of the pure liquids can be calculated from the Antoine equation (see Chapter 8):

At 35°C (308 K)	
EDC	0.16 bar
Ethylene	70.7
H_2O	0.055

From the vapour pressures it can be seen that the EDC and water will be essentially totally condensed, and that the ethylene remains as vapour. Ethylene will, however, tend to be dissolved in the condensed EDC. As a first trial, assume all the ethylene stays in the gas phase.

Convert flows to mol/h.

	Mol wt.	kmol/h	
EDC	99	64	
C_2H_4	28	5.4	} 213.4
Inerts	32 (estimated)	208	
H_2O	18	61	

Take the "non-condensables" (ethylene and inerts) as the tie substance. Treat gas phase as ideal, and condensed EDC-water as immiscible.

Partial pressure of non-condensables = (total pressure) − (vapour pressure of EDC + vapour pressure of water)

$$= 4 - 0.16 - 0.055 = \underline{\underline{3.79\text{ bar}}}$$

$$\text{Flow of EDC in vapour} = \frac{\text{vapour press. EDC}}{\text{partial press. non-condensables}} \times \text{flow non-condensables}$$

$$= \frac{0.16}{3.79} \times 213.4 = \underline{\underline{9\text{ kmol/h}}}$$

$$\text{Similarly, flow of } H_2O \text{ in vapour} = \frac{0.055}{3.79} \times 213.4 = \underline{\underline{3.1\text{ kmol/h}}}$$

So composition of gas streams is

	kmol/h	Per cent mol	kg/h
EDC	9	4.0	891
H_2O	3.1	1.4	56
Inerts	208	92.3	6640
C_2H_4	5.4	2.3	150

Check on dissolved ethylene

Partial pressure of ethylene = total pressure × mol fraction

$$= 4 \times \frac{2.3}{100} = 0.092\text{ bar}$$

By assuming EDC and C_2H_4 form an ideal solution, the mol fraction of ethylene dissolved in the liquid can be estimated, from Raoults Law (see Chapter 8).

$$y_A = \frac{x_A P_A^\circ}{P}$$

y_A = gas phase mol fraction,

x_A = liquid phase mol fraction,

P_A° = sat. vapour pressure,

P = total pressure,

Substituting

$$\frac{2.3}{100} = \frac{x_A 70.7}{4}$$

$$x_A = 1.3 \times 10^{-3}$$

hence quantity of ethylene in liquid = kmol EDC × x_A

$$= (64 - 9) \times 1.3 \times 10^{-3} = 0.07\text{ kmol/h}$$

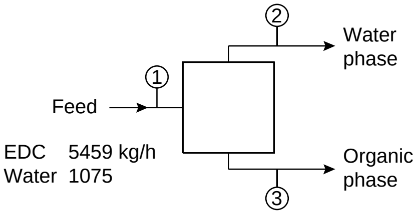
so kmol ethylene in gas phase $= 5.4 - 0.07 = \underline{\underline{5.33\text{ kmol/h}}}$

This is little different from calculated value and shows that initial assumption that no ethylene was condensed or dissolved was reasonable; so report ethylene in liquid as "trace".

Material balance	Flows (kg/h)		
Stream no.:	1	2	3
Title	Condenser feed	Condensate	Recycle gas
EDC	6350	5459	891
H_2O	1100	1044	56
Ethylene	150	Trace	150
Inerts	6640	—	6640
Total	14,240	6503	7737
Temp.°C	95	35	35
Pressure bar:	4	4	4

Example 4.3

This example illustrates the use of liquid-liquid phase equilibria in material balance calculations. The condensate stream from the condenser described in Example 4.2 is fed to a decanter to separate the condensed water and dichloroethane (EDC). Calculate the decanter outlet stream compositions.



Solution

Assume outlet phases are in equilibrium.

The solubilities of the components at 20°C are:

EDC in water	0.86 kg/100 kg
Water in EDC	0.16 kg/100 kg

Note the water will contain a trace of HCl, but as data on the solubility of EDC in dilute HCl are not available, the solubility in water will be used.

As the concentrations of dissolved water and EDC are small, the best approach to this problem is by successive approximation; rather than by setting up and solving equations for the unknown concentrations.

As a first approximation take organic stream flow = EDC flow in.

$$\text{Then water in EDC} = \frac{0.16}{100} \times 5459 = 8.73\ \text{kg/h}$$

$$\text{So water flow out} = 1075 - 8.73 = 1066.3\ \text{kg/h}$$

$$\text{and EDC dissolved in the water stream} = \frac{1066.3}{100} \times 0.86 = 9.2\ \text{kg/h}$$

$$\text{so, revised organic stream flow} = 5459 - 9.2 = \underline{\underline{5449.8\ \text{kg/h}}}$$

$$\begin{array}{l}\text{and quantity of water dissolved} \\ \text{in the stream}\end{array} = \frac{5449.8}{100} \times 0.16 = \underline{\underline{8.72\ \text{kg/h}}}$$

Which is not significantly lower than the first approximation. So stream flows, kg/h, will be:

Stream no. Title	1 Decanter feed	2 Organic phase	3 Aqueous phase
EDC	5459	5449.8	9.2
H_2O	1075	8.7	1066.3
Total	6534	5458.5	1075.5

Example 4.4

This example illustrates the manual calculation of a material and energy balance for a process involving several processing units.

Draw up a preliminary flow-sheet for the manufacture of 20,000 t/y nitric acid (basis 100 per cent HNO_3) from anhydrous ammonia, concentration of acid required 50 to 60 per cent.

The technology of nitric acid manufacture is well established and has been reported in several articles:

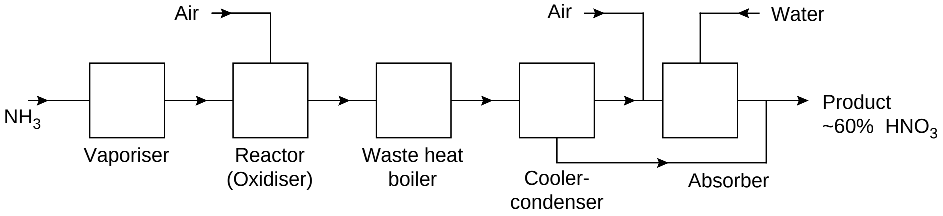
1. R. M. Stephenson: *Introduction to the Chemical Process Industries* (Reinhold, 1966).
2. C. H. Chilton: *The Manufacture of Nitric Acid by the Oxidation of Ammonia* (American Institute of Chemical Engineers).
3. S. Strelzoff: *Chem. Eng. NY* **63**(5), 170 (1956).
4. F. D. Miles: *Nitric Acid Manufacture and Uses* (Oxford University Press, 1961).

Three processes are used:

1. Oxidation and absorption at atmospheric pressure.
2. Oxidation and absorption at high pressure (approx. 8 atm).
3. Oxidation at atmospheric pressure and absorption at high pressure.

The relative merits of the three processes are discussed by Chilton (2), and Strelzoff (3).

For the purposes of this example the high-pressure process has been selected. A typical process is shown in the block diagram.



Schematic (block) diagram; production of nitric acid by oxidation of ammonia

The principal reactions in the reactor (oxidiser) are:

Reaction 1. $NH_3(g) + \frac{5}{4}O_2(g) \rightarrow NO(g) + \frac{3}{2}H_2O(g) \quad \Delta H^{\circ}_{298} = -226{,}334$ kJ/kmol

Reaction 2. $NH_3(g) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(g) \quad \Delta H^{\circ}_{298} = -316{,}776$ kJ/kmol

The nitric oxide formed can also react with ammonia:

Reaction 3. $NH_3(g) + \frac{3}{2}NO(g) \rightarrow \frac{5}{4}N_2(g) + \frac{3}{2}H_2O(g) \quad \Delta H^{\circ}_{298} = -452{,}435$ kJ/kmol

The oxidation is carried out over layers of platinum-rhodium catalyst; and the reaction conditions are selected to favour reaction 1. Yields for the oxidation step are reported to be 95 to 96 per cent.

Solution

Basis of the flow-sheet calculations

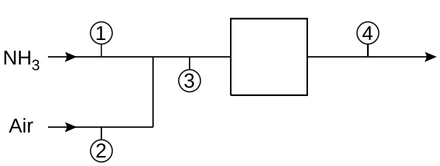
Typical values, taken from the literature cited:

1. 8000 operating hours per year.
2. Overall plant yield on ammonia 94 per cent.
3. Oxidiser (reactor) chemical yield 96 per cent.
4. Acid concentration produced 58 per cent w/w HNO_3.
5. Tail gas composition 0.2 per cent v/v NO.

Material balances

Basis: 100 kmol NH_3 feed to reactor.

Oxidiser



From reaction 1, at 96 per cent yield,

$$\text{NO produced} = 100 \times \frac{96}{100} = 96 \text{ kmol}$$

$$\text{oxygen required} = 96 \times \tfrac{5}{4} = 120 \text{ kmol}$$

$$\text{water produced} = 96 \times \tfrac{3}{2} = 144 \text{ kmol}$$

The remaining 4 per cent ammonia reacts to produce nitrogen; production of 1 mol of N_2 requires $\frac{3}{2}$ mol of O_2, by either reaction 2 or 1 and 3 combined.

$$\text{nitrogen produced} = \tfrac{4}{2} = 2 \text{ kmol}$$

$$\text{oxygen required} = 2 \times \tfrac{3}{2} = 3 \text{ kmol}$$

All the oxygen involved in these reactions produces water,

$$\text{water produced} = 3 \times 2 = 6 \text{ kmol}$$

So, total oxygen required and water produced;

$$\text{water} = 144 + 6 = 150 \text{ kmol}$$

$$\text{oxygen (stoichiometric)} = 120 + 3 = 123 \text{ kmol}$$

Excess air is supplied to the oxidiser to keep the ammonia concentration below the explosive limit (see Chapter 9), reported to be 12 to 13 per cent (Chilton), and to provide oxygen for the oxidation of NO to NO_2.

$$\text{Reaction 4.}\quad NO(g) + \tfrac{1}{2}O_2 \rightarrow NO_2(g) \quad \Delta H^\circ_{298} = 57{,}120 \text{ kJ/kmol}$$

The inlet concentration of ammonia will be taken as 11 per cent v/v.

$$\text{So, air supplied} = \frac{100}{11} \times 100 = 909 \text{ kmol}$$

Composition of air: 79 per cent N_2, 21 per cent O_2, v/v.
So, oxygen and nitrogen flows to oxidiser:

$$\text{oxygen} = 909 \times \frac{21}{100} = 191 \text{ kmol}$$

$$\text{nitrogen} = 909 \times \frac{79}{100} = 718 \text{ kmol}$$

And the oxygen unreacted (oxygen in the outlet stream) will be given by:

$$\text{oxygen unreacted} = 191 - 123 = 68 \text{ kmol}$$

The nitrogen in the outlet stream will be the sum of the nitrogen from the air and that produced from ammonia:

$$\text{nitrogen in outlet} = 718 + 2 = 720 \text{ kmol}$$

Summary, stream compositions:

	Feed (3)		Outlet (4)	
	kmol	kg	kmol	kg
NH_3	100	1700	nil	
NO	nil		96	2880
H_2O	trace		150	2700
O_2	191	6112	68	2176
N_2	718	20,104	720	20,016
Total		27,916		27,916

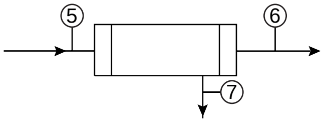
Notes

(1) The small amount of water in the inlet air is neglected.
(2) Some NO_2 will be present in the outlet gases, but at the oxidiser temperature used, 1100 to 1200 K, the amount will be small, typically <1 per cent.
(3) It is good practice always to check the balance across a unit by calculating the totals; total flow in must equal total flow out.

Waste-heat boiler (WHB) and cooler-condenser

The temperature of the gases leaving the oxidiser is reduced in a waste-heat boiler and cooler-condenser. There will be no separation of material in the WHB but the composition will change, as NO is oxidised to NO_2 as the temperature falls. The amount oxidised will depend on the residence time and temperature (see Stephenson). The oxidation is essentially complete at the cooler-condenser outlet. The water in the gas condenses in the cooler-condenser to form dilute nitric acid, 40 to 50 per cent w/w.

Balance on cooler-condenser



The inlet stream (5) will be taken as having the same composition as the reactor outlet stream (4).

Let the cooler-condenser outlet temperature be 40°C. The maximum temperature of the cooling water will be about 30°C, so this gives a 10°C approach temperature.

If the composition of the acid leaving the unit is taken as 45 per cent w/w (a typical value) the composition of the gas phase can be estimated by assuming that the gas and condensed liquid are in equilibrium at the outlet temperature.

At 40°C the vapour pressure of water over 45 per cent HNO_3 is 29 mmHg (Perry's *Chemical Engineers Handbook*, 5th edn, pp. 3–65). Take the total pressure as 8 atm. The mol fraction of water in the outlet gas stream will be given by the ratio of the vapour pressure to the total pressure:

$$\text{mol fraction water} = \frac{29}{760 \times 8} = 4.77 \times 10^{-3}$$

As a first trial, assume that all the water in the inlet stream is condensed, then:

$$\text{water condensed} = 150 \text{ kmol} = 2700 \text{ kg}$$

NO_2 combines with this water to produce a 45 per cent solution:

$$\text{Reaction 5.} \quad 3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

For convenience, take as a subsidiary basis for this calculation 100 kmol of HNO_3 (100 per cent basis) in the condensate.

From reaction 5, the mols of water required to form 100 kmol HNO_3 will be:

$$50 \text{ kmol} = 900 \text{ kg}$$

$$\text{mass of 100 kmol } HNO_3 = 100 \times 63 = 6300 \text{ kg}$$

$$\text{water to dilute this to 45 per cent} = \frac{6300 \times 55}{45} = 7700 \text{ kg}$$

So, total water to form dilute acid $= 900 + 7700 = 8600$ kg.

Changing back to the original basis of 100 kmol NH_3 feed:

$$HNO_3 \text{ formed} = 100 \times \frac{\text{Water condensed per 100 kmol } NH_3 \text{ feed}}{\text{Total water to form 45 per cent acid, per 100 kmol } HNO_3}$$

$$= 100 \times \frac{2700}{8600} = 31.4 \text{ kmol}$$

$$\begin{aligned} NO_2 \text{ consumed (from reaction 5)} &= 31.4 \times \tfrac{3}{2} = 47.1 \text{ kmol} \\ NO \text{ formed} &= 31.4 \times \tfrac{1}{2} = 15.7 \text{ kmol} \\ H_2O \text{ reacted} &= 15.7 \text{ kmol} \end{aligned}$$

Condensed water not reacted with $NO_2 = 150 - 15.7 = 134.3$ kmol.

The quantity of unoxidised NO in the gases leaving the cooler-condenser will depend on the residence time and the concentration of NO and NO_2 in the inlet stream. For simplicity in this preliminary balance the quantity of NO in the outlet gas will be taken as equal to the quantity formed from the absorption of NO_2 in the condensate to form nitric acid:

$$NO \text{ in outlet gas} = 15.7 \text{ kmol}$$

The unreacted oxygen in the outlet stream can be calculated by making a balance over the unit on the nitric oxides, and on oxygen.

Balance on oxides

$$\text{Total } (NO + NO_2) \text{ entering} = NO \text{ in stream } 4 = 96 \text{ kmol}$$

Of this, 31.4 kmol leaves as nitric acid, so $(NO + NO_2)$ left in the gas stream $= 96 - 31.4 = 64.6$ kmol.

Of this, 15.7 kmol is assumed to be NO, so NO_2 in exit gas $= 64.6 - 15.7$
$= 48.9$ kmol.

Balance on oxygen

Let unreacted O_2 be x kmol. Then oxygen out of the unit will be given by:

$$\left[\frac{NO}{2} + NO_2 + x\right]_{\substack{\text{gas}\\ \text{stream (6)}}} + \left[\frac{3}{2}HNO_3 + \frac{H_2O}{2}\right]_{\substack{\text{acid}\\ \text{stream (7)}}}$$

$$= \left(\frac{15.7}{2} + 48.9 + x\right) + \left(\frac{3}{2} \times 31.4 + \frac{134.3}{2}\right) = (171 + x) \text{ kmol}$$

$$\text{Oxygen into the unit} = \left[\frac{NO}{2} + O_2 + H_2O\right]_{\text{stream (5)}}$$

$$= \frac{96}{2} + 68 + \frac{150}{2} = 191 \text{ kmol}$$

Equating O_2 in and out:

$$\text{unreacted } O_2, x, = 191 - 171 = 20.0 \text{ kmol}$$

As a first trial, all the water vapour was assumed to condense; this assumption will now be checked.

The quantity of water in the gas stream will be given by:

$$\text{mol fraction} \times \text{total flow.}$$

The total flow of gas (neglecting water) = 804.6 kmol, and the mol fraction of water was estimated to be 4.77×10^{-3}.

$$\text{So, water vapour} = 4.77 \times 10^{-3} \times 804.6 = 3.8 \text{ kmol}$$

And, mols of water condensed $= 134.3 - 3.8 = 130.5$ kmol.

The calculations could be repeated using this adjusted value for the quantity of water condensed, to get a better approximation, but the change in the acid, nitric oxides, oxygen and water flows will be small. So, the only change that will be made to the original estimates will be to reduce the quantity of condensed water by that estimated to be in the gas stream:

$$\text{Water in stream (6) } 3.8 \text{ kmol} = 68.4 \text{ kg}$$

So, water in stream (7) $= 134.3 - 3.8 = 130.5$ kmol $= 2349$ kg.

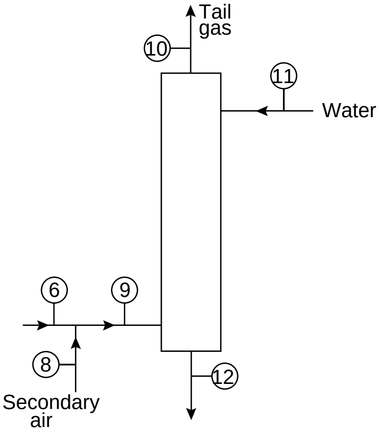
Summary, stream compositions:

	Gas (6)		Acid (7)	
	kmol	kg	kmol	kg
NO	15.7	471.0	Trace	
NO_2	48.9	2249.4	Trace	
O_2	20.0	640	—	
N_2	720	20,160		
HNO_3	—	—	31.4	1978.2
H_2O	3.8	68.4	130.5	2349.0
Total		23,588.4		4327.2

Total, stream (6) + (7) = 23,588.4 + 4327.2 = 27,915.6 kg, checks with inlet stream (4) total of 27,915.

Absorber

In the absorber the NO_2 in the gas stream is absorbed in water to produce acid of about 60 per cent w/w. Sufficient oxygen must be present in the inlet gases to oxidise the NO formed to NO_2. The rate of oxidation will be dependent on the concentration of oxygen, so an excess is used. For satisfactory operation the tail gases from absorber should contain about 3 per cent O_2 (Miles).



From stream (6) composition:

$$\text{NO in inlet stream to absorber} = 15.7 \text{ kmol} \quad \text{and } O_2 = 20.0 \text{ kmol}$$

Note: Though the NO/NO_2 ratio in this stream is not known exactly, this will not affect the calculation of the oxygen required; the oxygen is present in the stream either as free, uncombined oxygen or combined in the NO_2.

So, O_2 required to oxidise the NO in the inlet to stream to NO_2, from reaction 4, $= 15.7 \times \frac{1}{2} = 7.85$ kmol.

Hence, the "free" oxygen in the inlet stream $= 20.0 - 7.85 = 12.15$ kmol.

Combining reactions (4) and (5) gives the overall reaction for the absorption of NO_2 to produce HNO_3.

$$\text{Reaction 6.}\quad 4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

Using this reaction, the oxygen required to oxidise the NO formed in the absorber can be calculated:

$$\begin{aligned} O_2 \text{ required to oxidise NO formed} &= \{(NO + NO_2) \text{ in stream } (6)\} \times \tfrac{1}{4} \\ &= (48.9 + 15.7) \times \tfrac{1}{4} = 16.15 \text{ kmol} \end{aligned}$$

So O_2 required for complete oxidation, in addition to that in inlet gas

$$= 16.15 - 12.15 = 4 \text{ kmol}$$

Let the secondary air flow be y kmol. Then the O_2 in the secondary air will be $= 0.21\ y$ kmol. Of this, 4 kmol react with NO in the absorber, so the free O_2 in the tail gases will be $= 0.21\ y - 4$ kmol.

N_2 passes through the absorber unchanged, so the N_2 in the tail gases = the N_2 entering the absorber from the cooler-condenser and the secondary air. Hence:

$$N_2 \text{ in tail gas} = 720 + 0.79\ y \text{ kmol.}$$

The tail gases are essentially all N_2 and O_2 (the quantity of other constituents is negligible) so the percentage O_2 in the tail gas will be given by:

$$O_2 \text{ per cent} = 3 = \frac{(0.21\ y - 4)100}{(720 + 0.79\ y) + (0.21\ y - 4)}$$

from which

$$y = 141.6 \text{ kmol}$$

and the O_2 in the tail gases $= 141.6 \times 0.21 - 4 = 25.7$ kmol
and the N_2 in the tail gases $= 720 + 111.8 = 831.8$ kmol.

Tail gas composition, the tail gases will contain from 0.2 to 0.3 per cent NO, say 0.2 per cent, then:

$$\begin{aligned} \text{NO in tail gas} &= \text{total flow} \times \frac{0.2}{100} = (N_2 + O_2) \text{ flow} \times 0.002 \\ &= (831.8 + 25.7)0.002 = \underline{\underline{1.7 \text{ kmol}}} \end{aligned}$$

The quantity of the secondary air was based on the assumption that all the nitric oxides were absorbed. This figure will not be changed as it was calculated from an assumed (approximate) value for the concentration of the O_2 in the tail gases. The figure for O_2 in the tail gases must, however, be adjusted to maintain the balance.

The unreacted O_2 can be calculated from Reactions (4) and (6). 1.7 kmol of NO are not oxidised or absorbed, so the adjusted O_2 in tail gases $= 25.7 + 1.7(\frac{1}{4} + \frac{1}{2}) = \underline{\underline{27.0 \text{ kmol}}}$.

The tail gases will be saturated with water at the inlet water temperature, say 25°C. Partial pressure of water at $25°\text{C} = 0.032$ atm. The absorber pressure will be approximately 8 atm, so mol fraction water $= 0.032/8 = 4 \times 10^{-3}$ and H_2O in tail gas $= 857.5 \times 4 \times 10^{-3} = \underline{\underline{3.4\ \text{kmol}}}$.

Water required, stream (11).

The nitrogen oxides absorbed, allowing for the NO in the tail gases, will equal the HNO_3 formed

$$= (48.9 + 15.7) - 1.7 = 62.9\ \text{kmol} = 3962.7\ \text{kg}$$

Stoichiometric H_2O required, from reaction 6

$$= \frac{62.9}{4} \times 2 = 31.5\ \text{kmol}$$

The acid strength leaving the absorber will be taken as 60 per cent w/w. Then, water required for dilution

$$= \frac{3962.7}{0.6} \times 0.4 = 2641.8\ \text{kg} = 146.8\ \text{kmol}$$

So, total water required, allowing for the water vapour in the inlet stream (6), but neglecting the small amount in the secondary air

$$= 31.5 + 146.8 + 3.4 - 3.8 = 177.9\ \text{kmol}$$

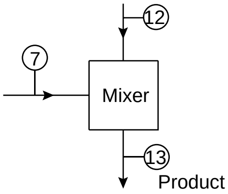
Summary, stream compositions:

Stream	Secondary air (8)		Inlet (9)		Acid (12)		Tail gas (10)		Water feed (11)	
	kmol	kg	kmol	kg	kmol	kg	kmol	kg	kmol	kg
NO	—	—	15.7	471.0	—	—	1.7	51.0	—	—
NO_2	—	—	48.9	2249.4	trace	—	—	—	—	—
O_2	29.7	950.4	49.7	1590.4	—	—	27.0	864	—	—
N_2	111.8	3130.4	831.8	23,290.0	—	—	831.8	23,290.4	—	—
HNO_3	—	—	—	—	62.9	3962.7	—	—	—	—
H_2O	trace	—	3.8	68.4	146.8	2641.8	3.4	61.2	177.9	3202.2
Total		4080.8		27,669.2		6604.5		24,266.6		3202.6

Check on totals: Stream (6) + (8) = (9)? 4080.8 + 23,588.4 = 27,669.2
27,669.2 = 27,669.2 checks

Stream (9) + (11) = (10) + (12)? 27,669.2 + 3203.2 = 24,266.6 + 6604.5
30,871.4 = 30,871.1 near enough.

Acid produced



$$\begin{array}{llrlr}
\text{From cooler-condenser} & HNO_3 = & 31.4\ \text{kmol} & = & 1978.2\ \text{kg} \\
 & H_2O\ = & 130.5\ \text{kmol} & = & 2349.0\ \text{kg} \\
\text{From absorber} & HNO_3 = & 62.9\ \text{kmol} & = & 3962.7\ \text{kg} \\
 & H_2O\ = & 146.8\ \text{kmol} & = & 2641.8\ \text{kg} \\
\text{Totals} & HNO_3 = & 1978.2 + 3962.7 & = & 5940.9\ \text{kg} \\
 & H_2O\ = & 2349.0 + 2641.8 & = & 4990.8\ \text{kg} \\
\hline
 & & & & 10{,}931.7\ \text{kg}
\end{array}$$

So, concentration of mixed acids $= \dfrac{5940.9}{10{,}931.7} \times 100 = 54$ per cent.

Summary, stream composition:

	Acid product (13)	
Stream	kmol	kg
HNO_3	94.3	5940.3
H_2O	277.3	4990.8
		10,931.7

Overall plant yield

The overall yield can be calculated by making a balance on the combined nitrogen:

$$\text{Yield} = \frac{\text{mols } N_2 \text{ in } HNO_3 \text{ produced}}{\text{mols } N_2 \text{ in } NH_3 \text{ feed}} = \frac{94.3/2}{100/2} = 94.3 \text{ per cent}$$

Note: the acid from the cooler-condenser could be added to the acid flow in the absorber, on the appropriate tray, to produce a more concentrated final acid. The secondary air flow is often passed through the acid mixer to strip out dissolved NO.

Scale-up to the required production rate

Production rate, 20,000 t/y HNO_3 (as 100 per cent acid).
With 8000 operating hours per year

$$\text{kg/h} = \frac{20{,}000 \times 10^3}{8000} = 2500 \text{ kg/h}$$

From calculations on previous basis:
100 kmol NH_3 produces 5940.9 kg HNO_3.

$$\text{So, scale-up factor} = \frac{2500}{5940.9} = 0.4208$$

To allow for unaccounted physical yield losses, round off to 0.43

All the stream flows, tabulated, were multiplied by this factor and are shown on the flowsheet, Figure 4.2. A sample calculation is given below:

Stream (6) gas from condenser

	Mass 100 kmol NH_3 basis (kg)		Mass flow for 20,000 t/y (kg/h)
NO	471		202.5
NO_2	2249.4		967.2
O_2	640.0	×0.43 =	275.2
N_2	20,160.0		8668.0
H_2O	68.4		29.4
Total	23,588.8		10,143.1

Energy balance

Basis 1 hour.

Compressor

Calculation of the compressor power and energy requirements (see Chapter 3).

$$\text{Inlet flow rate, from flow sheet} = \frac{13{,}027.7}{29 \times 3600} = 0.125 \text{ kmol/s}$$

Volumetric flow rate

$$\text{at inlet conditions, } 15^\circ\text{C, 1 bar} = 0.125 \times 22.4 \times \frac{288}{273} = 2.95 \text{ m}^3/\text{s}$$

From Figure 3.6, for this flow rate a centrifugal compressor would be used, $E_p = 74$ per cent.

$$\text{Work (per kmol)} = Z_1 T_1 \mathbf{R} \frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] \tag{3.31}$$

$$\text{Outlet temperature, } T_2 = T_1 \left(\frac{P_2}{P_1}\right)^m \tag{3.35}$$

As the conditions are well away from the critical conditions for air, equations (3.36a) and (3.38a) can be used

$$m = \frac{(\gamma - 1)}{\gamma E_p} \tag{3.36a}$$

$$n = \frac{1}{1 - m} \tag{3.38a}$$

γ for air can be taken as 1.4

$$m = \frac{1.4 - 1}{1.4 \times 0.74} = 0.39$$

$$n = \frac{1}{1 - 0.39} = 1.64$$

The inlet air will be at the ambient temperature, take as 15°C. With no intercooling

$$T_2 = 288 \times 8^{0.39} = \underline{\underline{648\ \text{K}}}$$

This is clearly too high and intercooling will be needed. Assume compressor is divided into two sections, with approximately equal work in each section. Take the intercooler gas outlet temperature as 60°C (which gives a reasonable approach to the normal cooling water temperature of 30°C).

For equal work in each section the interstage pressure

$$= \sqrt{\frac{P_{\text{out}}}{P_{\text{in}}}} = \sqrt{8} = 2.83$$

Taking the interstage pressure as 2.83 atm will not give exactly equal work in each section, as the inlet temperatures are different; however, it will be near enough for the purposes of this example.

$$\text{First section work, inlet } 15^\circ\text{C} = 1 \times 288 \times 8.314 \times \frac{1.64}{1.64 - 1}\left[(2.83)^{(1.64-1)/1.64} - 1\right]$$

$$= 3072.9\ \text{kJ/kmol}$$

$$\text{Second section work, inlet } 60^\circ\text{C} = 1 \times 333 \times 8.314 \times \frac{1.64}{1.64 - 1}\left[(2.83)^{(1.64-1)/1.64} - 1\right]$$

$$= 3552.6\ \text{kJ/kmol}$$

Total work $= 3072.9 + 3552.6 = 6625.5$ kJ/kmol

$$\text{Compressor power} = \frac{\text{work/kmol} \times \text{kmol/s}}{\text{efficiency}} = \frac{6625.5 \times 0.125}{0.74}$$

$$= 1119\ \text{kJ/s} = 1.12\ \text{MW}$$

Energy required per hour $= 1.12 \times 3600 = 4032$ MJ

$$\text{Compressor outlet temperature} = 333(2.83)^{0.39} = 500\ \text{K}$$

say, 230°C

This temperature will be high enough for no preheating of the reactor feed to be needed (Strelzoff).

Ammonia vaporiser

The ammonia will be stored under pressure as a liquid. The saturation temperature at 8 atm is 20°C. Assume the feed to the vaporiser is at ambient temperature, 15°C.

Specific heat at 8 bar = 4.5 kJ/kgK
Latent heat at 8 bar = 1186 kJ/kg
Flow to vaporiser = 731.0 kg/h

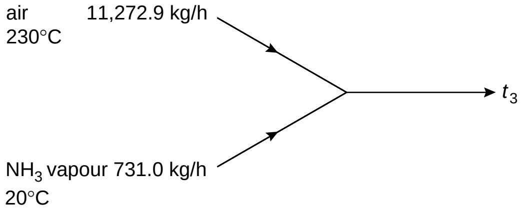
Heat input required to raise to 20°C and vaporise

$$= 731.0[4.5(20 - 15) + 1186] = 883{,}413.5\ \text{kJ/h}$$

add 10 per cent for heat losses $= 1.1 \times 883{,}413.5 = 971{,}754.9$ kJ/h

say, 972 MJ

Mixing tee



C_p air = 1 kJ/kgK,
C_p ammonia vapour 2.2 kJ/kgK.

Note: as the temperature of the air is only an estimate, there is no point in using other than average values for the specific heats at the inlet temperatures.

Energy balance around mixing tee, taking as the datum temperature the inlet temperature to the oxidiser, t_3.

$$11{,}272.9 \times 1(230 - t_3) + 731 \times 2.2(20 - t_3) = 0$$

$$t_3 = 204^\circ\text{C}$$

Oxidiser

The program ENERGY 1 (see Chapter 3) was used to make the balance over on the oxidiser. Adiabatic operation was assumed (negligible heat losses) and the outlet temperature found by making a series of balances with different outlet temperatures to find the value that reduced the computed cooling required to zero (adiabatic operation). The data used in the program are listed below:

$$\Delta H_r^\circ \text{ reaction 1} = -226{,}334 \text{ kJ/kmol (per kmol NH}_3\text{ reacted)}$$

$$\Delta H_r^\circ \text{ reaction 2} = -316{,}776 \text{ kJ/kmol (per kmol NH}_3\text{ reacted)}$$

All the reaction yield losses were taken as caused by reaction 2.

NH_3 reacted, by reaction 1

$$\text{Flow of NH}_3\text{ to oxidiser} \times \text{reactor yield} = \frac{731.0 \times 0.96}{17} = 41.3 \text{ kmol/h}$$

$$\text{balance by reaction 2} = \frac{731.0 \times 0.04}{17} = 1.7 \text{ kmol/h}$$

Summary, flows and heat capacity data:

Stream component	Feed (3) kmol/h	Product (4) kmol/h	C_p° kJ/kmol K			
			a	*b*	*c*	*d*
NH_3	43	—	27.32	23.83E-3	17.07E-6	−11.85E-9
O_2	82.1	29.2	28.11	−3.68E-6	17.46E-6	−10.65E-9
N_2	308.7	309.6	31.15	−1.36E-2	26.80E-6	−11.68E-9
NO	—	41.3	29.35	−0.94E-3	9.75E-6	−4.19E-9
H_2O	—	64.5	32.24	19.24E-4	10.5E-6	−3.60E-9
Temp. K	477	T_4				

The outlet temperature T_4 was found to be 1180 K = 907°C.

Waste-heat boiler (WHB)

As the amount of NO oxidised to NO_2 in this unit has not been estimated, it is not possible to make an exact energy balance over the unit. However, the maximum possible quantity of steam generated can be estimated by assuming that all the NO is oxidised; and the minimum quantity by assuming that none is. The plant steam pressure would be typically 150 to 200 psig $\approx$ 11 bar, saturation temperature 184°C. Taking the approach temperature of the outlet gases (difference between gas and steam temperature) to be 50°C, the gas outlet temperature will be $= 184 + 50 = 234$°C (507 K).

From the flow-sheet, NO entering WHB $= \dfrac{1238.4}{30} = 41.3$ kmol

$$O_2 \text{ entering} = \frac{935.7}{32} = 29.2 \text{ kmol/h}$$

If all the NO is oxidised, reaction 4, the oxygen leaving the WHB will be reduced to

$$29.2 - \frac{41.3}{2} = 8.6 \text{ kmol/h}$$

$$\Delta H_r^\circ = -57{,}120 \text{ kJ/kmol, NO oxidised}$$

If no NO is oxidised the composition of the outlet gas will be the same as the inlet. The inlet gas has the same composition as the reactor outlet, which is summarised above. Summarised below are the flow changes if the NO is oxidised:

		C_p° (kJ/kmol K)			
	(kmol/h)	*a*	*b*	*c*	*d*
O_2	7.46		as above		
NO_2	41.3	24.23	4.84 E-2	−20.81 E-2	0.29 E-9
Temp.	507K				

Using the program ENERGY 1, the following values were calculated for the heat transferred to the steam:

no NO oxidised	9.88 GJ/h
all NO oxidised	12.29 GJ/h

Steam generated; take feed water temperature as 20°C,

enthalpy of saturated steam at 11 bar = 2781 kJ/kg

enthalpy of water at 20°C = 84 kJ/kg

heat to form 1 kg steam = 2781 − 84 = 2697 kJ

$$\text{steam generated} = \frac{\text{heat transferred}}{\text{enthalpy change per kg}}$$

$$\text{so, minimum quantity generated} = \frac{9{,}880{,}000}{2697} = 3662 \text{ kg/h}$$

$$\text{maximum} = \frac{12{,}290{,}000}{2697} = 4555 \text{ kg/h}$$

Note: in practice superheated steam would probably be generated, for use in a turbine driving the air compressor.

Cooler-condenser

The sources of heat to be considered in the balance on this unit are:

1. Sensible heat: cooling the gases from the inlet temperature of 234°C to the required outlet temperature (the absorber inlet temperature) 40°C.
2. Latent heat of the water condensed.
3. Exothermic oxidation of NO to NO_2.
4. Exothermic formation of nitric acid.
5. Heat of dilution of the nitric acid formed, to 40 per cent w/w.
6. Sensible heat of the outlet gas and acid streams.

So that the magnitude of each source can be compared, each will be calculated separately. Take the datum temperature as 25°C.

1. Gas sensible heat

The program ENERGY 1 was used to calculate the sensible heat in the inlet and outlet gas streams. The composition of the inlet stream and the heat capacity data will be the same as that for the WHB outlet given above. Outlet stream flows from flow-sheet, converted to kmol/h:

Condenser outlet (6)	
	kmol/h
O_2	8.6
N_2	309.6
NO	6.75
NO_2	21.03
H_2O	1.63
Temp. 313 K	

Sensible heat inlet stream (5) = 2.81 GJ/h,
outlet stream (6) = 0.15 GJ/h.

2. Condensation of water

Water condensed = (inlet H_2O − outlet H_2O) = (1161 − 29) = 1131.6 kg/h
Latent heat of water at the inlet temperature, 230°C = 1812 kJ/kg

The steam is considered to condense at the inlet temperature and the condensate then cooled to the datum temperature.

$$\begin{aligned}\text{Heat from condensation} = 1131.6 \times 1812 &= 2.05 \times 10^6 \text{ kJ/h}\\ \text{Sensible heat to cool condensate} &= 1131.6 \times 4.18(230 - 25)\\ &= 0.97 \times 10^6 \text{ kJ/h}\\ \text{Total, condensation and cooling} &= (2.05 + 0.97)10^6 \text{ kJ/h}\\ &= 3.02 \text{ GJ/h}\end{aligned}$$

3. Oxidation of NO

The greatest heat load will occur if all the oxidation occurs in the cooler-condenser (i.e. none in the WHB) which gives the worst condition for the cooler-condenser design.

$$\begin{aligned}\text{Mols of NO oxidised} = \text{mols in} - \text{mols out} &= 41.3 - 6.75 = 34.55 \text{ kmol/h}\\ \text{From reaction 4, heat generated} &= 34.55 \times 57{,}120\\ &= 1.97 \times 10^6 \text{ kJ/h} = 1.97 \text{ GJ/h}\end{aligned}$$

4. Formation of nitric acid

$$\text{HNO}_3 \text{ formed, from flow sheet,} = \frac{850.6}{63} = 13.50 \text{ kmol/h}$$

The enthalpy changes in the various reactions involved in the formation of aqueous nitric acid are set out below (Miles):

$$2NO_2(g) \rightarrow N_2O_4(g) \qquad \Delta H = -57.32 \text{ kJ} \qquad (6a)$$

$$N_2O_4(g) + H_2O(l) + \tfrac{1}{2}O_2(g) \rightarrow 2HNO_3(g) \qquad \Delta H = +\ 9.00 \text{ kJ} \qquad (6b)$$

$$HNO_3(g) \rightarrow HNO_3(l) \qquad \Delta H = -39.48 \text{ kJ} \qquad (7)$$

Combining reactions 6*a*, 6*b* and 7.

Reaction 8. $2NO_2(g) + H_2O(l) + \frac{1}{2}O_2 \rightarrow 2HNO_3(l)$

$$\begin{aligned}\text{overall enthalpy change} &= -57.32 + 9.00 + 2(-39.48)\\ &= -127.28 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{heat generated per kmol of HNO}_3\text{(l) formed} &= \frac{127.28}{2} \times 10^3\\ &= 63{,}640 \text{ kJ}\\ \text{heat generated} = 13.50 \times 63{,}640 &= 0.86 \times 10^6 \text{ kJ/h}\\ &= 0.86 \text{ GJ/h}\end{aligned}$$

Note, the formation of N_2O_4 and the part played by N_2O_4 in the formation of nitric acid was not considered when preparing the flow-sheet, as this does not affect the calculation of the components flow-rates.

5. Heat of dilution of HNO_3

The heat of dilution was calculated from an enthalpy—concentration diagram given in Perry's *Chemical Engineers Handbook,* 5th edn, p. 3.205, Figure 3.42.

The reference temperature for this diagram is 32°F (0°C). From the diagram:

$$\begin{aligned}\text{enthalpy of 100 per cent HNO}_3 &= 0\\ \text{enthalpy of 45 per cent HNO}_3 &= -80 \text{ Btu/lb solution}\\ \text{specific heat 45 per cent HNO}_3 &= 0.67\end{aligned}$$

So, heat released on dilution, at 32°F = $80 \times 4.186/1.8 = 186$ kJ/kg soln.
Heat to raise solution to calculation datum temperature of 25°C = $0.67(25 - 0)4.186$
$= 70.1$ kJ/kg.
So, heat generated on dilution at 25°C = $186 - 70.1 = 115.9$ kJ/kg soln.

$$\text{Quantity of solution produced by dilution of 1 kmol 100 per cent } HNO_3 = \frac{63}{45} \times 100 = 140 \text{ kg},$$

$$\text{so, heat generated on dilution of 1 kmol} = 140 \times 115.9 = 16{,}226 \text{ kJ},$$

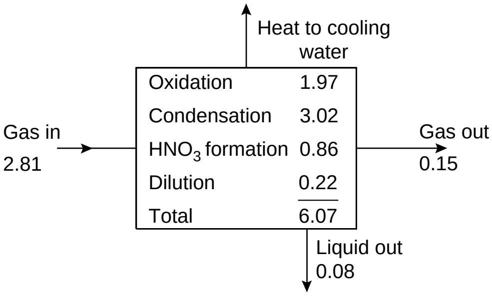
$$\text{so, total heat generated} = 13.5 \times 16{,}226 = 219{,}051 \text{ kJ/h} = 0.22 \text{ GJ/h}.$$

6. Sensible heat of acid

Acid outlet temperature was taken as 40°C, which is above the datum temperature.

Sensible heat of acid $= 0.67 \times 4.186(40 - 25) \times 1860.7 = 78{,}278$ kJ/h $= 0.08$ GJ/h

Heat balance (GJ/h)



$$\text{Heat transferred to cooling water} = 2.81 + 6.07 - 0.15 - 0.08 = 8.65 \text{ GJ/h}$$

Air cooler

The secondary air from the compressor must be cooled before mixing with the process gas stream at the absorber inlet; to keep the absorber inlet temperature as low as possible. Take the outlet temperature as the same as exit gases from the cooler condenser, 40°C.

Secondary air flow, from flow-sheet, 1754.8 kg/h
Specific heat of air 1 kJ/kgK
Heat removed from secondary air $= 1754.8 \times 1 \times (230 - 40) = 333{,}412$ kJ/h $= 0.33$ GJ/h

Absorber

The sources of heat in the absorber will be the same as the cooler-condenser and the same calculation methods have been used. The results are summarised below:

Sensible heat in inlet gases from cooler-condenser $= 0.15$ GJ/h
Sensible heat in secondary air $= 1754.8 \times 1.0(40 - 25) = 0.018$ GJ/h
Sensible heat in tail gases (at datum) $= 0$
Sensible heat in water feed (at datum) $= 0$

$$\text{NO oxidised} = \frac{202.5 - 21.9}{30} = 6.02 \text{ kmol/h}$$

$$\text{Heat generated} = 6.02 \times 57{,}120 = 0.34 \text{ GJ/h}$$

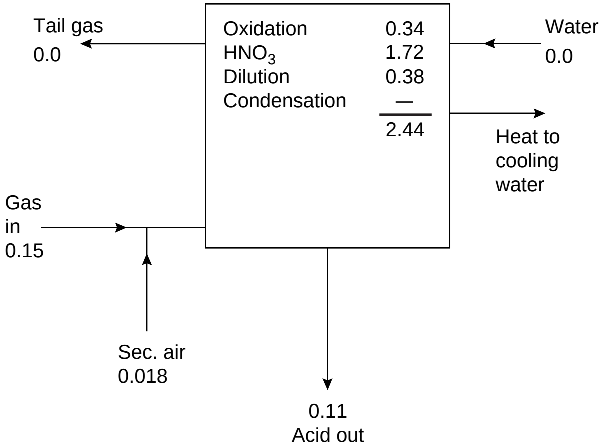
$$\text{HNO}_3 \text{ formed} = \frac{1704}{63} = 27.05 \text{ kmol/h}$$

$$\text{Heat generated} = 27.05 \times 63{,}640 = 1.72 \text{ GJ/h}$$

Heat of dilution to 60 per cent at 25°C = 27.05 × 14,207 = 0.38 GJ/h
Water condensed = 29.4 − 26.3 = 3.1 kg/h
Latent heat at 40°C = 2405 kJ/h
Sensible heat above datum temperature = 4.18 (40 − 25) = 63 kJ/kg
Heat released = $3.1(2405 + 63) = 7.6 \times 10^{-3}$ GJ/h (negligible)
Sensible heat in acid out, specific heat 0.64, take temperature out as same as gas inlet, 40°C

$$= 0.64(40 - 25)4.18 \times 2840 = 0.11 \text{ GJ/h}$$

Heat balance (GJ/h)



Heat transferred to cooling water = 0.15 + 0.018 + 2.44 − 0.11 = $\underline{\underline{2.5 \text{ GJ/h}}}$

Mixer

Calculation of mixed acid temperature.

Taking the datum as 0°C for this calculation, so the enthalpy-concentration diagram can be used directly.

From diagram:

enthalpy 45 per cent acid at 0°C = −186 kJ/kg
specific heat = 0.67 kcal/kg°C
enthalpy 60 per cent acid at 0°C = −202 kJ/kg
specific heat = 0.64 kcal/kg°C

So, enthalpy 45 per cent acid at 40°C $= -186 + 0.67 \times 4.186(40) = -73.8$ kJ/kg
and enthalpy 60 per cent acid at 40°C $= -202 + 0.64 \times 4.186(40) = -94.8$ kJ/kg

$$\text{Enthalpy of mixed acid} = \frac{(-73.8 \times 1860.7) + (-94.8 \times 2840.0)}{(1860.7 + 2840.0)}$$

$$= -86.5 \text{ kJ/kg}$$

From enthalpy-concentration diagram, enthalpy of mixed acid
(54 per cent) at 0°C $= -202$ kJ/kg; specific heat $= 0.65$ kcal/kg°C
so, "sensible" heat in mixed acid above datum of 0°C

$$= -86.5 - (-202) = 115.5 \text{ kJ/kg}$$

$$\text{and, mixed acid temperature} = \frac{115.5}{0.65 \times 4.186} = 43^\circ\text{C}$$

Energy recovery

In an actual nitric acid plant the energy in the tail gases would normally be recovered by expansion through a turbine coupled to the air compressor. The tail gases would be preheated before expansion, by heat exchange with the process gas leaving the WHB.

4.4. COMPUTER-AIDED FLOW-SHEETING

The computer programs available for flow-sheeting in process design can be classified into two basic types:

1. Full simulation programs, which require powerful computing facilities.
2. Simple material balance programs requiring only a relatively small core size.

The full simulation programs are capable of carrying out rigorous simultaneous heat and material balances, and preliminary equipment design: producing accurate and detailed flow-sheets. In the early stages of a project the use of a full simulation package is often not justified and a simple material balance program is more suitable. These are an aid to manual calculations and enable preliminary flow-sheets to be quickly, and cheaply, produced.

4.5. FULL STEADY-STATE SIMULATION PROGRAMS

Complex flow-sheeting programs, that simulate the operation and a complete process, or individual units, have been developed by several commercial software organisations. The names of the principal packages available, and the contact address, are listed in Table 4.1. Many of the commercial programs have been made available by the proprietors to university and college departments for use in teaching, at nominal cost.

Table 4.1. Simulation packages

Acronym	Type	Source	Internet address http//www.—
ASPEN Aspen DPS	steady-state	Aspen Technology Inc. Ten Canal Park, Cambridge, MA 02141-2201, USA	Aspentech.com
DESIGN II	steady-state	WinSim Inc. P.O. Box 1885, Houston, TX 77251-1885, USA	winsim.com
HYSYS	steady-state dynamic	Hyprotech Suite 900, 125-9 Avenue SE, Calgary, Alberta, T2G-OP6, Canada Merged with Aspen Tech	hyprotech.com
PRO/II DYNSIM	steady-state dynamic	SimSci-Esscor 5760 Fleet Street, Suite 100, Carlsbad, CA 92009, USA	simsci.com
CHEMCAD	steady-state	Chemstations Inc. 2901 Wilcrest, Suite 305, Houston, TX 77042 USA	chemstations.net

Note: Contact the web site to check the full features of the current versions of the programs.

Detailed discussion of these programs is beyond the scope of this book. For a general review of the requirements, methodology and application of process simulation programs the reader is referred to the books by: Husain (1986), Wells and Rose (1986), Leesley (1982), Benedek (1980), Mah and Seider (1980), Westerberg *et al*. (1979) and Crowe *et al*. (1971); and the paper by Panelides (1988).

Process simulation programs can be divided into two basic types:

Sequential-modular programs: in which the equations describing each process unit (module) are solved module-by-module in a stepwise manner; and iterative techniques used to solve the problems arising from the recycle of information.

They simulate the steady-state operation of the process and can be used to draw-up the process flow sheet, and to size individual items of equipment, such as distillation columns.

Equation based programs: in which the entire process is described by a set of differential equations, and the equations solved simultaneously: not stepwise, as in the sequential approach. Equation based programs can simulate the unsteady-state operation of processes and equipment.

In the past, most simulation programs available to designers were of the sequential-modular type. They were simpler to develop than the equation based programs, and required only moderate computing power. The modules are processed sequentially, so essentially only the equations for a particular unit are in the computer memory at one time. Also, the process conditions, temperature, pressure, flow-rate, are fixed in time.

But, computational difficulties can arise due to the iterative methods used to solve recycle problems and obtain convergence. A major limitation of modular-sequential simulators is the inability to simulate the dynamic, time dependent, behaviour of a process.

Equation based, dynamic, simulators require appreciably more computing power than steady-state simulators; to solve the thousands of differential equations needed to describe a process, or even a single item of equipment. However, with the development of fast powerful machines this is no longer a restriction. By their nature, equation based programs do not experience the problems of recycle convergence inherent in sequential simulators. But, as temperature, pressure and flow-rate are not fixed and the input of one unit is not determined by the calculated output from the previous unit in the sequence, as with steady-state simulators, equation based programs are more time demanding on computer time. This has led to the development of hybrid programs in which the steady-state simulator is used to generate the initial conditions for the dynamic simulation.

The principal advantage of equation based, dynamic, simulators is their ability to model the unsteady-state conditions that occur at start-up and during fault conditions. Dynamic simulators are being increasingly used for safety studies and in the design of control systems.

The structure of a typical simulation program is shown in Figure 4.4.

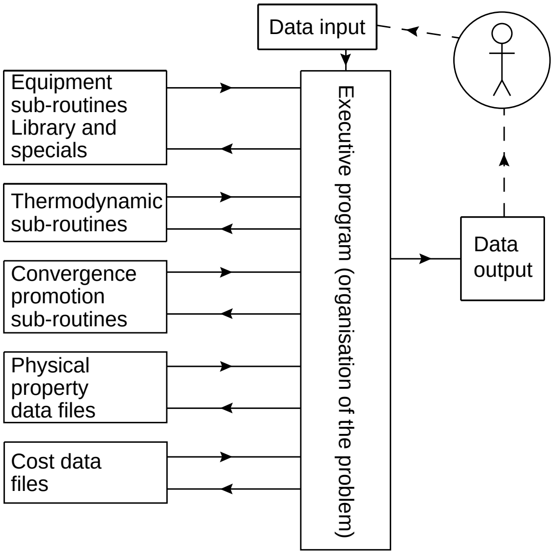


Figure 4.4. A typical simulation program

The program consists of:

1. A main executive program; which controls and keeps track of the flow-sheet calculations and the flow of information to and from the sub-routines.

2. A library of equipment performance sub-routines (modules); which simulate the equipment and enable the output streams to be calculated from information on the inlet streams.
3. A data bank of physical properties. To a large extent the utility of a sophisticated flow-sheeting program will depend on the comprehensiveness of the physical property data bank. The collection of the physical property data required for the design of a particular process, and its transformation into a form suitable for a particular flow-sheeting program can be very time-consuming.
4. Sub-programs for thermodynamic routines; such as the calculation of vapour-liquid equilibria and stream enthalpies.
5. Sub-programs and data banks for costing; the estimation of equipment capital costs and operating costs. Full simulation flow-sheeting programs enable the designer to consider alternative processing schemes, and the cost routines allow quick economic comparisons to be made. Some programs include optimisation routines. To make use of a costing routine, the program must be capable of producing at least approximate equipment designs.

In a sequential-modular program the executive program sets up the flow-sheet sequence, identifies the recycle loops, and controls the unit operation calculations: interacting with the unit operations library, physical property data bank and the other sub-routines. It will also contain procedures for the optimum ordering the calculations and routines to promote convergence.

In an equation based simulators the executive program sets up the flow-sheet and the set of equations that describe the unit operations, and then solves the equations; taking data from the unit operations library and physical property data bank and the file of thermodynamic sub-routines.

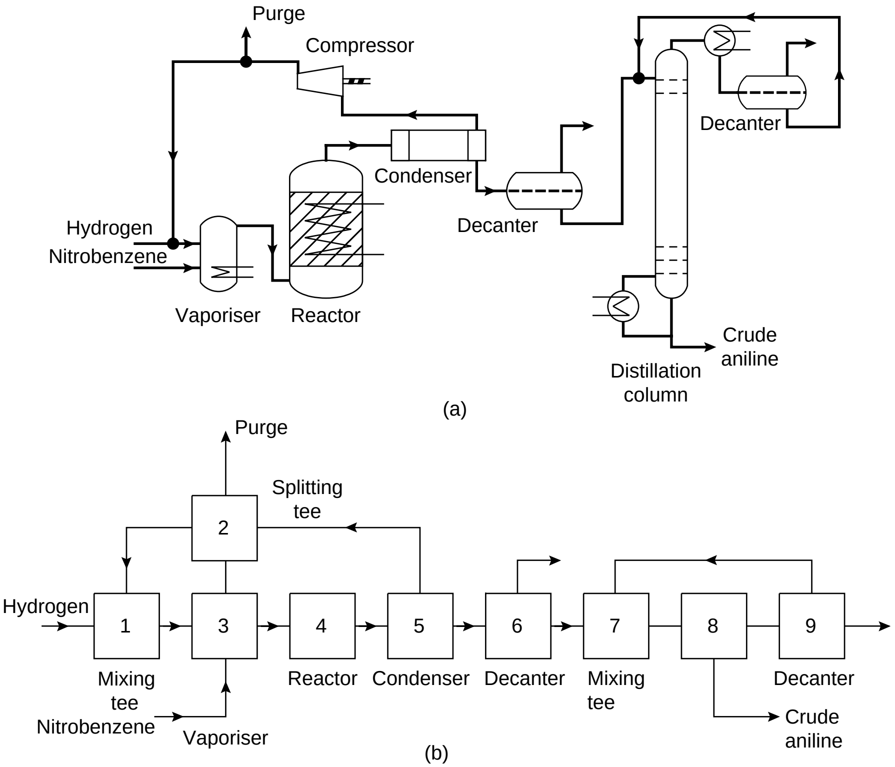
Many of the proprietary flow-sheeting packages are now front-ended with a graphical user interface to display the flow-sheet and facilitate the input of information to the package.

4.5.1. Information flow diagrams

To present the problem to the computer, the basic process flow diagram, which shows the sequence of unit operations and stream connections, must be transformed into an information flow diagram, such as that shown in Figure 4.5*b*. Each block represents a calculation module in the simulation program; usually a process unit or part of a unit. Units in which no change of composition, or temperature or pressure, occurs are omitted from the information flow diagram. But other operations not shown on the process flow diagram as actual pieces of equipment, but which cause changes in the stream compositions, such as mixing tees, must be shown.

The lines and arrows connecting the blocks show the flow of information from one subprogram to the next. An information flow diagram is a form of directed graph (a diagraph).

The calculation topology defined by the information diagram is transformed into a numerical form suitable for input into the computer, usually as a matrix.



Note: (1) Modules have been added to represent mixing and separation tees.
(2) The compressor is omitted.
(3) The distillation module includes the condenser and reboiler.

Figure 4.5. (*a*) Process flow diagram: hydrogenation of nitrobenzene to aniline (*b*) Information flow diagram hydrogenation of nitrobenzene to aniline (Figure 4.5*a*)

4.6. MANUAL CALCULATIONS WITH RECYCLE STREAMS

If a proprietary simulation program is not available, problems involving recycle streams can be solved on a spreadsheet using the procedure described below.

The procedure is based on the theory of recycle processes published by Nagiev (1964). The concept of split-fractions is used to set up the set of simultaneous equations that define the material balance for the process. This method has also been used by Rosen (1962) and is described in detail in the book by Henley and Rosen (1969).

4.6.1. The split-fraction concept

In an information flow diagram, such as that shown in Figure 4.5*b*, each block represents a calculation module; that is, the set of equations that relate the outlet stream component flows to the inlet flows. The basic function of most chemical processing units (unit operations) is to divide the inlet flow of a component between two or more outlet streams; for example, a distillation column divides the components in the feed between the overhead and bottom product streams, and any side streams. It is therefore convenient, when setting up the equations describing a unit operation, to express the flow of any component in any outlet stream as a fraction of the flow of that component in the inlet stream.

The block shown in Figure 4.6 represents any unit in an information flow diagram, and shows the nomenclature that will be used in setting up the material balance equations.

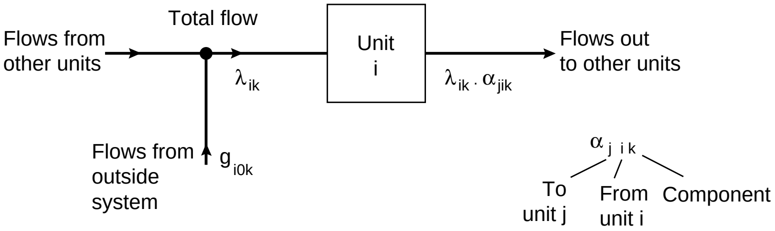


Figure 4.6.

i = the unit number,
$\lambda_{i,k}$ = the total flow into the unit i of the component k,
$\alpha_{j,i,k}$ = the *fraction* of the total flow of component k entering unit i that leaves in the outlet stream connected to the unit j; the "split-fraction coefficient",
$g_{i,0,k}$ = any fresh feed of component k into unit i; flow from outside the system (from unit 0).

The flow of any component from unit i to unit j will equal the flow into unit i multiplied by the split-fraction coefficient.

$$= \lambda_{i,k} \times \alpha_{j,i,k}$$

The value of the split-fraction coefficient will depend on the nature of the unit and the inlet stream composition.

The outlet streams from a unit can feed forward to other units, or backward (recycle).

An information flow diagram for a process consisting of three units, with two recycle streams is shown in Figure 4.7. The nomenclature defined in Figure 4.6 is used to show the stream flows.

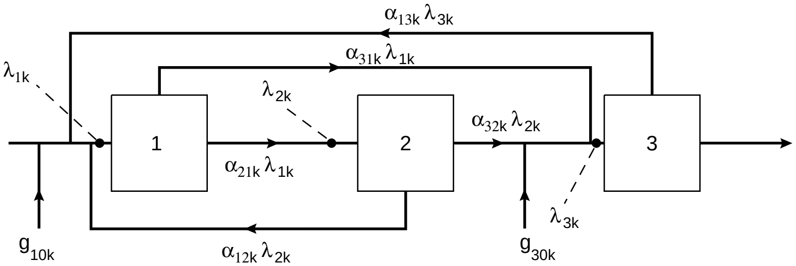


Figure 4.7.

Consider the streams entering unit 1.

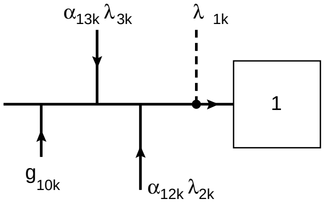


Figure 4.8.

A material balance gives:

$$g_{10k} + \alpha_{13k}\lambda_{3k} + \alpha_{12k}\lambda_{2k} = \lambda_{1k} \tag{4.1}$$

A similar material balance can be written at the inlet to each unit:

$$\text{unit 2:}\quad \alpha_{21k}\lambda_{1k} = \lambda_{2k} \tag{4.2}$$

$$\text{unit 3:}\quad \alpha_{32k}\lambda_{2k} + g_{30k} + \alpha_{31k}\lambda_{1k} = \lambda_{3k} \tag{4.3}$$

Rearranging each equation

$$\lambda_{1k} - \alpha_{12k}\lambda_{2k} - \alpha_{13k}\lambda_{3k} = g_{10k} \tag{4.1a}$$

$$-\alpha_{21k}\lambda_{1k} + \lambda_{2k} = 0 \tag{4.2b}$$

$$-\alpha_{31k}\lambda_{1k} - \alpha_{32k}\lambda_{2k} + \lambda_{3k} = g_{30k} \tag{4.3c}$$

This is simply a set of three simultaneous equations in the unknown flows λ_{1k}, λ_{2k}, λ_{3k}.

These equations are written in matrix form:

$$\begin{array}{cc} & \quad i \\ & \begin{array}{ccc} 1 & 2 & 3 \end{array} \\ j\begin{array}{c} 1 \\ 2 \\ 3 \end{array} & \begin{bmatrix} 1 & -\alpha_{12k} & -\alpha_{13k} \\ -\alpha_{21k} & 1 & 0 \\ -\alpha_{31k} & -\alpha_{32k} & 1 \end{bmatrix} \end{array} \times \begin{bmatrix} \lambda_{1k} \\ \lambda_{2k} \\ \lambda_{3k} \end{bmatrix} = \begin{bmatrix} g_{10} \\ 0 \\ g_{30} \end{bmatrix}$$

There will be a set of such equations for each component.

This procedure for deriving the set of material balance equations is quite general. For a process with n units there will be a set of n equations for each component.

The matrix form of the n equations will be as shown in Figure 4.9.

$$\begin{bmatrix} (1-\alpha_{11k}) - \alpha_{12k} & -\alpha_{13k} & \dots & -\alpha_{1nk} \\ -\alpha_{21k} & (1-\alpha_{22k}) - \alpha_{23k} & \dots & -\alpha_{2nk} \\ & & & \\ & & & \\ -\alpha_{n1k} \dots\dots\dots\dots\dots\dots & & \dots & (1-\alpha)_{nnk} \end{bmatrix} \times \begin{bmatrix} \lambda_{1k} \\ \lambda_{2k} \\ \\ \\ \lambda_{nk} \end{bmatrix} = \begin{bmatrix} g_{10k} \\ g_{20k} \\ \\ \\ g_{n0k} \end{bmatrix}$$

Figure 4.9. Matrix form of equations for n units

For practical processes most of the split-fraction coefficients are zero and the matrix is sparse.

In general, the equations will be non-linear, as the split-fractions coefficients (α's) will be functions of the inlet flows, as well as the unit function. However, many of the coefficients will be fixed by the process constraints, and the remainder can usually be taken as independent of the inlet flows (λ's) as a first approximation.

The fresh feeds will be known from the process specification; so if the split-fraction coefficients can be estimated, the equations can be solved to determine the flows of each component to each unit. Where the split-fractions are strongly dependent on the inlet flows, the values can be adjusted and the calculation repeated until a satisfactory convergence between the estimated values and those required by the calculated inlet flows is reached.

Processes with reaction

In a chemical reactor, components in the inlet streams are consumed and new components, not necessarily in the inlet streams, are formed. The components formed cannot be shown as split-fractions of the inlet flows and must therefore be shown as pseudo fresh-feeds.

A reactor is represented as two units (Figure 4.10). The split-fractions for the first unit are chosen to account for the loss of material by reaction. The second unit divides the reactor output between the streams connected to the other units. If the reactor has only one outlet stream (one connection to another unit), the second unit forming the reactor can be omitted.

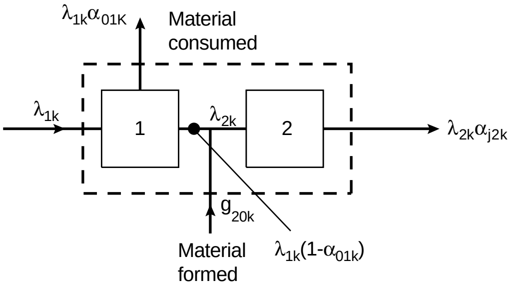


Figure 4.10. Reactor unit

Closed recycle systems

In some processes, a component may be recycled around two or more units in a closed loop. For example, the solvent in an absorption or liquid extraction process will normally be recovered by distillation and recycled. In this situation it will be necessary to introduce the solvent as a pseudo fresh-feed and the to remove it from the recycle loop by introducing a dummy stream divider, purging one stream.

As, in practice, some of the recycling component will always be lost, the amount purged should be adjusted to allow for any losses that are identified on the flow-sheet.

4.6.2. Illustration of the method

The procedure for setting up the equations and assigning suitable values to the split-fraction coefficients is best illustrated by considering a short problem: the manufacture of acetone from isopropyl alcohol.

Process description

Reaction: $$C_3H_7OH \xrightarrow[\text{cat.}]{\text{heat}} (CH_3)_2CO + H_2$$

Isopropyl alcohol is vaporised, heated and fed to a reactor, where it undergoes catalytic dehydrogenation to acetone. The reactor exit gases (acetone, water, hydrogen and unreacted isopropyl alcohol) pass to a condenser where most of the acetone, water and alcohol condense out. The final traces of acetone and alcohol are removed in a water scrubber. The effluent from the scrubber is combined with the condensate from the condenser, and distilled in a column to produce "pure" acetone and an effluent consisting of water and alcohol. This effluent is distilled in a second column to separate the excess water. The product from the second column is an azeotrope of water and isopropyl alcohol containing approximately 91 per cent alcohol. This is recycled to the reactor. Zinc oxide or copper is used as the catalyst, and the reaction carried out at 400 to 500°C and 40 to 50 psig pressure (4.5 bar). The yield to acetone is around 98 per cent, and the conversion of isopropyl alcohol per pass through the reactor is 85 to 90 per cent.

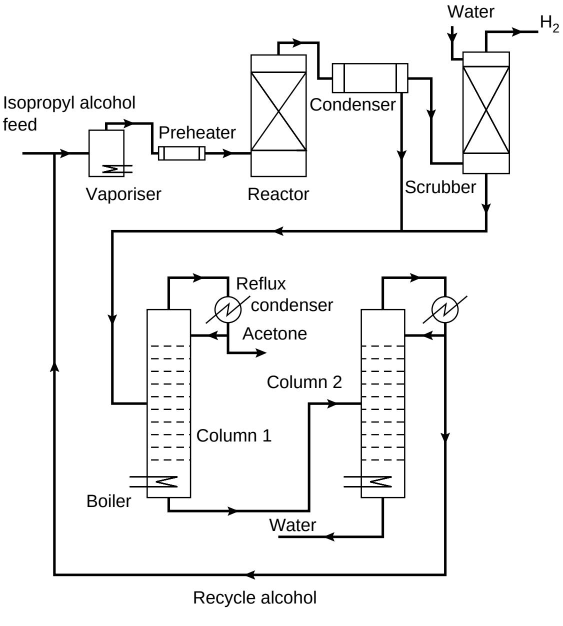


Figure 4.11. Process flow diagram

The process flow diagram is shown in Figure 4.11. This diagram is simplified and drawn as an information flow diagram in Figure 4.12. Only those process units in which there is a difference in composition between the inlet and outlet streams are shown. The

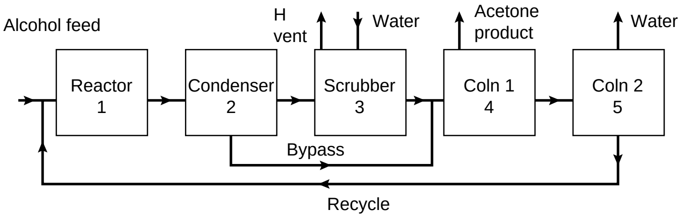


Figure 4.12. Information flow diagram

preheater and vaporiser are not shown, as there is no change in composition in these units and no division of the inlet stream into two or more outlet streams.

Figure 4.12 is redrawn in Figure 4.13, showing the fresh feeds, split-fraction coefficients and component flows. Note that the fresh feed g_{20k} represents the acetone and hydrogen generated in the reactor. There are 5 units so there will be 5 simultaneous equations. The equations can be written out in matrix form (Figure 4.14) by inspection of Figure 4.13. The fresh feed vector contains three terms.

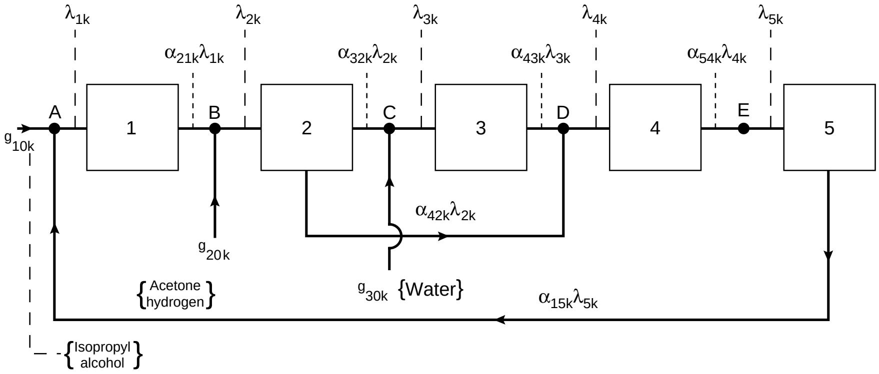


Figure 4.13. Split-fractions and fresh feeds

$$\begin{array}{c} \\ 1\\2\\3\\4\\5 \end{array}
\begin{array}{c}
\begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \end{array}\\
\left[\begin{array}{ccccc}
1 & 0 & 0 & 0 & -\alpha_{15k}\\
-\alpha_{21k} & 1 & 0 & 0 & 0\\
0 & -\alpha_{32k} & 1 & 0 & 0\\
0 & -\alpha_{42k} & -\alpha_{43k} & 1 & 0\\
0 & 0 & 0 & -\alpha_{54k} & 1
\end{array}\right]
\end{array}
\times \begin{bmatrix} \lambda_{1k}\\ \lambda_{2k}\\ \lambda_{3k}\\ \lambda_{4k}\\ \lambda_{5k} \end{bmatrix} = \begin{bmatrix} g_{10k}\\ g_{20k}\\ g_{30k}\\ 0\\ 0 \end{bmatrix}$$

Figure 4.14. The set of equations

Estimation of the split-fraction coefficients

The values of the split-fraction coefficients will depend on the function of the processing unit and the constraints on the stream flow-rates and compositions. Listed below are suggested first trial values, and the basis for selecting the particular value for each component.

Component 1, isopropyl alcohol ($k = 1$)

Unit 1, Reactor. The conversion per pass is given as 90 per cent, so for each mol entering only 10 per cent leave, hence α_{211} is fixed at 0.1. For this example it is assumed that the conversion is independent of the feed stream composition.

Unit 2, Condenser. Most of the alcohol will condense as its boiling point is 82°C. Assume 90 per cent condensed, $\alpha_{421} = 0.9$ (liquid out) and $\alpha_{321} = 0.1$ (vapour out). The actual amounts will depend on the condenser design.

Unit 3, Scrubber. To give a high plant yield, the scrubber would be designed to recover most of the alcohol in the vent stream. Assume 99 per cent recovery, allowing for the small loss that must theoretically occur, $\alpha_{431} = 0.99$.

Unit 4, First column. The fraction of alcohol in the overheads would be fixed by the amount allowed in the acetone product specification. Assume 1 per cent loss to the acetone is acceptable, which will give less than 1 per cent alcohol in the product; fraction in the bottoms 99 per cent, $\alpha_{541} = 0.99$.

Unit 5, Second column. No distillation column can be designed to give complete separation of the components. However, the volatilities for this system are such that a high recovery of alcohol should be practicable. Assume 99 per cent recovery, alcohol recycled, $\alpha_{151} = 0.99$.

Component 2, Acetone ($k = 2$)

Unit 1. Assume that any acetone in the feed passes through the reactor unchanged, $\alpha_{212} = 1$.

Unit 2. Most of the acetone will condense (b.p. 56°C) say 80 per cent, $\alpha_{322} = 0.2$, $\alpha_{422} = 0.8$.

Unit 3. As for alcohol, assume 99 per cent absorbed, allows for a small loss, $\alpha_{432} = 0.99$.

Unit 4. Assume 99 per cent recovery of acetone as product, $\alpha_{542} = 0.01$.

Unit 5. Because of its high volatility in water all but a few ppm of the acetone will go overhead, put $\alpha_{152} = 0.01$.

Component 3, Hydrogen ($k = 3$)

Unit 1. Passes through unreacted, $\alpha_{213} = 1$.

Unit 2. Non-condensable, $\alpha_{323} = 1$, $\alpha_{423} = 0$.

Unit 3. None absorbed, $\alpha_{433} = 0$.

Unit 4. Any present in the feed would go out with the overheads, $\alpha_{543} = 1$.

Unit 5. As for unit 4, $\alpha_{153} = 1$.

Component 4, Water ($k = 4$)

Unit 1. Passes through unreacted, $\alpha_{214} = 1$.

Unit 2. A greater fraction of the water will condense than the alcohol or acetone (b.p. 100°C) assume 95 per cent condensed, $\alpha_{324} = 0.05$, $\alpha_{423} = 0.95$.

Unit 3. There will be a small loss of water in the vent gas stream, assume 1 per cent lost, $\alpha_{434} = 0.99$.

Unit 4. Some water will appear in the acetone product; as for the alcohol this will be fixed by the acetone product specification. Putting $\alpha_{544} = 0.99$ will give less than 1 per cent water in the product.

Unit 5. The overhead composition will be close to the azeotropic composition, approximately 9 per cent water. The value of α_{154} (recycle to the reactor) must be selected so that the overheads from this unit approximate to the azeotropic composition, as a first try put $\alpha_{154} = 0.05$.

Estimation of fresh feeds

1. Isopropyl alcohol, take the basis of the flow sheet as 100 mol feed, $g_{101} = 100$.
2. Acetone formed in the reaction. The overall yield to acetone is approximately 98 per cent, so acetone formed $= 100 \times \frac{98}{2} = 980$ mol, $g_{202} = 98$ mol.
3. Hydrogen, it is formed in equimolar proportion to acetone, so $g_{203} = 98$ mol.
4. Water, the feed of water to the scrubber will be dependent on the scrubber design. A typical design value for mG_m/L_m for a scrubber is 0.7 (see Volume 2, Chapter 4). For the acetone absorption this would require a value of L_m of 200 mol, $g_{304} = 200$ mol.

Matrices

Substituting the values for alcohol ($k = 1$) into the matrix (Figure 4.14) gives the following set of equations for the flow of alcohol into each unit;

$$\begin{bmatrix} 1 & 0 & 0 & 0 & -0.99 \\ -0.1 & 1 & 0 & 0 & 0 \\ 0 & -0.1 & 1 & 0 & 0 \\ 0 & -0.9 & -0.99 & 1 & 0 \\ 0 & 0 & 0 & -0.99 & 1 \end{bmatrix} \times \begin{bmatrix} \lambda_{11} \\ \lambda_{21} \\ \lambda_{31} \\ \lambda_{41} \\ \lambda_{51} \end{bmatrix} = \begin{bmatrix} 100 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Substitution of the values of the split-fraction coefficients for the other components will give the sets of equations for the component flows to each unit. The values of the split-fraction coefficients and fresh feeds are summarised in Table 4.2.

Table 4.2. Split-fraction coefficients and feeds

α	$k =$ 1	2	3	4
21k	−0.1	−1	−1	−1.0
32k	−0.1	−0.2	−1	−0.05
42k	−0.9	−0.8	0	−0.95
43k	−0.99	−0.99	0	−0.99
54k	−0.99	−0.01	−1	−0.99
15k	−0.99	−0.01	−1	−0.05
	g_{101}	g_{202}	g_{203}	g_{304}
Mol	100	98	98	200

Solution of the equations

The most convenient way to set up and solve the equations is to use a spreadsheet; but any of the standard procedures and programs available for the solution of linear simultaneous equations can be used; Westlake (1968), Mason (1984).

Most proprietary spreadsheets include a routine for the inversion of matrices and the solution of sets of linear simultaneous equations. By using cell references, with cell copying and cell pointing, it is a simple procedure to set up the split fraction matrices and fresh feed vectors; solve the equations; and use the results to calculate and check the values of any stream composition.

Once the spreadsheet has been set up it is easy to change the values of the split fractions and fresh feeds, and iterate until the design constraints for the problem are satisfied.

The sample problem was solved using an inexpensive, but versatile, spreadsheet package “AS-EASY-AS”(1). The procedure used is illustrated below.

Procedure

Step 1: Set up the table of split-fractions and fresh feeds, Figure 4.15.

```
A ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
 1 |
 2 |        MASSBAL EXAMPLE USING SPREAD SHEET “AS-EASY-AS”
 3 |        TO SOLVE EQUATIONS
 4 |        ______________________________________________________________
 5 |
 6 |        Split fraction coefficients and fresh feeds
 7 |
 8 |        alpha / k          1             2             3             4
 9 |
10 |        21k            −0.10         −1.00         −1.00         −1.00
11 |        32k            −0.10         −0.20         −1.00         −0.05
12 |        42k            −0.90         −0.80          0.00         −0.95
13 |        43k            −0.99         −0.99          0.00         −0.99
14 |        54k            −0.99         −0.01         −1.00         −0.99
15 |        15k            −0.99         −0.01         −1.00         −0.05
16 |
17 |                        g101          g202          g203          g304
18 |
19 |        mol            100.00         98.00         98.00        200.00
20 |     ___________________________________________________________
```

Figure 4.15.

Step 2: Set up an identity matrix of the dimensions needed, $n \times n$; a matrix with 1’s on the leading diagonal and 0’s elsewhere. For this problem there are 5 unis so a 5×5 matrix is needed, Figure 4.16.

```
A  ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
20 |          _________________________________________________________
21 |
22 |          Identity matric
23 |
24 |                 1          2          3          4          5          g          Flows
25 |
26 |      1        1.00       0.00       0.00       0.00       0.00       0.00
27 |      2        0.00       1.00       0.00       0.00       0.00       0.00
28 |      3        0.00       0.00       1.00       0.00       0.00       0.00
29 |      4        0.00       0.00       0.00       1.00       0.00       0.00
30 |      5        0.00       0.00       0.00       0.00       1.00       0.00
31 |          _________________________________________________________
```

Figure 4.16.

---

(1) AS-EASY-AS is copyright software developed by TRUIS Inc., North Andover, Massachusetts, USA. Check their web site to download the latest version: www.truisinc.com.

Step 3: Make a copy of the identity matrix, one for each component. For this problem there are 4 components so 4 copies are needed.

Step 4: Copy the appropriate split-fractions and fresh feeds from the table of split-fractions and fresh feeds, Figure 4.15, into the component matrices, Figure 4.17. Copy the cell references, not the actual values. Using the cell references ensures that subsequent changes in the values in the primary table, Figure 4.15, will be copied automatically to the appropriate matrix.

For example, in Figure 4.17 the contents of cell F72 are (F15), not −0.05.

```
A  ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
31 |         ____________________________________________________________
32 |
33 |         Matrix equations
34 |
35 |         k = 1
36 |
37 |               1         2         3         4         5          g         Flows
38 |
39 |   1        1.00      0.00      0.00      0.00     −0.99     100.00       110.85
40 |   2       −0.10      1.00      0.00      0.00      0.00       0.00        11.09
41 |   3        0.00     −0.10      1.00      0.00      0.00       0.00         1.11
42 |   4        0.00     −0.90     −0.99      1.00      0.00       0.00        11.07
43 |   5        0.00      0.00      0.00     −0.99      1.00       0.00        10.96
44 |         ____________________________________________________________
45 |
46 |         k = 2
47 |
48 |               1         2         3         4         5          g         Flows
49 |
50 |   1        1.00      0.00      0.00      0.00     −0.01       0.00         0.01
51 |   2       −1.00      1.00      0.00      0.00      0.00      98.00        98.01
52 |   3        0.00     −0.20      1.00      0.00      0.00       0.00        19.60
53 |   4        0.00     −0.80     −0.99      1.00      0.00       0.00        97.81
54 |   5        0.00      0.00      0.00     −0.01      1.00       0.00         0.98
55 |         ____________________________________________________________
56 |
57 |         k = 3
58 |
59 |               1         2         3         4         5          g         Flows
60 |
61 |   1        1.00      0.00      0.00      0.00     −1.00       0.00         0.00
62 |   2       −1.00      1.00      0.00      0.00      0.00      98.00        98.00
63 |   3        0.00     −1.00      1.00      0.00      0.00       0.00        98.00
64 |   4        0.00      0.00      0.00      1.00      0.00       0.00         0.00
65 |   5        0.00      0.00      0.00     −1.00      1.00       0.00         0.00
66 |         ____________________________________________________________
67 |
68 |         k = 4
69 |
70 |               1         2         3         4         5          g         Flows
71 |
72 |   1        1.00      0.00      0.00      0.00     −0.05       0.00        10.31
73 |   2       −1.00      1.00      0.00      0.00      0.00       0.00        10.31
74 |   3        0.00     −0.05      1.00      0.00      0.00     200.00       200.52
75 |   4        0.00     −0.95     −0.99      1.00      0.00       0.00       208.31
76 |   5        0.00      0.00      0.00     −0.99      1.00       0.00       206.22
77 |         ____________________________________________________________
78 |
```

Figure 4.17.

Step 5: Use the equation solving routine (E-solve with AS-EASY-AS) to solve the equations and put the results, the flows into each unit, into a column headed “flows”, column H in Figure 4.17; repeat for each component matrix.

Step 6: Transfer (COPY) the component flows into a table and use the SUM function to total the flows in a column, Figure 4.18. Copy the cell references into the table not the values. Examples, from Figure 4.18:

cell C84 contents: (H40)
cell C85 contents: (H41)
cell G84 contents: SUM(C84. .F84)

```
A  ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
77 |            ___________________________________________________
78 |
79 |         Flow and Compositions
80 |
81 |         Component       1         2         3         4      Totals
82 |   Unit
83 |    1                110.85      0.01      0.00     10.31    121.17
84 |    2                 11.09     98.01     98.00     10.31    217.41
85 |    3                  1.11     19.60     98.00    200.52    319.23
86 |    4                 11.07     97.81      0.00    208.31    317.19
87 |    5                 10.96      0.98      0.00    206.22    218.16
88 |
89 |
90 |            Unit         1         2         3         4         5
91 |
92 |  Comp.%      1        91.48      5.10      0.35      3.49      5.03
93 |              2         0.01     45.08      6.14     30.84      0.45
94 |              3         0.00     45.08     30.70      0.00      0.00
95 |              4         8.51      4.74     62.81     65.67     94.53
96 |
97 |            Total     100.00    100.00    100.00    100.00    100.00
   |         ______________________________________________________
```

Figure 4.18.

Step 7: Set up a table to calculate the percentage composition of the stream into each unit; by copying from the table of component flows. The results are shown in Figure 4.18. Example, from Figure 4.18:

cell C92 contents: (C83/G83) $*$ 100

Step 8: Set up the calculations for any values which are design constraints. For example, the overheads, recycle flow, from the second column which should approximate to the azeotropic composition; see Table 4.4. The calculations giving the composition of this stream are shown in Figure 4.19*a*.

```
A ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
 98 |        ______________________________________________________________________
 99 |
100 |
101 |        Recycle flow composition
102 |
103 |          alpha 1, 5, 4 = −0.05
104 |
105 |        Component         1          2          3          4          Total
106 |
107 |        Flow            10.85       0.01       0.00      10.31       21.17
108 |
109 |        Percent         51.26       0.05       0.00      48.70
110 |
111 |        ______________________________________________________________________
112 |
```

Figure 4.19*a*.

```
A ] . . . . . . . .A/. . . . . . . .B/. . . . . . . .C/. . . . . . . .D/. . . . . . . .E/. . . . . . . .F/. . . . . . . .G/. . . . . . . .H
 98 |        ______________________________________________________________________
 99 |
100 |
101 |        Recycle flow composition
102 |
103 |          alpha 1, 5, 4 = −0.0053
104 |
105 |        Component         1          2          3          4          Total
106 |
107 |        Flow            10.85       0.01       0.00       1.08       11.94
108 |
109 |        Per cent        90.88       0.08       0.00       9.04
110 |
111 |        ______________________________________________________________________
112 |
```

Figure 4.19*b*.

Step 9: Change the values of the appropriate split fractions, or fresh feeds, in the primary table, Figure 4.15, and observe the changes to the calculated values: which will carry through the spread sheet automatically. Iterate on the values until the desired result is obtained.

Comments on the first trial solutions

Table 4.3 shows the feed of each component and the total flow to each unit. The composition of any other stream of interest can be calculated from these values and the split-fraction coefficients. The compositions and flows should be checked for compliance with the process constraints, the split-fraction values adjusted, and the calculation repeated, as necessary, until a satisfactory fit is obtained. Some of the constraints to check in this example are discussed below.

Table 4.3. Solution of equations, feeds to units

Unit	Component	1	2	3	4	Total
1	λ_{1k}	110.85	0.01	0.0	10.31	121.17
2	λ_{2k}	11.09	98.01	98.0	10.31	217.41
3	λ_{3k}	1.11	19.6	98.0	200.51	319.22
4	λ_{4k}	11.07	97.81	0.0	208.3	317.19
5	λ_{5k}	10.96	0.98	0.0	206.22	218.16

Recycle flow from the second column

This should approximate to the azeotropic composition (9 per cent alcohol, 91 per cent water). The flow of any component in this stream is given by multiplying the feed to the column (λ_{5k}) by the split-fraction coefficient for the recycle stream (α_{15k}). The calculated flows for each component are shown in Table 4.4.

Table 4.4. Calculation of recycle stream flow

Component	1	2	3	4	Total
λ_{5k}	10.96	0.98	0.0	206.22	
α_{15k}	0.99	0.01	1	0.05	
Flow					
$\alpha_{15k}\lambda_{5k}$	10.85	0.01	0	10.31	21.17
Per cent	51.3	0.05	0	48.7	

Calculated percentage alcohol = 51.3 per cent, required value 91 per cent. Clearly the initial value selected for α_{154} was too high; too much recycle. Iteration, using the spreadsheet, shows the correct value of α_{154} to be 0.0053, see Figure 4.19*b*.

Reactor conversion and yield

$$\text{Conversion} = \frac{\text{alcohol in} - \text{alcohol out}}{\text{alcohol in}} = \frac{\lambda_{11} - \lambda_{21}}{\lambda_{11}} = \frac{110.85 - 11.09}{110.85}$$

$$= 90 \text{ per cent, which is the value given}$$

$$\text{Yield} = \frac{\text{acetone out}}{\text{alcohol in} - \text{alcohol out}} = \frac{\lambda_{22}}{\lambda_{11} - \lambda_{21}} = \frac{98.01}{110.85 - 11.09}$$

$$= 98.3 \text{ per cent, near enough.}$$

Condenser vapour and liquid composition

The liquid and vapour streams from the partial condenser should be approximately in equilibrium.

The component flows in the vapour stream $= \alpha_{32k}\lambda_{2k}$ and in the liquid stream $= \alpha_{42k}\lambda_{2k}$. The calculation is shown in Table 4.5.

These compositions should be checked against the vapour-liquid equilibrium data for acetone-water and the values of the split-fraction coefficients adjusted, as necessary.

Table 4.5. Condenser vapour and liquid compositions

Component k	1	2	3	4	Total
λ_{2k}	11.09	98.01	98.0	10.31	
α_{32k}	0.1	0.2	1	0.05	
Vapour flow					
$\alpha_{32k}\lambda_{2k}$	1.11	19.6	98.0	0.52	119.23
Per cent	0.9	16.4	82.2	0.4	
α_{42k}	0.9	0.8	0	0.95	
Liquid flow					
$\alpha_{42k}\lambda_{2k}$	9.98	78.41	0	9.79	98.18
Per cent	10.2	79.9	0	10.0	

4.6.3. Guide rules for estimating split-fraction coefficients

The split-fraction coefficients can be estimated by considering the function of the process unit, and by making use of any constraints on the stream flows and compositions that arise from considerations of product quality, safety, phase equilibria, other thermodynamic relationships; and general process and mechanical design considerations. The procedure is similar to the techniques used for the manual calculation of material balances discussed in Section 4.3.

Suggested techniques for use in estimating the split-fraction coefficients for some of the more common unit operations are given below.

1. Reactors

The split-fractions for the reactants can be calculated directly from the percentage conversion. The conversion may be dependent on the relative flows of the reactants (feed composition) and, if so, iteration may be necessary to determine values that satisfy the feed condition.

Conversion is not usually very dependent on the concentration of any inert components.

The pseudo fresh feeds of the products formed in the reactor can be calculated from the specified, or estimated, yields for the process.

2. Mixers

For a unit that simply combines several inlet streams into one outlet stream, the split-fraction coefficients for each component will be equal to 1. $\alpha_{j,i,k} = 1$.

3. Stream dividers

If the unit simply divides the inlet stream into two or more outlet streams, each with the same composition as the inlet stream, then the split-fraction coefficient for each component will have the same value as the fractional division of the total stream. A purge stream is an example of this simple division of a process stream into two streams: the main stream and the purge. For example, for a purge rate of 10 per cent the split-fraction coefficients for the purge stream would be 0.1.

4. Absorption or stripping columns

The amount of a component absorbed or stripped in a column is dependent on the column design (the number of stages), the component solubility, and the gas and liquid rates. The fraction absorbed can be estimated using the absorption factor method, attributed to Kremser (1930) (see Volume 2, Chapter 12). If the concentration of solute in the solvent feed to the column is zero, or can be neglected, then for the solute component the fraction absorbed =

$$\frac{(L_m/mG_m)^{s+1} - L_m/mG_m}{(L_m/mG_m)^{s+1} - 1}$$

and for a stripping column, the fraction stripped =

$$\frac{(mG_m/L_m)^{s+1} - (mG_m/L_m)}{(mG_m/L_m)^{s+1} - 1}$$

where G_m = gas flow rate, kmol m^{-2} h^{-1},
L_m = liquid flow rate, kmol m^{-2} h^{-1},
m = slope of the equilibrium curve,
s = the number of stages.

For a packed column the chart by Colburn (1939) can be used (see Volume 2, Chapter 11). This gives the ratio of the inlet and outlet concentrations, y_1/y_2, in terms of the number of transfer units and mG_m/L_m.

The same general approach can be used for solvent extraction processes.

5. Distillation columns

A distillation column divides the feed stream components between the top and bottom streams, and any side streams. The product compositions are often known; they may be specified, or fixed by process constraints, such as product specifications, effluent limits or an azeotropic composition. For a particular stream, “s”, the split-fraction coefficient is given by:

$$\frac{x_{sk} r_s}{x_{fk}}$$

where x_{sk} = the concentration of the component k in the stream, s,
x_{fk} = the concentration component k in the feed stream,
r_s = the fraction of the total feed that goes to the stream, s.

If the feed composition is fixed, or can be estimated, the value of r_s can be calculated from a mass balance.

The split-fraction coefficients are not very dependent on the feed composition, providing the reflux flow-rate is adjusted so that the ratio of reflux to feed flow is held constant; Vela (1961), Hachmuth (1952).

It is not necessary to specify the reflux when calculating a preliminary material balance; the system boundary can be drawn to include the reflux condenser.

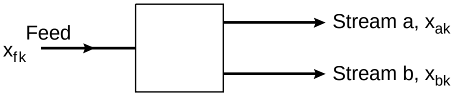
For a column with no side streams the fraction of the total feed flow going to the overheads is given by:

$$r_{\text{overheads}} = \frac{x_{fk} - x_{wk}}{x_{dk} - x_{wk}}$$

where x is the component composition and the suffixes f, d, w refer to feed, overheads and bottoms respectively.

6. Equilibrium separators

This is a stream divider with two outlet streams, a and b, which may be considered to be in equilibrium.



where x_{ak} = concentration of component k in stream a,
x_{bk} = concentration of component k in stream b,
x_{fk} = concentration of component k in the feed stream.

If the equilibrium relationship can be expressed by a simple equilibrium constant, K_k, such that:

$$x_{ak} = K_k x_{bk}$$

Then the split-fraction coefficients can be calculated from a material balance.

$$\text{Split fraction for stream } a = \frac{K_k}{K_k - 1} \frac{(x_{fk} - x_{bk})}{x_{fk}}.$$

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4.8. NOMENCLATURE

		Dimensions in **MLT**
G_m	Molar flow-rate of gas per unit area	$\mathbf{ML^{-2}T^{-1}}$
g_{iok}	Fresh feed to unit i of component k	$\mathbf{MT^{-1}}$
K_k	Equilibrium constant for component k	—
L_m	Liquid flow-rate per unit area	$\mathbf{ML^{-2}T^{-1}}$
m	Slope of equilibrium line	—
r_s	Fraction of total feed that goes to stream s	—
s	Number of stages	—
x_{ak}	Concentration of component k in stream a	—
x_{bk}	Concentration of component k in stream b	—
x_{dk}	Concentration of component k in distillate	—
x_{fk}	Concentration of component k in feed	—
x_{wk}	Concentration of component k in bottom product	—
λ_{ik}	Total flow of component k to unit i	$\mathbf{MT^{-1}}$
α_{jik}	Split-fraction coefficient : fraction of component k flowing from unit i to unit j	—

4.9. PROBLEMS

4.1. Monochlorobenzene is produced by the reaction of benzene with chlorine. A mixture of monochlorobenzene and dichlorobenzene is produced, with a small amount of trichlorobenzene. Hydrogen chloride is produced as a by-product. Benzene is fed to the reactor in excess to promote the production of monochlorobenzene.

The reactor products are fed to a condenser where the chlorobenzenes and unreacted benzene are condensed. The condensate is separated from the non-condensable gases in a separator. The non-condensables, hydrogen chloride and unreacted chlorine, pass to an absorption column where the hydrogen chloride is absorbed in water. The chlorine leaving the absorber is recycled to the reactor.

The liquid phase from the separator, chlorobenzenes and unreacted benzene, is fed to a distillation column, where the chlorobenzenes are separated from the unreacted benzene. The benzene is recycle to the reactor.

Using the data given below, calculate the stream flows and draw up a preliminary flow-sheet for the production of 1.0 tonne monochlorobenzene per day.
Hint: start the material balance at the reactor inlet (after the addition of the recycle streams) and use a basis of 100 kmol/h benzene at this point.
Data
Reactor

Reactions: $C_6H_6 + Cl_2 \rightarrow C_6H_5 + HCl$

$$C_6H_6 + 2Cl_2 \rightarrow C_6H_4\ Cl_2 + 2HCl$$

mol ratio $Cl_2 : C_6H_6$ at inlet to reactor = 0.9
overall conversion of benzene = 55.3 per cent
yield of monochlorobenzene = 73.6 per cent
yield of dichlorobenzene = 27.3 per cent
production of other chlorinated compounds can be neglected.

Condenser

Assume that all the chlorobenzenes and unreacted benzene condenses. Assume that the vapour pressure of the liquid at the condenser temperature is not significant; i.e. that no chlorobenzene or benzene are carried over in the gas stream.

Separator

Assume complete separation of the liquid and gas phases.

Absorber

Assume 100 per cent absorption of hydrogen chloride, and that 98 per cent of the chlorine is recycled, the remainder being dissolved in the water. The water supply to the absorber is set to produce a 30 per cent w/w strength hydrochloric acid.

Distillation column

Take the recovery of benzene to be 95 per cent, and complete separation of the chlorobenzenes.

4.2. Methyl tertiary butyl ether (MTBE) is used as an anti-knock additive in petrol (gasoline).
It is manufactured by the reaction of isobutene with methanol. The reaction is highly selective and practically any C_4 stream containing isobutene can be used as a feedstock

$$CH_2{=\!=}C(CH_3)_2 + CH_3OH \rightarrow (CH_3)_3{-\!-}C{-\!-}O{-\!-}CH_3$$

A 10 per cent excess of methanol is used to suppress side reactions.
In a typical process, the conversion of isobutene in the reactor stage is 97 per cent. The product is separated from the unreacted methanol and any C_4's by distillation. The essentially pure, liquid, MTBE leaves the base of the distillation column and is sent to storage. The methanol and C_4's leave the top of the column as vapour and pass to a column where the methanol is separated by absorption in water. The C_4's leave the top of the absorption column, saturated with water, and are used as a fuel gas. The methanol is separated from the water solvent by distillation and recycled to the reactor stage. The water, which leaves the base of the column, is

recycled to the absorption column. A purge is taken from the water recycle stream to prevent the build-up of impurities.

1. Draw up an information flow diagram for this process.
2. Estimate the split faction coefficients and fresh feeds for each stage.
3. Set up the resulting material balance equations, in matrix form.
4. Solve the equations using a suitable spread-sheet.
5. Adjust the values chosen for the split-fractions and feeds, so the results meet the constraints,
6. Draw a flow-sheet for the process.

Treat the C_4's, other than isobutene, as one component.

Data:

1. Feedstock composition, mol per cent: n-butane = 2, butene-1 = 31, butene-2 = 18, isobutene = 49.
2. Required production rate of MTBE, 7000 kg/h.
3. Reactor conversion of isobutene, 97 per cent.
4. Recovery of MTBE from the distillation column, 99.5 per cent.
5. Recovery of methanol in the absorption column, 99 per cent.
6. Concentration of methanol in the solution leaving the absorption column, 15 per cent.
7. Purge from the water recycle stream, to waste treatment, 10 per cent of the flow leaving the methanol recovery column.
8. The gases leave the top of the absorption column saturated with water at 30 °C.
9. Both columns operate at essentially atmospheric pressure.

4.3. Water and ethanol form a low boiling point azeotrope. So, water cannot be completely separated from ethanol by straight distillation. To produce absolute (100 per cent) ethanol it is necessary to add an entraining agent to break the azeotrope. Benzene is an effective entrainer and is used where the product is not required for food products. Three columns are used in the benzene process.

Column 1. This column separates the ethanol from the water. The bottom product is essentially pure ethanol. The water in the feed is carried overhead as the ternary azeotrope of ethanol, benzene and water (24 per cent ethanol, 54 per cent benzene, 22 per cent water). The overhead vapour is condensed and the condensate separated in a decanter into, a benzene-rich phase (22 per cent ethanol, 74 per cent benzene, 4 per cent water) and a water-rich phase (35 per cent ethanol, 4 per cent benzene, 61 per cent water). The benzene-rich phase is recycled to the column as reflux. A benzene make-up stream is added to the reflux to make good any loss of benzene from the process. The water-rich phase is fed to the second column.

Column 2. This column recovers the benzene as the ternary azeotrope and recycles it as vapour to join the overhead vapour from the first column. The bottom product from the column is essentially free of benzene (29 per cent ethanol, 51 per cent water). This stream is fed to the third column.

Column 3. In this column the water is separated and sent to waste treatment. The overhead product consists of the azeotropic mixture of ethanol and water (89 per cent ethanol, 11 per cent water). The overheads are condensed and recycled to join the feed to the first column. The bottom product is essentially free of ethanol.

From the compositions given, calculate the stream flows for the production of absolute alcohol from 100 kmol/h raw alcohol feed, composition 89 per cent ethanol, balance water. Take the benzene losses to total 0.1 kmol/h. Draw a preliminary flow-sheet for the process.

All the compositions given are mol percentage.

4.4. A plant is required to produce 10,000 tonnes per year of anhydrous hydrogen chloride from chlorine and hydrogen. The hydrogen source is impure: 90 per cent hydrogen, balance nitrogen.

The chlorine is essentially pure chlorine, supplied in rail tankers.

The hydrogen and chlorine are reacted in a burner at 1.5 bar pressure.

$$H_2 + Cl_2 \rightarrow 2HCl$$

Hydrogen is supplied to the burner in 3 per cent excess over the stoichiometric amount. The conversion of chlorine is essentially 100 per cent. The gases leaving the burner are cooled in a heat exchanger.

The cooled gases pass to an absorption column where the hydrogen chloride gas is absorbed in dilute hydrochloric acid. The absorption column is designed to recover 99.5 per cent of the hydrogen chloride in the feed.

The unreacted hydrogen and inerts pass from the absorber to a vent scrubber where any hydrogen chloride present is neutralised by contact with a dilute, aqueous solution, of sodium hydroxide. The solution is recirculated around the scrubber. The concentration of sodium hydroxide is maintained at 5 per cent by taking a purge from the recycle loop and introducing a make up stream of 25 per cent concentration. The maximum concentration of hydrogen chloride discharged in the gases vented from the scrubber to atmosphere must not exceed 200 ppm (parts per million) by volume.

The strong acid from the absorption column (32 per cent HCl) is fed to a stripping column where the hydrogen chloride gas is recovered from the solution by distillation. The diluted acid from the base of this column (22 per cent HCl), is recycled to the absorption column.

The gases from the top of the stripping column pass through a partial condenser, where the bulk of the water vapour present is condensed and returned to the column as reflux. The gases leaving the column will be saturated with water vapour at 40 °C.

The hydrogen chloride gas leaving the condenser is dried by contact with concentrated sulphuric acid in a packed column. The acid is recirculated over the packing. The concentration of sulphuric acid is maintained at 70 per cent by taking a purge from the recycle loop and introducing a make up stream of strong acid (98 per cent H_2SO_4).

The anhydrous hydrogen chloride product is compressed to 5 bar and supplied as a feed to another process.

Using the information provided, calculate the flow-rates and compositions of the main process streams, and draw a flow-sheet for this process.

There is no need to calculate the reflux flow to the distillation column; that will be determined by the column design.

4.5. Ammonia is synthesised from hydrogen and nitrogen. The synthesis gas is usually produced from hydrocarbons. The most common raw materials are oil or natural gas; though coal, and even peat can be used.

When produced from natural gas the synthesis gas will be impure, containing up to 5 per cent inerts, mainly methane and argon. The reaction equilibrium and rate are favoured by high pressure. The conversion is low, about 15 per cent and so, after removal of the ammonia produced, the gas is recycled to the converter inlet.

A typical process would consist of: a converter (reactor) operating at 350 bar; a refrigerated system to condense out the ammonia product from the recycle loop; and compressors to compress the feed and recycle gas. A purge is taken from the recycle loop to keep the inert concentration in the recycle gas at an acceptable level.

Using the data given below, draw an information flow diagram of the process and calculate the process stream flow-rates and compositions for the production of 600 t/d ammonia. Use either the 'Nagiev' split fraction method, with any suitable spreadsheet; or manual calculations.

Data:

Composition of synthesis gas, mol fraction:

N_2	H_2	CH_4	A
24.5	73.5	1.7	0.3

Temperature and operating pressure of liquid ammonia–gas separator, 340 bar and −28 °C.

Inert gas concentration in recycle gas, not greater than 15 per cent mol per cent.

4.6. Methyl ethyl ketone (MEK) is manufactured by the dehydrogenation of 2-butanol. A simplified description of the processes listing the various units used is given below:

1. A reactor in which the butanol is dehydrated to produce MEK and hydrogen, according to the reaction:

$$CH_3CH_2CH_3CHOH \rightarrow CH_3CH_2CH_3CO + H_2$$

   The conversion of alcohol to MEK is 88 per cent and the yield can be taken as 100 per cent.
2. A cooler-condenser, in which the reactor off-gases are cooled and most of the MEK and unreacted alcohol are condensed. Two exchangers are used but they can be modelled as one unit. Of the MEK entering the unit 84 per cent is condensed, together with 92 per cent of the alcohol. The hydrogen is non-condensable. The condensate is fed forward to the final purification column.
3. An absorption column, in which the uncondensed MEK and alcohol are absorbed in water.

   Around 98 per cent of the MEK and alcohol can be considered to be absorbed in this unit, giving a 10 per cent w/w solution of MEK. The water feed to the absorber is recycled from the next unit, the extractor. The vent stream from the absorber, containing mainly hydrogen, is sent to a flare stack.
4. An extraction column, in which the MEK and alcohol in the solution from the absorber are extracted into trichloroethylane (TCE). The raffinate, water

containing around 0.5 per cent w/w MEK, is recycled to the absorption column. The extract, which contains around 20 per cent w/w MEK, and a small amount of butanol and water, is fed to a distillation column.

5. A distillation column, which separates the MEK and alcohol from the solvent TCE.
   The solvent containing a trace of MEK and water is recycled to the extraction column.
6. A second distillation column, which produces a pure MEK product from the crude product from the first column. The residue from this column, which contains the bulk of the unreacted 2-butanol, is recycled to the reactor.

For a production rate of 1250 kg/h MEK:

1. Draw up an information flow diagram for this process.
2. Estimate the split-faction coefficients and fresh feeds for each stage.
3. Set up the resulting material balance equations, in matrix form.
4. Solve the equations using a suitable spread-sheet.
5. Adjust the values chosen for the split-fractions and feeds, so the results meet the constraints,
6. Draw a flow-sheet for the process.

Postscript: The design problems given in Appendix F provide more problems in flow-sheeting.

CHAPTER 6

Costing and Project Evaluation

6.1. INTRODUCTION

Cost estimation is a specialised subject and a profession in its own right. The design engineer, however, needs to be able to make quick, rough, cost estimates to decide between alternative designs and for project evaluation. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed.

In this chapter the various components that make up the capital cost of a plant and the components of the operating costs are discussed, and the techniques used for estimating reviewed briefly. Simple costing methods and some cost data are given, which can be used to make preliminary estimates of capital and operating costs at the flow-sheet stage. They can also be used to cost out alternative processing schemes and equipment.

For a more detailed treatment of the subject the reader should refer to the numerous specialised texts that have been published on cost estimation. The following books are particularly recommended: Happle and Jordan (1975) and Guthrie (1974), Page (1984), Garrett (1989).

6.2. ACCURACY AND PURPOSE OF CAPITAL COST ESTIMATES

The accuracy of an estimate depends on the amount of design detail available: the accuracy of the cost data available; and the time spent on preparing the estimate. In the early stages of a project only an approximate estimate will be required, and justified, by the amount of information by then developed.

Capital cost estimates can be broadly classified into three types according to their accuracy and purpose:

1. Preliminary (approximate) estimates, accuracy typically ±30 per cent, which are used in initial feasibility studies and to make coarse choices between design alternatives. They are based on limited cost data and design detail.
2. Authorisation (Budgeting) estimates, accuracy typically ±10–15 per cent. These are used for the authorisation of funds to proceed with the design to the point where an accurate and more detailed estimate can be made. Authorisation may also include funds to cover cancellation charges on any long delivery equipment ordered at this stage of the design to avoid delay in the project. In a contracting organisation this type of estimate could be used with a large contingency factor to obtain a price for tendering. Normally, however, an accuracy of about ±5 per cent would be needed

and a more detailed estimate would be made, if time permitted. With experience, and where a company has cost data available from similar projects, estimates of acceptable accuracy can be made at the flow-sheet stage of the project. A rough P and I diagram and the approximate sizes of the major items of equipment would also be needed.

3. Detailed (Quotation) estimates, accuracy ±5–10 per cent, which are used for project cost control and estimates for fixed price contracts. These are based on the completed (or near complete) process design, firm quotations for equipment, and a detailed breakdown and estimation of the construction cost.

The cost of preparing an estimate increases from about 0.1 per cent of the total project cost for ±30 per cent accuracy, to about 2 per cent for a detailed estimate with an accuracy of ±5 per cent.

6.3. FIXED AND WORKING CAPITAL

Fixed capital is the total cost of the plant ready for start-up. It is the cost paid to the contractors.

It includes the cost of:

1. Design, and other engineering and construction supervision.
2. All items of equipment and their installation.
3. All piping, instrumentation and control systems.
4. Buildings and structures.
5. Auxiliary facilities, such as utilities, land and civil engineering work.

It is a once-only cost that is not recovered at the end of the project life, other than the scrap value.

Working capital is the additional investment needed, over and above the fixed capital, to start the plant up and operate it to the point when income is earned.

It includes the cost of:

1. Start-up.
2. Initial catalyst charges.
3. Raw materials and intermediates in the process.
4. Finished product inventories.
5. Funds to cover outstanding accounts from customers.

Most of the working capital is recovered at the end of the project. The total investment needed for a project is the sum of the fixed and working capital.

Working capital can vary from as low as 5 per cent of the fixed capital for a simple, single-product, process, with little or no finished product storage; to as high as 30 per cent for a process producing a diverse range of product grades for a sophisticated market, such as synthetic fibres. A typical figure for petrochemical plants is 15 per cent of the fixed capital.

Methods for estimating the working capital requirement are given by Bechtel (1960), Lyda (1972) and Scott (1978).

6.4. COST ESCALATION (INFLATION)

The cost of materials and labour has been subject to inflation since Elizabethan times. All cost-estimating methods use historical data, and are themselves forecasts of future costs. Some method has to be used to update old cost data for use in estimating at the design stage, and to forecast the future construction cost of the plant.

The method usually used to update historical cost data makes use of published cost indices. These relate present costs to past costs, and are based on data for labour, material and energy costs published in government statistical digests.

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \tag{6.1}$$

To get the best estimate, each job should be broken down into its components and separate indices used for labour and materials. It is often more convenient to use the composite indices published for various industries in the trade journals. These produce a weighted average index combining the various components in proportions considered typical for the particular industry. Such an index for the chemical industry in the United Kingdom is published in the journal *Process Engineering*, Anon. (2004). The composition of this index is:

$$C = 0.45\text{Eq} + 0.1\text{Ci} + 0.19\text{Cn} + 0.26\text{Di}$$

where C = the composite index
Ci = civil engineering index
Cn = site engineering index
Di = design index

The base year used for the index is revised about every 5 years. The base for the current index is January 2000 = 100; see Anon. (2002). Care must be taken when updating costs over a period that includes a change in the index base; see Example 6.1.

The Process Engineering index, over a ten-year period (January to January), is shown in Figure 6.1*a*.

Process Engineering also publishes monthly cost indices for several other countries, including the United States, Japan, Australia and many of the EU countries.

A composite index for the United States process plant industry is published monthly in the journal *Chemical Engineering*, the CPE plant cost index. This journal also publishes the Marshall and Swift index (M and S equipment cost index), base year 1926. The CPE index over a ten-year period is shown in Figure 6.1*b*.

All cost indices should be used with caution and judgement. They do not necessarily relate the true make-up of costs for any particular piece of equipment or plant; nor the effect of supply and demand on prices. The longer the period over which the correlation is made the more unreliable the estimate. Between 1970 and 1990 prices rose dramatically. Since then the annual rise has slowed down and is now averaging around 2 to 3 per cent per year.

To estimate the future cost of a plant some prediction has to be made of the future annual rate of inflation. This can be based on the extrapolation of one of the published indices, tempered by the engineer's own assessment of what the future may hold.

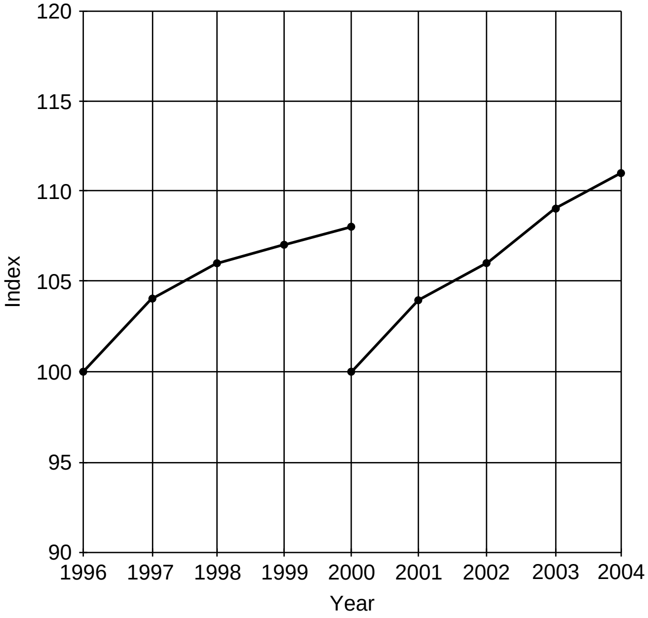


Figure 6.1a. Process Engineering index

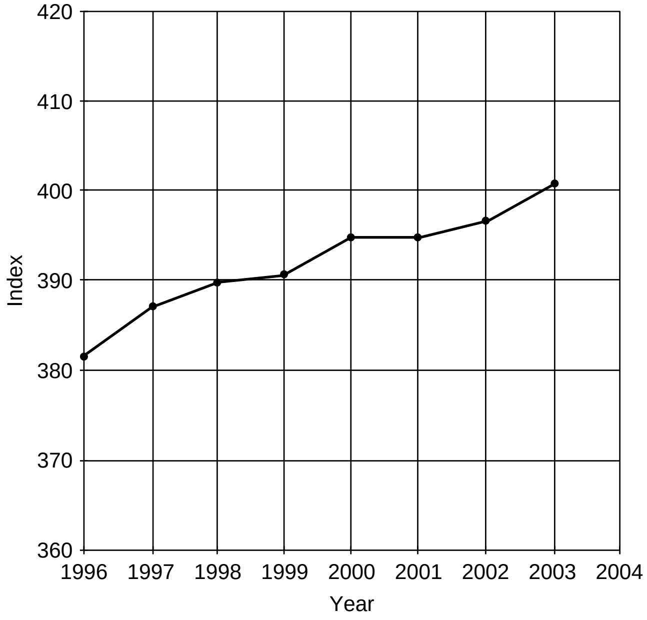


Figure 6.1b. CPE index

Example 6.1

The purchased cost of a shell and tube heat exchanger, carbon shell, stainless steel tubes, heat transfer area 500 m^2, was £7600 in January 1998; estimate the cost in January 2006. Use the *Process Engineering* plant index.

Solution

From Figure 6.1:

$$\begin{aligned}\text{Index in } 1998 &= 106\\ 2000 &= 108, 100 \text{ (change of base)}\\ 2004 &= 111\end{aligned}$$

So, estimated cost in January 2000 $= 7600 \times 108/106 = £7743$,

and in 2004 $= 7743 \times 111/100 = £8595$

From Figure 6.1, the average increase in costs is about 2.5 per cent per year. Use this value to predict the exchanger cost in 2006.

Cost in 2006 $= 8595 \times (1.025)^2 = £9030$

Say $\underline{\underline{£9000}}$.

6.5. RAPID CAPITAL COST ESTIMATING METHODS

6.5.1. Historical costs

An approximate estimate of the capital cost of a project can be obtained from a knowledge of the cost of earlier projects using the same manufacturing process. This method can be used prior to the preparation of the flow-sheets to get a quick estimate of the investment likely to be required.

The capital cost of a project is related to capacity by the equation

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \tag{6.2}$$

where C_2 = capital cost of the project with capacity S_2,
C_1 = capital cost of the project with capacity S_1.

The value of the index n is traditionally taken as 0.6; the well-known six-tenths rule. This value can be used to get a rough estimate of the capital cost if there are not sufficient data available to calculate the index for the particular process. Estrup (1972) gives a critical review of the six-tenths rule. Equation 6.2 is only an approximation, and if sufficient data are available the relationship is best represented on a log-log plot. Garrett (1989) has published capital cost-plant capacity curves for over 250 processes.

Example 6.2

Obtain a rough estimate of the cost of a plant to produce 750 tonnes per day of sulphuric acid, from sulphur. Use the costs given by Garrett (1989) reproduced in Figure 6.2.

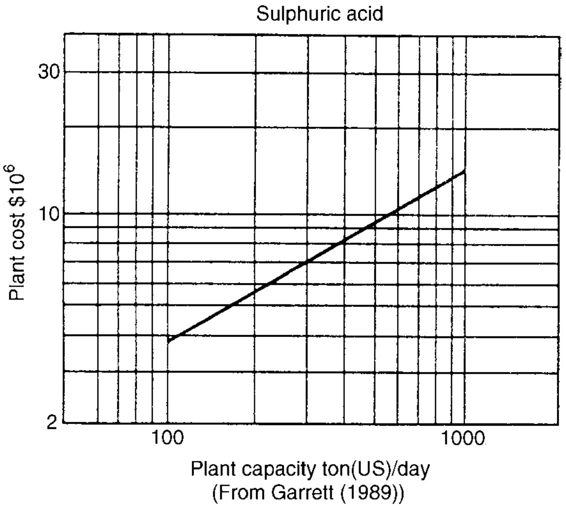


Figure 6.2. Capital Cost *v*. Capacity

Solution

Garret's units are US dollars and US tons, and refer to 1987 (*Chemical Engineering Index* quoted as 320).

$$1 \text{ US ton} = 2000 \text{ lb} = 0.91 \text{ tonne } (1000 \text{ kg})$$

$$\text{So, } 750 \text{ tonne per day} = 750/0.91 = 824 \text{ US t/d}$$

From Figure 6.2 the fixed capital cost for this capacity, for production from sulphur, is 13×10^6 US dollars.
There are two possible ways to convert to UK costs:

1. Convert at the 1987 exchange rate and update using a UK index.
2. Update using a US index and convert using the current exchange rate.

1. In 1987 (January) the rate of exchange was \$1.64 = £1, and UK and US cost can be taken as roughly equivalent.

$$1987 \text{ cost} = \frac{13 \times 10^6}{1.64} = £7.93 \times 10^6$$

Updating this cost using the index published in *Process Engineering* (basis 100 at end 1990)

$$\text{Index } 1987 \text{ (January)} = 78$$

$$2004 \text{ (January)} = 154 \text{ (basis adjusted to 1990)}$$

$$\text{So, capital cost of plant early } 2004 = 7.93 \times 10^6 \times \frac{154}{78} = £15.67 \times 10^6$$

$$\text{say, } \underline{\underline{£16{,}000{,}000}}$$

2. Garrett quotes the *Chemical Engineering Index* for his costs as 320 (January 1987).

The value in January 2004 was, approximately, 405, so the dollar cost of the plant in early 2004 will be:

$$13 \times 10^6 \times \frac{405}{320} = \$16.45 \times 10^6$$

The rate of exchange in January 2004 was $1.82, so the cost in pounds sterling will be

$$\frac{16.45 \times 10^6}{1.82} = £9.04 \times 10^6$$

$$\text{say, } \underline{\underline{\$9{,}000{,}000}}$$

Widely different from that estimated by method 1. This is not surprising as inflation in the UK has been very much greater than that in the US over this period.

Where UK, or other local, indexes and historical exchange rates are available, it is probably better to convert costs to the local currency using the rate of exchange ruling at the date of the costs and update using the local index: method 1 in the Example 6.2. In the United Kingdom historical values for exchange rates can be found in the government publication *Economic Trends* (Central Statistical Office, HMSO). Current and historical values for most currencies can be found on the Internet/World Wide Web.

As a rough guide US costs can be taken as equivalent to local prices, converted to local currency, for Western European countries, but construction costs may be significantly greater in less developed parts of the world.

Location factors can be used to make allowance for the variation in costs in different countries; see IChemE (1987).

6.5.2. Step counting methods

Step counting estimating methods provide a way of making a quick, *order of magnitude*, estimate of the capital cost of a proposed project.

The technique is based on the premise that the capital cost is determined by a number of significant processing steps in the overall process. Factors are usually included to allow for the capacity, and complexity of the process: material of construction, yield, operating pressure and temperature.

A number of workers have published correlations based on a step counting approach: Taylor (1977), Wilson (1971). These and other correlations are reviewed and compared in the Institution of Chemical Engineers booklet, IChemE (1988).

Bridgwater, IChemE (1988), gives a developed relatively simple correlation for plants that are predominantly liquid and/or solid phase handing processes.

His equation, adjusted to 2004 prices is:

for plant capacities under 60,000 tonne per year:

$$C = 150{,}000\ N\ (Q/s)^{0.30} \tag{6.3}$$

and above 60,000 t/y:

$$C = 170\ N\ (Q/s)^{0.675} \tag{6.4}$$

where C = capital cost in pounds sterling
N = Number of functional units

Q = plant capacity, tonne per year
s = reactor conversion

Reactor conversion is defined as:

$$s = \frac{\text{mass of desired product}}{\text{mass reactor input}}$$

Timms, IChemE (1988) gives a simple equation for gas phase processes; updated to 1998:

$$C = 9000\ N\ Q^{0.615} \tag{6.5}$$

where the symbols are the same as for equations 6.3 and 6.4.

In US dollars

$$C' = 14{,}000\ N\ Q^{0.615} \tag{6.5a}$$

Where C' = captial cost in US dollars

Example 6.3

Estimate the capital cost for the nitric acid plant shown in Figure 4.2, Chapter 4.

Solution

Number of significant processing steps 6.

Capacity 100,000 tonne per year

$$C = 9000 \times 6 \times 100{,}000^{0.615} = 64.2 \times 10^6 \tag{6.5}$$

say, $\underline{\underline{\text{£65 million.}}}$

$$C' = 14{,}000 \times 6 \times 100{,}000^{0.615} = 99.8 \times 10^6$$

say, $\underline{\underline{\text{\$100 million.}}}$

Clearly, step counting methods can only, at best, give a very approximate idea of the probable cost of a plant. They are useful in the conceptual stage of process design, when comparisons between alternative process routes are being made.

6.6. THE FACTORIAL METHOD OF COST ESTIMATION

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost. The accuracy of this type of estimate will depend on what stage the design has reached at the time the estimate is made, and on the reliability of the data available on equipment costs. In the later stages of the project design, when detailed equipment specifications are available and firm quotations have been obtained, an accurate estimation of the capital cost of the project can be made.

6.6.1. Lang factors

The factorial method of cost estimation is often attributed to Lang (1948). The fixed capital cost of the project is given as a function of the total purchase equipment cost by the equation:

$$Cf = f_L Ce \tag{6.6}$$

where Cf = fixed capital cost,
Ce = the total delivered cost of all the major equipment items: storage tanks, reaction vessels, columns, heat exchangers, etc.,
f_L = the "Lang factor", which depends on the type of process.

f_L = 3.1 for predominantly solids processing plant
f_L = 4.7 for predominantly fluids processing plant
f_L = 3.6 for a mixed fluids-solids processing plant

The values given above should be used as a guide; the factor is best derived from an organisation's own cost files.

Equation 6.6 can be used to make a quick estimate of capital cost in the early stages of project design, when the preliminary flow-sheets have been drawn up and the main items of equipment roughly sized.

6.6.2. Detailed factorial estimates

To make a more accurate estimate, the cost factors that are compounded into the "Lang factor" are considered individually. The direct-cost items that are incurred in the construction of a plant, in addition to the cost of equipment are:

1. Equipment erection, including foundations and minor structural work.
2. Piping, including insulation and painting.
3. Electrical, power and lighting.
4. Instruments, local and control room.
5. Process buildings and structures.
6. Ancillary buildings, offices, laboratory buildings, workshops.
7. Storages, raw materials and finished product.
8. Utilities (Services), provision of plant for steam, water, air, firefighting services (if not costed separately).
9. Site, and site preparation.

The contribution of each of these items to the total capital cost is calculated by multiplying the total purchased equipment by an appropriate factor. As with the basic "Lang factor", these factors are best derived from historical cost data for similar processes. Typical values for the factors are given in several references, Happle and Jordan (1975) and Garrett (1989). Guthrie (1974), splits the costs into the material and labour portions and gives separate factors for each. In a booklet published by the Institution of Chemical Engineers, IChemE (1988), the factors are shown as a function of plant size and complexity.

The accuracy and reliability of an estimate can be improved by dividing the process into sub-units and using factors that depend on the function of the sub-units; see Guthrie (1969). In Guthrie's detailed method of cost estimation the installation, piping and instrumentation costs for each piece of equipment are costed separately. Detailed costing is only justified if the cost data available are reliable and the design has been taken to the point where all the cost items can be identified and included.

Typical factors for the components of the capital cost are given in Table 6.1. These can be used to make an approximate estimate of capital cost using equipment cost data published in the literature.

In addition to the direct cost of the purchase and installation of equipment, the capital cost of a project will include the indirect costs listed below. These can be estimated as a function of the direct costs.

Indirect costs

1. Design and engineering costs, which cover the cost of design and the cost of “engineering” the plant: purchasing, procurement and construction supervision. Typically 20 per cent to 30 per cent of the direct capital costs.
2. Contractor’s fees, if a contractor is employed his fees (profit) would be added to the total capital cost and would range from 5 per cent to 10 per cent of the direct costs.
3. Contingency allowance, this is an allowance built into the capital cost estimate to cover for *unforeseen* circumstances (labour disputes, design errors, adverse weather). Typically 5 per cent to 10 per cent of the direct costs.

The indirect cost factors are included in Table 6.1.

The capital cost required for the provision of utilities and other plant services will depend on whether a new (green field) site is being developed, or if the plant is to be built on an existing site and will make use of some of the existing facilities. The term

Table 6.1. Typical factors for estimation of project fixed capital cost

Item	Process type		
	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
*f_6 Utilities	0.50	0.45	0.25
*f_7 Storages	0.15	0.20	0.25
*f_8 Site development	0.05	0.05	0.05
*f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC)			
PPC = PCE $(1 + f_1 + \cdots + f_9)$			
= PCE ×	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor’s fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$			
= PPC ×	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

"battery limits" is used to define a contractor's responsibility. The main processing plant, within the battery limits, would normally be built by one contractor. The utilities and other ancillary equipment would often be the responsibility of other contractors and would be said to be outside the battery limits. They are often also referred to as "off-sites".

6.7. ESTIMATION OF PURCHASED EQUIPMENT COSTS

The cost of the purchased equipment is used as the basis of the factorial method of cost estimation and must be determined as accurately as possible. It should preferably be based on recent prices paid for similar equipment.

The relationship between size and cost given in equation 6.2 can also be used for equipment, but the relationship is best represented by a log-log plot if the size range is wide. A wealth of data has been published on equipment costs; see Guthrie (1969, 1974), Hall *et al*. (1982), Page (1984), Ulrich (1984), Garrett (1989) and Peters *et al*. (2003). Articles giving the cost of process equipment are frequently published in the journals *Chemical Engineering* and *Hydrocarbon Processing*. Equipment prices can also be found on various web sites, such as: MatchesMSN@msn.com.

The cost of specialised equipment, which cannot be found in the literature, can usually be estimated from the cost of the components that make up the equipment. For example, a reactor design is usually unique for a particular process but the design can be broken down into standard components (vessels, heat-exchange surfaces, spargers, agitators) the cost of which can be found in the literature and used to build up an estimate of the reactor cost.

Pikulik and Diaz (1977) give a method of costing major equipment items from cost data on the basic components: shells, heads, nozzles, and internal fittings. Purohit (1983) gives a detailed procedure for estimating the cost of heat exchangers.

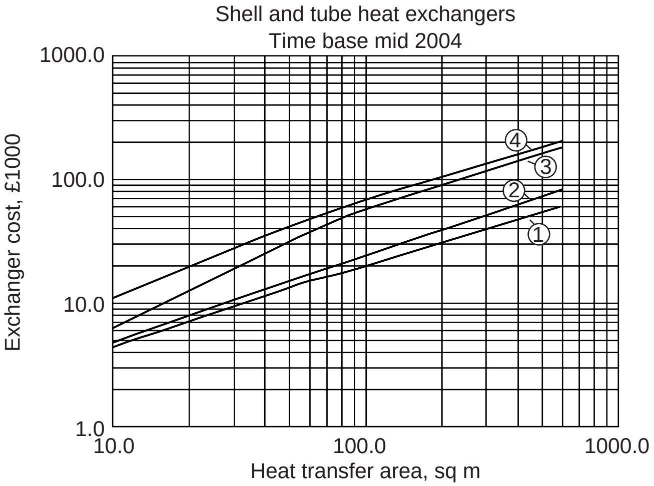
Almost all the information on costs available in the open literature is in American journals and refers to dollar prices in the US. Some UK equipment prices were published in the journals *British Chemical Engineering* and *Chemical and Process Engineering* before they ceased publication. The only comprehensive collection of UK prices available is given in the Institution of Chemical Engineers booklet, IChemE (2000).

Up to 1970 US and UK prices for equipment could be taken as roughly equivalent, converting from dollars to pounds using the rate of exchange ruling on the date the prices were quoted. Since 1970 the rate of inflation in the US has been significantly lower than in the UK, and rates of exchange have fluctuated since the pound was floated in 1972.

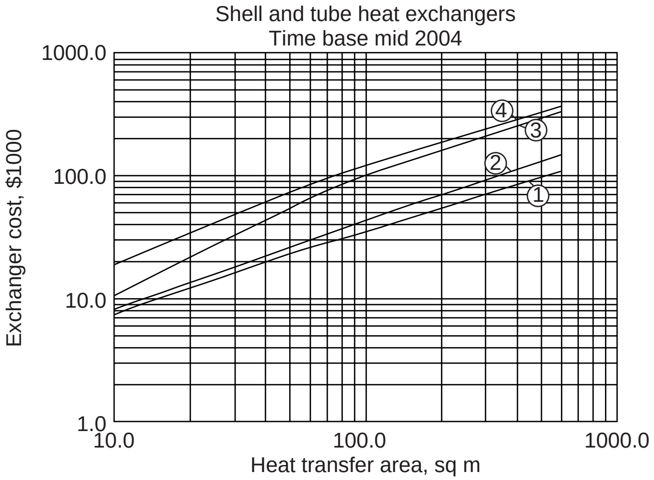
If it can be assumed that world market forces will level out the prices of equipment, the UK price can be estimated from the US price by bringing the cost up to date using a suitable US price index, converting to pounds sterling at the current rate of exchange, and adding an allowance for freight and duty.

If an estimate is being made to compare two processes, the costing can be done in dollars and any conclusion drawn from the comparison should still be valid for the United Kingdom and other countries.

The cost data given in Figures 6.3 to 6.7, and Table 6.2 have been compiled from various sources. They can be used to make preliminary estimates. The base date is mid-2004, and the prices are thought to be accurate to within ±25 per cent.



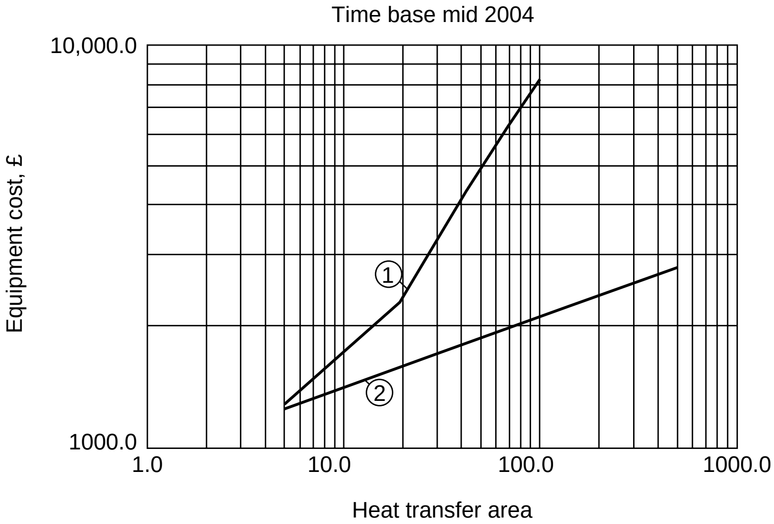
(*a*) Pounds sterling



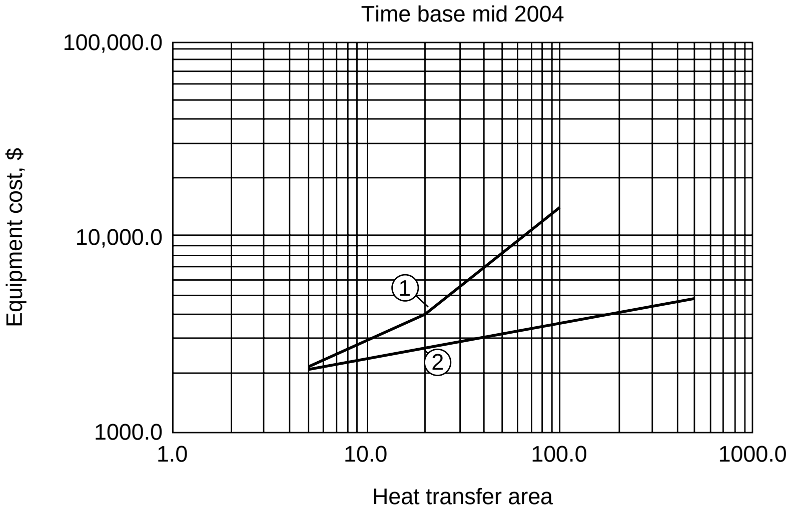
(*b*) US dollars

Materials			Pressure factors		Type factors	
	Shell	Tubes				
			1–10 bar	× 1.0	Floating head	× 1.0
①	Carbon steel	Carbon steel	10–20	× 1.1	Fixed tube sheet	× 0.8
②	C.S.	Brass	20–30	× 1.25	U tube	× 0.85
③	C.S.	Stainless steel	30–50	× 1.3	Kettle	× 1.3
④	S.S.	S.S.	50–70	× 1.5		

Figure 6.3*a*, *b*. Shell and tube heat exchangers. Time base mid-2004
Purchased cost = (bare cost from figure) × Type factor × Pressure factor



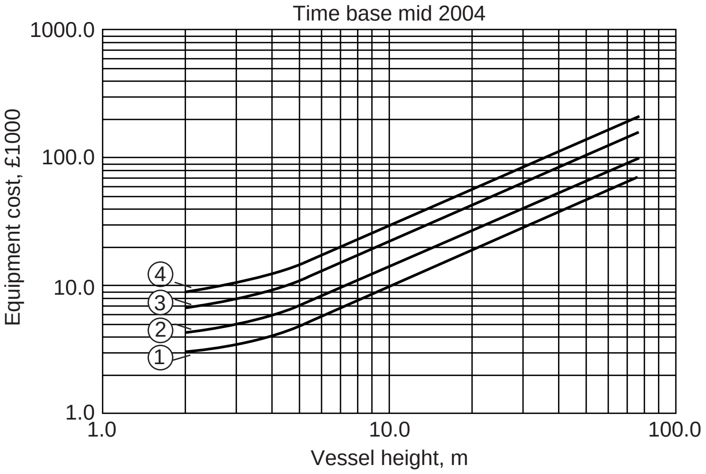
(*a*) Pounds sterling



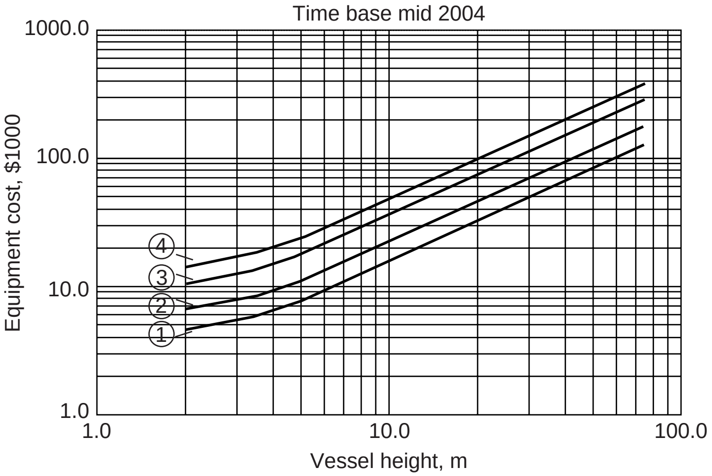
(*b*) US dollars

Type	Area scale	Material
(1) Gasketed plate	m^2	Stainless steel
(2) Double pipe	$m^2 \times 10$	Carbon steel

Figure 6.4*a*, *b*. Gasketed plate and frame and double pipe heat exchangers, Time base mid-2004



(*a*) Pounds sterling



(*b*) US dollars

Diameter, m

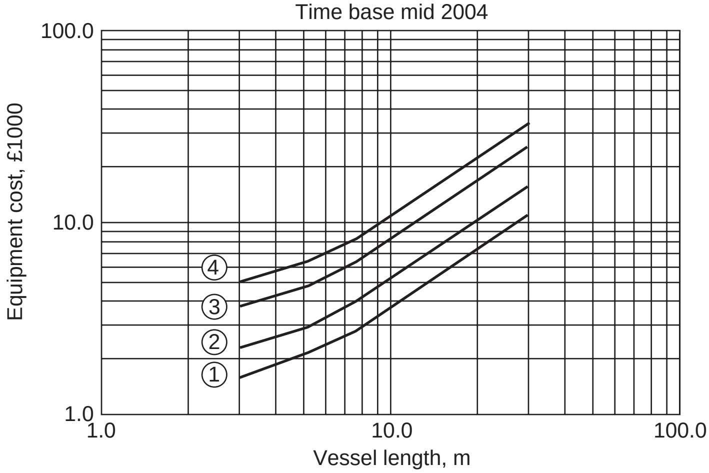
① — 0.5 ③ — 2.0
② — 1.0 ④ — 3.0

Material factors	
C.S.	× 1.0
S.S.	× 2.0
Monel	× 3.4
S.S. clad	× 1.5
Monel clad	× 2.1

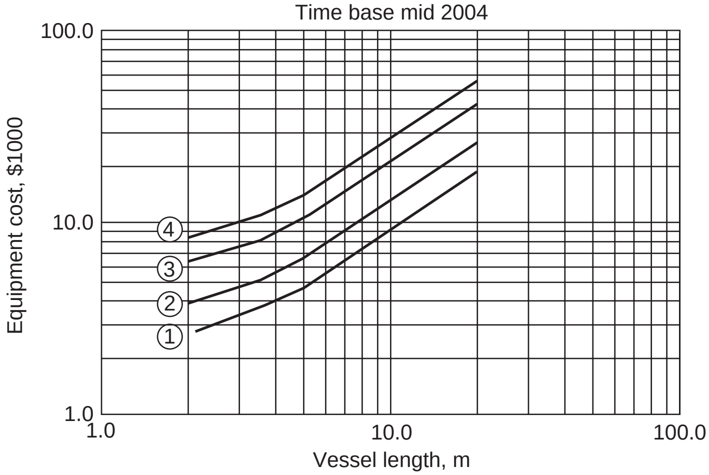
Pressure factors	
1–5 bar	× 1.0
5–10	× 1.1
10–20	× 1.2
20–30	× 1.4
30–40	× 1.6
40–50	× 1.8
50–60	× 2.2

Temperature up to 300°C

Figure 6.5*a*, *b*. Vertical pressure vessels. Time base mid-2004.
Purchased cost = (bare cost from figure) × Material factor × Pressure factor



(*a*) Pounds sterling



(*b*) US dollars

Diameter, m

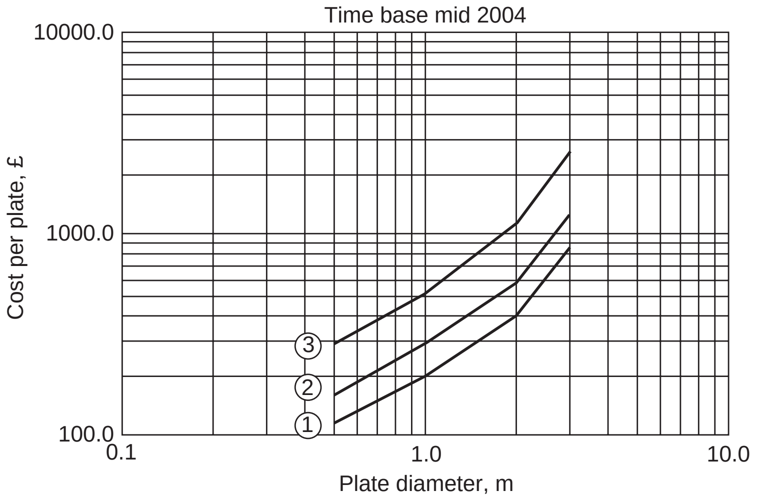
①—0.5 ③—2.0
②—1.0 ④—3.0

Material factors	
C.S.	× 1.0
S.S.	× 2.0
Monel	× 3.4
S.S. clad	× 1.5
Monel clad	× 2.1

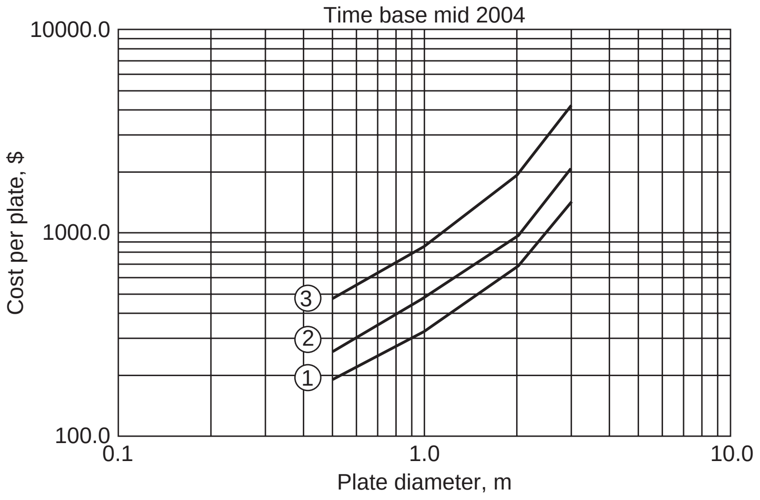
Pressure factors	
1–5 bar	× 1.0
5–10	× 1.1
10–20	× 1.2
20–30	× 1.4
30–40	× 1.6
40–50	× 1.8
50–60	× 2.2

Temperature up to 300°C

Figure 6.6*a*, *b*. Horizontal pressure vessels. Time base mid-2004.
Purchase cost = (bare cost from figure) × Material factor × Pressure factor



(*a*) Pound sterling



(*b*) US dollars

Type	Material factors
① Sieve	C.S. × 1.0
② Valve	S.S. × 1.7
③ Bubble cap	

Figure 6.7*a*, *b*. Column plates. Time base mid-2004 (for column costs see Figure 6.4)
Installed cost = (cost from figure) × Material factor

Table 6.2. Purchase cost of miscellaneous equipment, cost factors for use in equation 6.7. Cost basis mid 2004

Equipment	Size unit, S	Size range	Constant C,£	C,$	Index n	Comment
Agitators						
Propeller	driver	5–75	1200	1900	0.5	
Turbine	power, kW		1800	3000	0.5	
Boilers						
Packaged						oil or gas fired
up to 10 bar	kg/h steam	$(5-50) \times 10^3$	70	120	0.8	
10 to 60 bar			60	100	0.8	
Centrifuges						
Horizontal basket	dia., m	0.5–1.0	35,000	58,000	1.3	carbon steel
Vertical basket			35,000	58,000	1.0	×1.7 for ss
Compressors						
Centrifugal	driver power, kW	20–500	1160	1920	0.8	electric, max. press.
Reciprocating			1600	2700	0.8	50 bar
Conveyors						
Belt	length, m	2–40				
0.5 m wide			1200	1900	0.75	
1.0 m wide			1800	2900	0.75	
Crushers						
Cone	t/h	20–200	2300	3800	0.85	
Pulverisers	kg/h		2000	3400	0.35	
Dryers						
Rotary	area, m^2	5–30	21,000	35,000	0.45	direct
Pan		2–10	4700	7700	0.35	gas fired
Evaporators						
Vertical tube	area, m^2	10–100	12,000	20,000	0.53	carbon steel
Falling film			6500	10,000	0.52	
Filters						
Plate and frame	area, m^2	5–50	5400	8800	0.6	cast iron
Vacuum drum		1–10	21,000	34,000	0.6	carbon steel
Furnaces						
Process						
Cylindrical	heat abs, kW	10^3–10^4	330	540	0.77	carbon steel
Box		10^3–10^5	340	560	0.77	×2.0 ss
Reactors						
Jacketed,	capacity, m^3	3–30	9300	15,000	0.40	carbon steel
agitated			18,500	31,000	0.45	glass lined
Tanks						
Process	capacity, m^3					
vertical		1–50	1450	2400	0.6	atmos. press.
horizontal		10–100	1750	2900	0.6	carbon steel
Storage						
floating roof		50–8000	2500	4350	0.55	×2 for
cone roof		50–8000	1400	2300	0.55	stainless

Table 6.3. Cost of column packing. Cost basis mid 2004

	Cost	£/m^3 (\$/m^3)	
Size, mm	25	38	50
Saddles, stoneware	840 (1400)	620 (1020)	580 (960)
Pall rings, polypropylene	650 (1080)	400 (650)	250 (400)
Pall rings, stainless steel	1500 (2500)	1500 (2500)	830 (1360)

To use Table 6.2, substitute the values given for the particular type of equipment into the equation:

$$Ce = CS^n \tag{6.7}$$

where Ce = purchased equipment cost, £,
S = characteristic size parameter, in the units given in Table 6.2,
C = cost constant from Table 6.2,
n = index for that type of equipment.

6.8. SUMMARY OF THE FACTORIAL METHOD

Many variations on the factorial method are used. The method outlined below can be used with the data given in this chapter to make a quick, approximate, estimate of the investment need for a project.

Procedure

1. Prepare material and energy balances, draw up preliminary flow-sheets, size major equipment items and select materials of construction.
2. Estimate the purchase cost of the major equipment items. Use Figures 6.3 to 6.6 and Tables 6.2 and 6.3, or the general literature.
3. Calculate the total physical plant cost (PPC), using the factors given in Table 6.1

$$\text{PPC} = \text{PCE}(1 + f_1 + \cdots + f_9) \tag{6.8}$$

4. Calculate the indirect costs from the direct costs using the factors given in Table 6.1.
5. The direct plus indirect costs give the total fixed capital.
6. Estimate the working capital as a percentage of the fixed capital; 10 to 20 per cent.
7. Add the fixed and working capital to get the total investment required.

6.9. OPERATING COSTS

An estimate of the operating costs, the cost of producing the product, is needed to judge the viability of a project, and to make choices between possible alternative processing schemes. These costs can be estimated from the flow-sheet, which gives the raw material and service requirements, and the capital cost estimate.

The cost of producing a chemical product will include the items listed below. They are divided into two groups.

1. Fixed operating costs: costs that do not vary with production rate. These are the bills that have to be paid whatever the quantity produced.
2. Variable operating costs: costs that are dependent on the amount of product produced.

Fixed costs

1. Maintenance (labour and materials).
2. Operating labour.
3. Laboratory costs.
4. Supervision.
5. Plant overheads.

6. Capital charges.
7. Rates (and any other local taxes).
8. Insurance.
9. Licence fees and royalty payments.

Variable costs

1. Raw materials.
2. Miscellaneous operating materials.
3. Utilities (Services).
4. Shipping and packaging.

The division into fixed and variable costs is somewhat arbitrary. Certain items can be classified without question, but the classification of other items will depend on the accounting practice of the particular organisation.

The items may also be classified differently in cost sheets and cost standards prepared to monitor the performance of the operating plant. For this purpose the fixed-cost items should be those over which the plant supervision has no control, and the variable items those for which they can be held accountable.

The costs listed above are the direct costs of producing the product at the plant site. In addition to these costs the site will have to carry its share of the Company's general operating expenses. These will include:

1. General overheads.
2. Research and development costs.
3. Sales expense.
4. Reserves.

How these costs are apportioned will depend on the Company's accounting methods. They would add about 20 to 30 per cent to direct production costs at the site.

6.9.1. Estimation of operating costs

In this section the components of the fixed and variable costs are discussed and methods given for their estimation.

It is usually convenient to do the costing on an annual basis.

Raw materials

These are the major (essential) materials required to manufacture the product. The quantities can be obtained from the flow-sheet and multiplied by the operating hours per year to get the annual requirements.

The price of each material is best obtained by getting quotations from potential suppliers, but in the preliminary stages of a project prices can be taken from the literature.

The American journal *Chemical Marketing Reporter*, CMR (2004), publishes a weekly review of prices for most chemicals. The prices for a limited number of chemicals in Europe can be found in *European Chemical News*, ECN (2004). U.S. prices, converted to the local currency at the current rate of exchange, can be used as a guide to the probable price in other countries. An indication of the prices of a selected range of chemicals is given in Table 6.4 (see p. 263).

Miscellaneous materials (plant supplies)

Under this heading are included all the miscellaneous materials required to operate the plant that are not covered under the headings raw materials or maintenance materials.

Miscellaneous materials will include:

1. Safety clothing: hard hats, safety glasses etc.
2. Instrument charts and accessories
3. Pipe gaskets
4. Cleaning materials

An accurate estimate can be made by detailing and costing all the items needed, based on experience with similar plants. As a rough guide the cost of miscellaneous materials can be taken as 10 per cent of the total maintenance cost.

Utilities (services)

This term includes, power, steam, compressed air, cooling and process water, and effluent treatment; unless costed separately. The quantities required can be obtained from the energy balances and the flow-sheets. The prices should be taken from Company records, if available. They will depend on the primary energy sources and the plant location. The figures given in Table 6.5 can be used to make preliminary estimates. The current cost of utilities supplied by the utility companies: electricity, gas and water, can be obtained from their local area offices.

Shipping and packaging

This cost will depend on the nature of the product. For liquids collected at the site in the customer's own tankers the cost to the product would be small; whereas the cost of packaging and transporting synthetic fibres or polymers to a central distribution warehouse would add significantly to the product cost.

Maintenance

This item will include the cost of maintenance labour, which can be as high as the operating labour cost, and the materials (including equipment spares) needed for the maintenance of the plant. The annual maintenance costs for chemical plants are high, typically 5 to 15 per cent of the installed capital costs. They should be estimated from a knowledge of the maintenance costs on similar plant. As a first estimate the annual maintenance cost can be taken as 10 per cent of the fixed capital cost; the cost can be considered to be divided evenly between labour and materials.

Operating labour

This is the manpower needed to operate the plant: that directly involved with running the process.

The costs should be calculated from an estimate of the number of shift and day personnel needed, based on experience with similar processes. It should be remembered that to operate three shifts per day, at least five shift crews will be needed. The figures used for

Table 6.4. Raw material and product costs

Typical prices for bulk purchases, mid-1998. All deliveries by rail or road tanker, and all materials technical/industrial grade; unless otherwise stated

Chemical, and state	Cost unit	Cost £/unit	Cost $/unit
Acetaldehyde, 99%	kg	0.53	0.48
Acetic acid	kg	0.60	1.10
Acetic anhydride	kg	0.70	1.15
Acetone	kg	0.63	1.03
Acrylonitrile	kg	1.20	1.90
Ally alcohol	kg	1.40	2.30
Ammonia, anhydrous	t	180	280
Ammonium nitrate, bulk	t	100	170
Ammonium sulphate, bulk	t	90	150
Amyl alcohol, mixed isomers	kg	0.67	1.20
Aniline	kg	0.52	0.84
Benzaldehyde, drums	kg	1.95	3.21
Benzene	kg	0.20	0.33
Benzoic acid, drums	kg	2.20	3.60
Butene-1	kg	0.30	0.40
n-Butyl alcohol	kg	0.75	1.30
n-Butyl ether, drums	kg	1.95	3.20
Calcium carbide, bulk	t	320	530
Calcium carbonate, bulk, coarse	t	105	145
Calcium chloride, bulk	t	200	275
Calcium hydroxide (lime), bulk	t	55	90
Carbon disulphide	t	370	500
Carbon tetrachloride, drums	kg	0.50	0.83
Chlorine	t	140	200
Chloroform	kg	0.45	0.70
Cupric chloride, anhydrous	kg	3.30	5.5
Dichlorobenzene	kg	0.95	1.54
Diethanolamine	kg	1.20	1.70
Ethanol, 90%	kg	4.20	6.50
Ethyl ether	kg	0.80	1.35
Ethylene, contract	kg	0.46	0.70
Ethylene glycol	kg	0.56	0.83
Ethylene oxide	kg	0.60	0.90
Formaldehyde, 37% w/w	kg	0.31	0.46
Formic acid, 94% w/w, drums	kg	0.63	1.05
Glycerine, 99.7%	kg	1.30	1.70
Heptane	kg	0.30	0.40
Hexane	kg	0.20	0.33
Hydrochloric acid, anhyd.	kg	1.00	1.70
Hydrochloric acid, 30% w/w	t	60	90
Hydrogen fluoride, anhydrous	kg	0.90	1.40
Hydrogen peroxide, 50% w/w	kg	0.50	0.80
Isobutanol, alcohol	kg	0.75	1.1
Isopropanol alcohol	kg	0.73	1.12
Maleic anhydride, drums	kg	1.80	2.90
Methanol	kg	0.63	1.00
Methyl ethyl ketone	kg	0.64	1.06
Monoethanolamine	kg	1.02	1.54
Methylstyrene	kg	0.70	1.15
Nitric acid, 50% w/w	t	130	220
98% w/w	t	220	370
Nitrobenzene	kg	0.47	0.78

(*continued overleaf*)

Table 6.4. (*continued*)

Chemical, and state	Cost unit	Cost £/unit	Cost $/unit
Oxalic acid, sacks	kg	0.58	0.96
Phenol	kg	0.90	1.53
Phosgene, cyl.	kg	1.09	1.62
Phosphoric acid 75% w/w	kg	0.47	0.78
Potassium bicarbonate, sacks	kg	0.45	0.75
Potassium carbonate, sacks	kg	0.56	0.92
Potassium chloride	t	70	110
Potassium chromate, sacks	kg	0.80	1.30
Potassium hydroxide	kg	2.00	3.70
Potassium nitrate, bulk	t	350	570
Propylene	kg	0.43	0.64
Propylene oxide	kg	1.00	1.60
n-Propanol	kg	0.93	1.438
Sodium carbonate, sacks	kg	0.35	0.58
Sodium chloride, drums	kg	0.40	0.65
Sodium hydroxide, drums	kg	1.60	2.60
Sodium sulphate, bulk	t	72	120
Sodium thiosulphate	kg	0.38	0.57
Sulphur, crude, 99.5%, sacks	t	85	140
Sulphuric acid, 98% w/w	t	40	65
Titanium dioxide, sacks	kg	1.50	2.50
Toluene	kg	0.32	0.47
Toluene diisocyanate	kg	2.20	3.20
Trichloroethane	kg	0.56	0.94
Trichloroethylene	kg	0.84	1.40
Urea, 46% nitrogen, bulk	t	120	160
Vinyl acetate	kg	0.65	1.08
Vinyl chloride	kg	0.44	0.66
Xylenes	kg	0.29	0.43

Anhyd. = anhydrous, cyl. = cylinder, refin. = refined

Caution: Use these prices only as a rough guide to the probable price range. Actual prices at a given time will vary considerably from these values, depending on location, contract quantities, and the prevailing market forces.

Table 6.5. Cost of utilities, typical figures mid-2004

Utility	UK	USA
Mains water (process water)	60 p/t	50 c/t
Natural gas	0.4 p/MJ	0.7 c/MJ
Electricity	1.0 p/MJ	1.5 c/MJ
Fuel oil	65 £/t	100 $/t
Cooling water (cooling towers)	1.5 p/t	1 c/t
Chilled water	5 p/t	8 c/t
Demineralised water	90 p/t	90 c/t
Steam (from direct fired boilers)	7 £/t	12 $/t
Compressed air (9 bar)	0.4 p/m^3 (Stp)	0.6 c/m^3
Instrument air (9 bar) (dry)	0.6 p/m^3 (Stp)	1 c/m^3
Refrigeration	1.0 p/MJ	1.5 c/MJ
Nitrogen	6 p/m^3 (Stp)	8 c/m^3

Note: £1 = 100p, 1$ = 100c, 1 t = 1000 kg = 2200 ib, stp = 1 atm, 0°C

These prices should be used only as a rough guide to the likely cost of utilities. The cost of water will be very dependent on the plant location, and the price of all utilities will be determined by the current cost of energy.

the cost of each man should include an allowance for holidays, shift allowances, national insurance, pension contributions and any other overheads. The current wage rates per hour in the UK chemical industry (mid-2004) are £15–20, to which must be added up to 50 per cent for the various allowances and overheads mentioned above.

Chemical plants do not normally employ many people and the cost of operating labour would not normally exceed 15 per cent of the total operating cost. The direct overhead charges would add 20 to 30 per cent to this figure.

Wessel (1952) gives a method of estimating the number of man-hours required based on the plant capacity and the number of discrete operating steps.

Supervision

This heading covers the direct operating supervision: the management directly associated with running the plant. The number required will depend on the size of the plant and the nature of the process. The site would normally be broken down into a number of manageable units. A typical management team for a unit would consist of four to five shift foremen, a general foreman, and an area supervisor (manager) and his assistant. The cost of supervision should be calculated from an estimate of the total number required and the current salary levels, including the direct overhead costs. On average, one “supervisor” would be needed for each four to five operators. Typical salaries, mid-2004, are £20,000 to £45,000, depending on seniority. An idea of current salaries can be obtained from the salary reviews published periodically by the Institution of Chemical Engineers.

Laboratory costs

The annual cost of the laboratory analyses required for process monitoring and quality control is a significant item in most modern chemical plants. The costs should be calculated from an estimate of the number of analyses required and the standard charge for each analysis, based on experience with similar processes.

As a rough estimate the cost can be taken as 20 to 30 per cent of the operating labour cost, or 2 to 4 per cent of the total production cost.

Plant overheads

Included under this heading are all the general costs associated with operating the plant not included under the other headings; such as, general management, plant security, medical, canteen, general clerical staff and safety. It would also normally include the plant technical personnel not directly associated with and charged to a particular operating area. This group may be included in the cost of supervision, depending on the organisation’s practice.

The plant overhead cost is usually estimated from the total labour costs: operating, maintenance and supervision. A typical range would be 50 to 100 per cent of the labour costs; depending on the size of the plant and whether the plant was on a new site, or an extension of an existing site.

Capital charges

The investment required for the project is recovered as a charge on the project. How this charge is shown on an organisation’s books will depend on its accounting practices.

Capital is often recovered as a depreciation charge, which sets aside a given sum each year to repay the cost of the plant. If the plant is considered to “depreciate” at a fixed rate over its predicted operating life, the annual sum to be included in the operating cost can be easily calculated. The operating life of a chemical plant is usually taken as 10 years, which gives a depreciation rate of 10 per cent per annum. The plant is not necessarily replaced at the end of the depreciation period. The depreciation sum is really an internal transfer to the organisation’s fund for future investment. If the money for the investment is borrowed, the sum set aside would be used to repay the loan. Interest would also be payable on the loan at the current market rates. Normally the capital to finance a particular project is not taken as a direct loan from the market but comes from the company’s own reserves. Any interest charged would, like depreciation, be an internal (book) transfer of cash to reflect the cost of the capital used.

Rather than consider the cost of capital as depreciation or interest, or any other of the accounting terms used, which will depend on the accounting practice of the particular organisation and the current tax laws, it is easier to take the cost as a straight, unspecified, capital charge on the operating cost. This would be typically around 10 per cent of the fixed capital, annually, depending on the cost of money. As an approximate estimate the “capital charge” can be taken as 2 per cent above the current minimum lending rate. For a full discussion on the nature of depreciation and the cost of capital see Happle and Jordan (1975), Holland *et al*. (1983), Valle-Riestra (1983).

Local taxes

This term covers local taxes, which are calculated on the value of the site. A typical figure would be 1 to 2 per cent of the fixed capital.

Insurance

The cost of the site and plant insurance: the annual insurance premium paid to the insurers; usually about 1 to 2 per cent of the fixed capital.

Royalties and licence fees

If the process used has not been developed exclusively by the operating company, royalties and licence fees may be payable. These may be paid as a lump sum, included in the fixed capital, or as an annual fee; or payments based on the amount of product sold.

The cost would add about 1 per cent to 5 per cent to the sales price.

Summary of production costs

The various components of the operating costs are summarised in Table 6.6. The typical values given in this table can be used to make an approximate estimate of production costs.

Table 6.6. Summary of production costs

Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	....
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	....
Direct production costs A + B	....
13. Sales expense	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	....
Annual production cost = A + B + C =	....

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Example 6.4

Preliminary design work has been done on a process to recover a valuable product from an effluent gas stream. The gas will be scrubbed with a solvent in a packed column; the recovered product and solvent separated by distillation; and the solvent cooled and recycled. The major items of equipment that will be required are detailed below.

1. Absorption column: diameter 1 m, vessel overall height 15 m, packed height 12 m, packing 25 mm ceramic intalox saddles, vessel carbon steel, operating pressure 5 bar.
2. Recovery column: diameter 1 m, vessel overall height 20 m, 35 sieve plates, vessel and plates stainless steel, operating pressure 1 bar.
3. Reboiler: forced convection type, fixed tube sheets, area 18.6 m^2, carbon steel shell, stainless-steel tubes, operating pressure 1 bar.
4. Condenser: fixed tube sheets, area 25.3 m^2, carbon steel shell and tubes, operating pressure 1 bar.
5. Recycle solvent cooler: U-tubes, area 10.1 m^2, carbon steel shell and tubes, operating pressure 5 bar.
6. Solvent and product storage tanks: cone roof, capacity 35 m^3, carbon steel.

Estimated service requirements:

Steam	200 kg/h
Cooling water	5000 kg/h
Electrical power	100 kWh/d (360 MJ/d)

Estimated solvent loss 10 kg/d; price £400/t. Plant attainment 95 per cent.
Estimate the capital investment required for this project, and the annual operating cost; date mid-2004.

Solution

Purchased cost of major equipment items.

Absorption column

Bare vessel cost (Figure 6.5*a*) £21,000; material factor 1.0, pressure factor 1.1
Vessel cost $= 21{,}000 \times 1.0 \times 1.1 =$ £23,000
Packing cost (Table 6.3) £840/m^3
Volume of packing $= (\pi/4) \times 12 = 9.4\ \text{m}^3$
Cost of column packing $= 9.4 \times 840 =$ £7896
Total cost of column $21{,}000 + 7896 = 28{,}896$, say £29,000

Recovery column

Bare vessel cost (Figure 6.5*a*) £26,000; material factor 2.0, pressure factor 1.0
Vessel cost $26{,}000 \times 2.0 \times 1.0 =$ £52,000
Cost of a plate (Figure 6.7*a*), material factor $1.7 = 200 \times 1.7 =$ £340
Total cost of plates $= 35 \times 340 =$ £11,900
Total cost of column $= 52{,}000 + 11{,}900 = 63{,}900$, say £64,000

Reboiler

Bare cost (Figure 6.3*a*) £11,000; type factor 0.8, pressure factor 1.0
Purchased cost $= 11{,}000 \times 0.8 \times 1.0 =$ £8800

Condenser

Bare cost (Figure 6.3*a*) £8500; type factor 0.8, pressure factor 1.0
Purchased cost $= 8500 \times 0.8 \times 1.0 =$ £6800

Cooler

Bare cost (Figure 6.3*a*) £4300; type factor 0.85, pressure factor 1.0
Purchased cost $= 4300 \times 0.85 \times 1.0 =$ £3700

Solvent tank

Purchase cost (Table 6.2) $= 1400 \times (35)^{0.55} =$ £9894, say £10,000

Product tank

Purchase cost same as solvent tank = £10,000

Total purchase cost of major equipment items (PCE)

Absorption column	29,000
Recovery column	64,000
Reboiler	8000
Condenser	6000
Cooler	3000
Solvent tank	10,000
Product tank	10,000
Total	£130,000

Estimation of fixed capital cost, reference Table 6.1, fluids processing plant:

PCE £130,000	—
f_1 Equipment erection	0.40
f_2 Piping	0.70
f_3 Instrumentation	0.20
f_4 Electrical	0.10
f_5 Buildings	none required
f_6 Utilities	not applicable
f_7 Storages	provided in PCE
f_8 Site development	not applicable
f_9 Ancillary buildings	none required

Total physical plant cost (PPC) $= 132{,}300(1 + 0.4 + 0.7 + 0.2 + 0.1) =$ £317,520

f_{10} Design and Engineering	0.30
f_{11} Contractor's Fee	none (unlikely to be used for a small, plant project)
f_{12} Contingencies	0.10

Fixed capital $= 317{,}520(1 + 0.3 + 0.1) = 44{,}528$ round up to £445,000

Working capital, allow 5% of fixed capital to cover the cost of the initial solvent charge $=$ $445{,}000 \times 0.05 =$ £22,250.

Total investment required for project $= 445{,}000 + 22{,}250 = 467{,}250$, say £468,000

Annual operating costs, reference Table 6.6:
Operating time, allowing for plant attainment $= 365 \times 0.95 = 347$ d/y, $347 \times 24 =$ 8328 h/y.

Variable costs:

1. Raw materials, solvent make-up $= 10 \times 347 \times 400/1000 =$	£ 1388
2. Miscellaneous materials, 10% of maintenance cost (item 5) $=$	£ 2200
3. Utilities, cost from Table 6.5:	
Steam, at 7£/t $= 7 \times 8328 \times 200/1000 =$	£11,659
Cooling water, at 1.5 p/t $= (1.5/100) \times 8328 \times 5000/1000 =$	£ 625
Power, at 1.2 p/MJ $= (1.2/100) \times 360 \times 347 =$	£ 1499
4. Shipping and packaging	not applicable
Variable costs $=$	£17,371

Fixed costs:

5.	Maintenance, take as 5% of fixed capital $= 445{,}000 \times 0.05 =$	£22,250
6.	Operating labour, allow one extra man on days. It is unlikely that one extra man per shift would be needed to operate this small plant, and one extra per shift would give a disproportionately high labour cost. Say, £30,000 per year, allowing for overheads =	£30,000
7.	Supervision, no additional supervision would be needed	
8.	Plant overheads, take as 50% of operating labour =	£15,000
9.	Laboratory, take as 30% of operating labour =	£ 9000
10.	Capital charges, 6% of fixed capital (bank rate 4%)	£26,700
11.	Insurance, 1% of fixed capital	£ 4450
12.	Local taxes	neglect
13.	Royalties	not applicable
	Fixed cost =	£107,400
	Direct production costs $= 17{,}396 + 107{,}400 =$	£124,796

14.	Sales expense	not applicable
15.	General overheads	not applicable
16.	Research and development	not applicable

Annual operating cost, rounded = £125,000

6.10. ECONOMIC EVALUATION OF PROJECTS

As the purpose of investing money in chemical plant is to earn money, some means of comparing the economic performance of projects is needed.

For small projects, and for simple choices between alternative processing schemes and equipment, the decisions can usually be made by comparing the capital and operating costs. More sophisticated evaluation techniques and economic criteria are needed when decisions have to be made between large, complex projects, particularly when the projects differ widely in scope, time scale and type of product. Some of the more commonly used techniques of economic evaluation and the criteria used to judge economic performance are outlined in this section. For a full discussion of the subject one of the many specialist texts that have been published should be consulted; Brennan (1998), Chauvel *et al.* (2003) and Vale-Riestra (1983). The booklet published by the Institution of Chemical Engineers, Allen (1991), is particularly recommended to students.

Making major investment decisions in the face of the uncertainties that will undoubtedly exist about plant performance, costs, the market, government policy, and the world economic situation, is a difficult and complex task (if not an impossible task) and in a large design organisation the evaluation would be done by a specialist group.

6.10.1. Cash flow and cash-flow diagrams

The flow of cash is the life blood of any commercial organisation. The cash flows in a manufacturing company can be likened to the material flows in a process plant.

The inputs are the cash needed to pay for research and development; plant design and construction; and plant operation. The outputs are goods for sale; and cash returns, are recycled, to the organisation from the profits earned. The "net cash flow" at any time is the difference between the earnings and expenditure. A cash-flow diagram, such as that shown in Figure 6.8, shows the forecast cumulative net cash flow over the life of a project. The cash flows are based on the best estimates of investment, operating costs, sales volume and sales price, that can be made for the project. A cash-flow diagram gives a clear picture of the resources required for a project and the timing of the earnings. The diagram can be divided into the following characteristic regions:

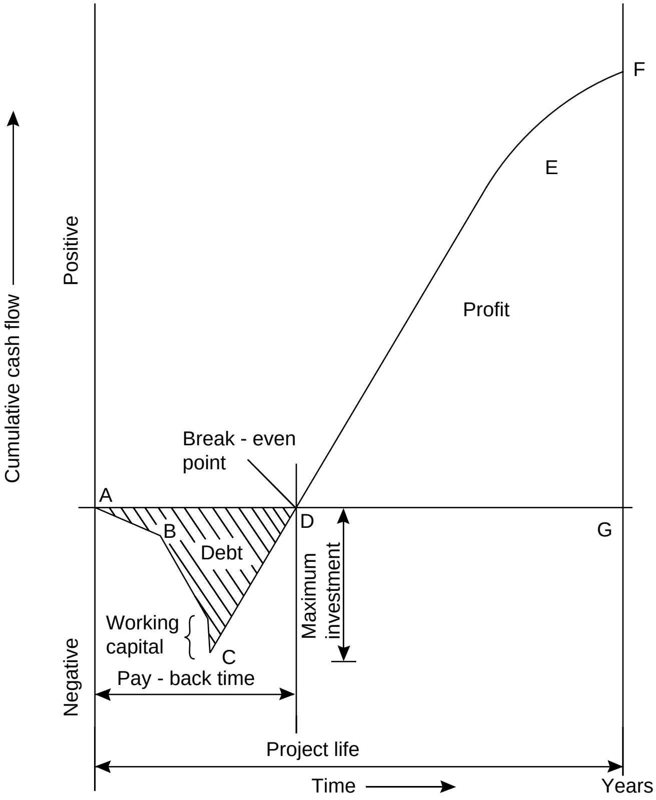


Figure 6.8. Project cash-flow diagram

A–B The investment required to design the plant.

B–C The heavy flow of capital to build the plant, and provide funds for start-up.

C–D The cash-flow curve turns up at C, as the process comes on stream and income is generated from sales. The net cash flow is now positive but the cumulative amount remains negative until the investment is paid off, at point D.

Point D is known as the *break-even point* and the time to reach the break-even point is called the *pay-back time*. In a different context, the term "break-even point" is used for the percentage of plant capacity at which the income equals the cost for production.

D–E In this region the cumulative cash flow is positive. The project is earning a return on the investment.

E–F Toward the end of project life the rate of cash flow may tend to fall off, due to increased operating costs and falling sale volume and price, and the slope of the curve changes.

The point F gives the final cumulative net cash flow at the end of the project life.

Net cash flow is a relatively simple and easily understood concept, and forms the basis for the calculation of other, more complex, measures of profitability.

6.10.2. Tax and depreciation

In calculating cash flows, as in Example 6.6, the project is usually considered as an isolated system, and taxes on profits and the effect of depreciation of the investment are not considered; tax rates are not constant and depend on government policy. In recent years, corporation (profits) tax has been running at around 30 per cent and this figure can be used to make an estimate of the cash flow after tax. Depreciation rates depend on government policy, and on the accounting practices of the particular company. At times, it has been government practice to allow higher depreciation rates for tax purposes in development areas; or to pay capital grants to encourage investment in these areas. The effect of government policy must clearly be taken into account at some stage when evaluating projects, particularly when considering projects in different countries.

6.10.3. Discounted cash flow (time value of money)

In Figure 6.8 the net cash flow is shown at its value in the year in which it occurred. So the figures on the ordinate show the "future worth" of the project: the cumulative "net future worth" (NFW).

The money earned in any year can be put to work (reinvested) as soon as it is available and start to earn a return. So money earned in the early years of the project is more valuable than that earned in later years. This "time value of money" can be allowed for by using a variation of the familiar compound interest formula. The net cash flow in each year of the project is brought to its "present worth" at the start of the project by discounting it at some chosen compound interest rate.

$$\begin{array}{c}\text{Net present worth (NPW)}\\ \text{of cash flow in year } n\end{array} = \frac{\text{Estimated net cash flow in year } n \text{ (NFW)}}{(1+r)^n} \tag{6.9}$$

where r is the discount rate (interest rate) per cent/100 and

$$\text{Total NPW of project} = \sum_{n=1}^{n=t} \frac{\text{NFW}}{(1+r)^n} \tag{6.10}$$

t = life of project, years.

The discount rate is chosen to reflect the earning power of money. It would be roughly equivalent to the current interest rate that the money could earn if invested.

The total NPW will be less than the total NFW, and reflects the time value of money and the pattern of earnings over the life of the project; see Example 6.6.

Most proprietary spreadsheets have procedures for calculating the cumulative NPW from a listing of the yearly net annual revenue (profit). Spreadsheets are useful tools for economic analysis and project evaluation.

6.10.4. Rate of return calculations

Cash-flow figures do not show how well the capital invested is being used; two projects with widely different capital costs may give similar cumulative cash-flow figures. Some way of measuring the performance of the capital invested is needed. Rate of return (ROR), which is the ratio of annual profit to investment, is a simple index of the performance of the money invested. Though basically a simple concept, the calculation of the ROR is complicated by the fact that the annual profit (net cash flow) will not be constant over the life of the project. The simplest method is to base the ROR on the average income over the life of the project and the original investment.

$$\text{ROR} = \frac{\text{Cumulative net cash flow at end of project}}{\text{Life of project} \times \text{original investment}} \times 100 \text{ per cent} \tag{6.11}$$

From Figure 6.8.

$$\begin{aligned} \text{Cumulative income} &= \text{F} - \text{C} \\ \text{Investment} &= \text{C} \\ \text{Life of project} &= \text{G} \\ \text{then, ROR} &= \frac{\text{F} - \text{C}}{\text{C} \times \text{G}} \times 100 \text{ per cent} \end{aligned}$$

The rate of return is often calculated for the anticipated best year of the project: the year in which the net cash flow is greatest. It can also be based on the book value of the investment, the investment after allowing for depreciation. Simple rate of return calculations take no account of the time value of money.

6.10.5. Discounted cash-flow rate of return (DCFRR)

Discounted cash-flow analysis, used to calculate the present worth of future earnings (Section 6.10.3), is sensitive to the interest rate assumed. By calculating the NPW for various interest rates, it is possible to find an interest rate at which the cumulative net present worth at the end of the project is zero. This particular rate is called the “discounted cash-flow rate of return” (DCFRR) and is a measure of the maximum rate that the project could pay and still break even by the end of the project life.

$$\sum_{n=1}^{n=t} \frac{\text{NFW}}{(1 + r')^n} = 0 \tag{6.12}$$

where r' = the discounted cash-flow rate of return (per cent/100),
NFW = the future worth of the net cash flow in year n,
t = the life of the project, years.

The value of r' is found by trial-and-error calculations. Finding the discount rate that just pays off the project investment over the project's life is analogous to paying off a mortgage. The more profitable the project, the higher the DCFRR that it can afford to pay.

DCFRR provides a useful way of comparing the performance of capital for different projects; independent of the amount of capital used and the life of the plant, or the actual interest rates prevailing at any time.

Other names for DCFRR are interest rate of return and internal rate of return.

6.10.6. Pay-back time

Pay-back time is the time required after the start of the project to pay off the initial investment from income; point D on Figure 6.7. Pay-back time is a useful criterion for judging projects that have a short life, or when the capital is only available for a short time.

It is often used to judge small improvement projects on operating plant. Typically, a pay-back time of 2 to 5 years would be expected from such projects.

Pay-back time as a criterion of investment performance does not, by definition, consider the performance of the project after the pay-back period.

6.10.7. Allowing for inflation

Inflation depreciates money in a manner similar to, but different from, the idea of discounting to allow for the time value of money. The effect of inflation on the net cash flow in future years can be allowed for in a similar manner to the net present worth calculation given by equation 6.9, using an inflation rate in place of, or added to, the discount rate r. However, the difficulty is to decide what the inflation rate is likely to be in future years. Also, inflation may well affect the sales price, operating costs and raw material prices differently. One approach is to argue that a decision between alternative projects made without formally considering the effect of inflation on future earnings will still be correct, as inflation is likely to affect the predictions made for both projects in a similar way.

6.10.8. Sensitivity analysis

The economic analysis of a project can only be based on the best estimates that can be made of the investment required and the cash flows. The actual cash flows achieved in any year will be affected by any changes in raw-materials costs, and other operating costs; and will be very dependent on the sales volume and price. A sensitivity analysis is a way of examining the effects of uncertainties in the forecasts on the viability of a project. To carry out the analysis the investment and cash flows are first calculated using what are considered the most probable values for the various factors; this establishes the base case for analysis. The cash flows, and whatever criteria of performance are to be used, are then calculated assuming a range of error for each of the factors in turn; for example, an error of, say, ±10 per cent on the sales price might be assumed. This will show how sensitive the cash flows and economic criteria are to errors in the forecast figures. It gives some idea of the degree of risk involved in making judgements on the forecast performance of the project.

6.10.9. Summary

The investment criteria discussed in this section are set out in Table 6.7, which shows the main advantage and disadvantage of each criterion.

There is no one best criterion on which to judge an investment opportunity. A company will develop its own methods of economic evaluation, using the techniques discussed in this section, and will have a "target" figure of what to expect for the criterion used, based on their experience with previous successful, and unsuccessful, projects.

Table 6.7. Investment criteria

Criterion	Abbreviation	Units	Main advantage	Main shortcoming
Investment	—	£, $	Shows financial resources needed	No indication of project performance
Net future worth	NFW	£, $	Simple. When plotted as cash-flow diagram, shows timing of investment and income	Takes no account of the time value of money
Pay-back time	—	years	Shows how soon investment will be recovered	No information on later years
Net present worth	NPW	£, $	As for NFW but accounts for timing of cash flows	Dependent on discount rate used
Rate of return	ROR	%	Measures performance of capital	Takes no account of timing of cash flows Dependent on definition of income (profit) and investment
Discounted cash-flow rate of return	DCFRR	%	Measures performance of capital allowing for timing of cash flows	No indication of the resources needed

A figure of 20 to 30 per cent for the return on investment (ROR) can be used as a rough guide for judging small projects, and when decisions have to be made on whether to install additional equipment to reduce operating costs. This is equivalent to saying that for a project to be viable the investment needed should not be greater than about 4 to 5 times the annual savings achieved.

As well as economic performance, many other factors have to be considered when evaluating projects; such as those listed below:

1. Safety.
2. Environmental problems (waste disposal).
3. Political considerations (government policies).
4. Location of customers.
5. Availability of labour.
6. Availability of supporting services.
7. Company experience in the particular technology.

Example 6.5

A plant is producing 10,000 t/y of a product. The overall yield is 70 per cent, on a mass basis (kg of product per kg raw material). The raw material costs £10/t, and the product sells for £35/t. A process modification has been devised that will increase the yield to 75 per cent. The additional investment required is £35,000, and the additional operating costs are negligible. Is the modification worth making?

Solution

There are two ways of looking at the earnings to be gained from the modification:

1. If the additional production given by the yield increase can be sold at the current price, the earnings on each additional ton of production will equal the sales price less the raw material cost.
2. If the additional production cannot be readily sold, the modification results in a reduction in raw material requirements, rather than increased sales, and the earnings (savings) are from the reduction in annual raw material costs.

The second way gives the lowest figures and is the safest basis for making the evaluation. At 10,000 t/y production

$$\begin{aligned}
\text{Raw material requirements at 70 per cent yield} &= \frac{10{,}000}{0.7} = 14{,}286 \\
\text{at 75 per cent yield} &= \frac{10{,}000}{0.75} = \underline{13{,}333} \\
&\quad \text{savings } \underline{\underline{953 \text{ t/y}}} \\
\text{Cost savings, at £10}/t, &= 953 \times 10 = £9530 \text{ per year} \\
\text{ROR} &= \frac{9530}{35{,}000} \times 100 = \underline{\underline{27 \text{ per cent}}}
\end{aligned}$$

Pay-back time (as the annual savings are constant, the pay-back time will be the reciprocal of the ROR)

$$= \frac{100}{27} = \underline{\underline{3.7 \text{ years}}}$$

On these figures the modification would be considered worthwhile.

Example 6.6

It is proposed to build a plant to produce a new product. The estimated investment required is 12.5 million pounds and the timing of the investment will be:

year 1	1.0 million (design costs)
year 2	5.0 million (construction costs)
year 3	5.0 million ” ”
year 4	1.5 million (working capital)

The plant will start up in year 4.

The forecast sales price, sales volume, and raw material costs are shown in Table 6.8.

Table 6.8. Summary of data and results for example 6.6

				During year		At year end	At commencement of project				
End of year	Forecast sales 10^3t	Forecast selling Price £/t	Raw material costs £/t product	Sale income less operating costs 10^6£	Net cash flow 10^6£	Cumulative cash flow 10^6£ (Project NFW)	Discounted cash flow at 15 per cent 10^6£	Cumulative DCF (Project NPW) 10^6£	Project NPW at 25 per cent discount rate	Project NPW at 35 per cent discount rate	Project NPW at 37 per cent discount rate
1	0	—	—	0	−1.0	−1.00	−0.87	−0.87	−0.80	−0.74	0.73
2	0	—	—	0	−5.0	−6.00	−3.78	−4.65	−4.00	−3.48	−3.39
3	0	—	—	0	−5.0	−11.00	−3.29	−7.94	−6.56	−5.52	−5.34
4	100	150	90	4.6	3.10	−7.90	1.77	−6.17	−5.29	−4.58	−4.46
5	105	150	90	4.85	4.85	−3.05	2.41	−4.03	−3.70	−3.50	−3.45
6	110	150	90	5.10	5.10	2.05	2.20	−1.83	−2.36	−2.66	−2.68
7	120	150	90	5.60	5.60	7.65	2.11	0.28	−1.19	−1.97	−2.06
8	130	150	90	6.10	6.10	13.75	1.99	2.27	−0.17	−1.42	−1.57
9	140	150	90	6.50	6.50	20.25	1.85	4.12	0.70	−0.98	−1.19
10	150	145	85	7.00	7.00	27.25	1.73	5.85	1.45	−0.64	−0.89
11	165	140	85	6.93	6.93	34.18	1.49	7.34	2.05	−0.38	−0.67
12	180	140	85	7.60	7.60	41.78	1.42	8.76	2.57	−0.17	−0.50
13	190	140	85	8.05	8.05	49.83	1.31	10.07	3.01	−0.01	−0.36
14	200	135	80	8.05	8.05	57.88	1.14	11.21	3.36	0.11	−0.27
15	190	130	75	7.62	7.62	65.50	0.94	12.15	3.63	0.19	−0.20
16	180	120	75	7.19	7.19	72.69	0.77	12.92	3.83	0.25	−0.15
17	170	115	70	5.06	5.06	77.75	0.47	13.39	3.95	0.28	−0.13
18	160	110	70	3.93	3.93	81.68	0.32	13.71	4.02	0.30	−0.12
19	150	100	70	2.15	2.15	83.83	0.15	13.86	4.05	0.31	−0.11

The fixed operating costs are estimated to be:

£400,000 per year up to year 9
£500,000 per year from year 9 to 13
£550,000 per year from year 13

The variable operating costs are estimated to be:

£10 per ton of product up to year 13
£13 per ton of product from year 13

Calculate:

1. The net cash flow in each year.
2. The future worth of the project, NFW.
3. The present worth, NPW, at a discount rate of 15 per cent.
4. The discounted cash-flow rate of return, DCFRR.
5. The pay-back time.

No account needs to be taken of tax in this exercise; or the scrap value of the equipment and value of the site at the end of the project life. For the discounting calculation, cash flows can be assumed to occur at the end of the year in which they actually occur.

Solution

The cash-flow calculations are summarised in Table 6.8. Sample calculations to illustrate the methods used are given below.

For year 4

$$\begin{aligned}
&\text{Investment (negative cash flow)} && = \text{£}1.5 \times 10^6\\
&\text{Sales income} = 100 \times 10^3 \times 150 && = \text{£}15.0 \times 10^6\\
&\text{Raw material costs} = 100 \times 10^3 \times 90 && = \text{£}9.0 \times 10^6\\
&\text{Fixed operating costs} && = \text{£}0.4 \times 10^6\\
&\text{Variable operating costs} = 100 \times 10^3 \times 10 && = \text{£}1.0 \times 10^6\\
&\text{Net cash flow} = \text{sales income} - \text{costs} - \text{investment} &&\\
&\qquad\qquad = 15.0 - 10.4 - 1.5 = 3.1 \text{ million pounds} &&\\
&\text{Discounted cash flow (at 15 per cent)} = \frac{3.1}{(1+0.15)^4} && = \text{£}1.77 \times 10^6
\end{aligned}$$

For year 8

$$\begin{aligned}
&\text{Investment} && \text{nil}\\
&\text{Sales income} = 130 \times 10^3 \times 150 && = \text{£}19.5 \times 10^6\\
&\text{Raw material costs} = 130 \times 10^3 \times 90 && = \text{£}11.7 \times 10^6\\
&\text{Fixed operating costs} && = \text{£}0.4 \times 10^6\\
&\text{Variable operating costs} = 130 \times 10^3 \times 10 && = \text{£}1.3 \times 10^6\\
&\text{Net cash flow} = 19.5 - 13.4 = 6.10 \text{ million pounds} &&\\
&\text{DCF} = \frac{6.1}{(1.15)^8} = 1.99 &&
\end{aligned}$$

DCFRR

This is found by trial-and-error calculations. The present worth has been calculated at discount rates of 25, 35 and 37 per cent. From the results shown in Table 6.8 it will be seen that the rate to give zero present worth will be around 36 per cent. This is the discounted cash-flow rate of return for the project.

6.11. COMPUTER METHODS FOR COSTING AND PROJECT EVALUATION

Most large manufacturing and contracting organisations use computer programs to aid in the preparation of cost estimates and in process evaluation. Many have developed their own programs, using cost data available from company records to ensure that the estimates are reliable. Of the packages available commercially, QUESTIMATE, marketed by the Icarus Corporation, is probably the most widely used.

Costing and economic evaluation programs also form part of some of the commercial process design packages; such as the ICARUS program which is available from Aspen Tech, see Chapter 4, Table 4.1.

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6.13. NOMENCLATURE

		Dimensions in **MT £** or **$**
A	Year in which cost is known (equation 6.1)	**T**
B	Year in which cost is to be estimated (equation 6.1)	**T**
C	Cost constant in equation 6.7	*
Ce	Purchased equipment cost	**£** or **$**
Cf	Fixed capital cost	**£** or **$**
C_1	Capital cost of plant 1	**£** or **$**
C_2	Capital cost of plant 2	**£** or **$**
f_L	Lang factors (equation 6.3)	—
$f_1 \ldots f_9$	Capital cost factors (Table 6.1)	—
N	Number of significant processing steps	—
n	Capital cost index in equation 6.4	—
Q	Plant capacity	$\mathbf{MT}^{-1}$
S	Equipment size unit in equation 6.4	*

S_1	Capacity of plant 1	$\mathbf{MT}^{-1}$
S_2	Capacity of plant 2	$\mathbf{MT}^{-1}$
s	Reactor conversion	—

Asterisk (*) indicates that these dimensions are dependent on the type of equipment.

6.14. PROBLEMS

6.1. The capital cost of a plant to produce 100 t per day of aniline was 8.5 million US dollars in mid-1992. Estimate the cost in pounds sterling in January 2004. Take the exchange rates as: £1 = \$2.0 in mid-1992 and £1 = \$1.8 in January 2004.

6.2. The process used in the manufacture of aniline from nitrobenzene is described in Appendix G, design problem G.8. The process involves six significant stages:
Vaporisation of the nitrobenzene
Hydrogenation of the nitrobenzene
Separation of the reactor products by condensation
Recovery of crude aniline by distillation
Purification of the crude nitrobenzene
Recovery of aniline from waste water streams

Estimate the capital cost of a plant to produce 20,000 tonne per year.

6.3. A reactor vessel cost £365,000 in June 1998, estimate the cost in mid-2004.

6.4. The cost of a distillation column was \$225,000 in early 1998, estimate the cost in January 2004.

6.5. Using the data on equipment costs given in this chapter, estimate the cost of the following equipment:

1. A shell and tube heat exchanger, heat transfer area 50 m^2, floating head type, carbon steel shell, stainless steel tubes, operating pressure 25 bar.
2. A kettle reboiler: heat transfer area 25 m^2, carbon steel shell and tubes, operating pressure 10 bar.
3. A horizontal, cylindrical, storage tank, 3 m diameter, 12 m long, used for liquid chlorine at 10 bar, material carbon steel.
4. A plate column: diameter 2 m height 25 m, stainless clad vessel, 20 stainless steel sieve plates, operating pressure 5 bar.

6.6. Compare the cost the following types of heat exchangers, to give a heat transfer area of 10 m^2. Take the construction material as carbon steel.

1. Shell and tube, fixed head
2. Double-pipe

6.7. Estimate the cost of the following items of equipment:

1. A packaged boiler to produce 20,000 kg/h of steam at 10 bar.
2. A centrifugal compressor, driver power 75 kW
3. A plate and frame filter press, filtration area 10 m^2

4. A floating roof storage tank, capacity 50,000 m^3
5. A cone roof storage tank, capacity 35,000 m^3

6.8. A storage tank is purged continuously with a stream of nitrogen. The purge stream leaving the tank is saturated with the product stored in the tank. A major part of the product lost in the purge could be recovered by installing a scrubbing tower to absorb the product in a solvent. The solution from the tower could be fed to a stage in the production process, and the product and solvent recovered without significant additional cost. A preliminary design of the purge recovery system has been made. It would consist of:

1. A small tower 0.5 m diameter, 4 m high, packed with 25 mm ceramic saddles, packed height 3 m.
2. A small storage tank for the solution, 5 m^3 capacity.
3. The necessary pipe work, pump, and instrumentation.

All materials of construction, carbon steel.
Using the following data, evaluate whether it would be economical to install the recovery system:

1. cost of product £5 per kg,
2. cost of solvent 20 p/kg,
3. additional solvent make-up 10 kg/d,
4. current loss of product 0.7 kg/h,
5. anticipated recovery of product 80 per cent,
6. additional service(utility) costs, negligible.

Other operating costs will be insignificant.

6.9. Make a rough estimate of the cost of steam per ton, produced from a packaged boiler. 10,000 kg per hour of steam are required at 15 bar. Natural gas will be used as the fuel, calorific value 39 MJ/m^3. Take the boiler efficiency as 80 per cent. No condensate will be returned to the boiler.

6.10. The production of methyl ethyl ketone (MEK) is described in Appendix G, problem G.3. A preliminary design has been made for a plant to produce 10,000 tonne per year. The major equipment items required are listed below. The plant attainment will be 8000 hours per year.
Estimate the capital required for this project, and the production cost.
The plant will be built on an existing site with adequate resources to provide the ancillary requirements of the new plant.

Major equipment items

1. Butanol vaporiser: shell and tube heat exchanger, kettle type, heat transfer area 15 m^2, design pressure 5 bar, materials carbon steel.
2. Reactor feed heaters, two off: shell and tube, fixed head, heat transfer area 25 m^2, design pressure 5 bar, materials stainless steel.
3. Reactor, three off: shell and tube construction, fixed tube sheets, heat transfer area 50 m^2, design pressure 5 bar, materials stainless steel.

4. Condenser: shell and tube heat exchanger, fixed tube sheets, heat transfer area 25 m^2, design pressure 2 bar, materials stainless steel.
5. Absorption column: packed column, diameter 0.5 m, height 6.0 m, packing height 4.5 m, packing 25 mm ceramic saddles, design pressure 2 bar, material carbon steel.
6. Extraction column: packed column, diameter 0.5 m, height 4 m, packed height 3 m, packing 25 mm stainless steel pall rings, design pressure 2 bar, material carbon steel.
7. Solvent recovery column: plate column, diameter 0.6 m, height 6 m, 10 stainless steel sieve plates, design pressure 2 bar, column material carbon steel.
8. Recover column reboiler: thermosyphon, shell and tube, fixed tube sheets, heat transfer area 4 m^2, design pressure 2 bar, materials carbon steel.
9. Recovery column condenser: double-pipe, heat transfer area 1.5 m^2, design pressure 2 bar, materials carbon steel.
10. Solvent cooler: double pipe exchanger, heat transfer area 2 m^2, materials stainless steel.
11. Product purification column: plate column, diameter 1 m^2, height 20 m, 15 sieve plates, design pressure 2 bar, materials stainless steel.
12. Product column reboiler: kettle type, heat transfer area 4 m^2, design pressure 2 bar, materials stainless steel.
13. Product column condenser: shell and tube, floating head, heat transfer area 15 m^2, design pressure 2 bar, materials stainless steel.
14. Feed compressor: centrifugal, rating 750 kW.
15. Butanol storage tank: cone roof, capacity 400 m^3, material carbon steel.
16. Solvent storage tank: horizontal, diameter 1.5 m, length 5 m, material carbon steel.
17. Product storage tank: cone roof, capacity 400 m^3, material carbon steel.

Raw materials

1. 2-butanol, 1.045 kg per kg of MEK, price £450/t ($750/t).
2. Solvent (trichloroethane) make-up 7000 kg per year, price 60p/kg. ($1.0/kg).

Utilities
Fuel oil, 3000 t per year
Cooling water, 120 t/hour
Steam, low pressure, 1.2 t/h
Electrical power, 1 MW

The fuel oil is burnt to provide flue gases for heating the reactor feed and the reactor. The cost of the burner need not be included in this estimate. Some of the fuel requirements could be provided by using the by-product hydrogen. Also, the exhaust flue gases could be used to generate steam. The economics of these possibilities need not be considered.

6.11. A plant is proposing to install a combined heat and power system to supply electrical power and process steam. Power is currently taken from a utility company and steam is generated using on-site boilers.

The capital cost of the CHP plant is estimated to be £3 million pounds (5 million dollars). Combined heat and power is expected to give net savings of £700,000 ($1,150,000) per year. The plant is expected to operate for 10 years after the completion of construction.

Calculate the cumulative net present worth of the project, at a discount rate of 8 per cent. Also, calculate the discounted cash flow rate of return.

Construction will take two years, and the capital will be paid in two equal increments, at the end of the first and second year. The savings (income) can be taken as paid at the end of each year. Production will start on the completion of construction.