وزارة التعليم العالي والبحث العلمي الجامعة
التقنية الشمالية
الجامعةالتقنيةالشمالية/كليةهندسة
تقنيات النفط و الغاز

الحقيبة التعليمية

القسم العلمي: **وقود وطاقة**

اسم المقرر: الكيمياء الفيزيائية

المرحلة / المستوى: **الثاني**

الفصل الدراسي: **الثاني**

السنة الدراسية: **2025-2024**

اسم	**الكيمياء الفيزيائية**
القسم	الوقود والطاقة
الكلية	كلية هندسة تقنيات النفط والغاز
المرحلة / المستوى	الثانيه
الفصل الدراسي	الثاني
عدد الساعات الاسبوعيه:	نظري 2 عملي 2
عدد الوحدات	
الرمز:	
نوع المادة	نظري عملي كلاهما *
هل يتوفر نظير للمقرر في الاقسام الاخرى	كلا
اسم المقرر النظير	-
القسم	-
رمز المقرر	-
معلومات تدريسي المادة	
اسم مدرس)مدرسي(المقرر:	**اية اوس سعد**
اللقب العلمي:	**مدرس مساعد**
سنة الحصول على اللقب	2024
الشهادة:	**ماجستير هندسة طاقة**
سنة الحصول على الشهادة	**2023**
عدد سنوات الخبره (تدريس)	**1**

الوصف العام للمقرر

This syllabus introduces the fundamental principles of physical chemistry, including thermodynamics, chemical kinetics, quantum mechanics, statistical mechanics, and spectroscopy. The syllabus covers the behavior of atoms and molecules, providing a clear explanation of molecular structure, reaction rates, and the laws governing chemical processes. It integrates both theoretical concepts and practical applications, with detailed examples, illustrations, and problem sets to reinforce learning. The text is known for its accessibility, modern approach, and focus on bridging the gap between microscopic behavior and macroscopic observations, making it an essential resource for students and professionals .in the field of chemistry

االهداف العامة

After studying the book, students will gain a deep understanding of core concepts in physical chemistry, including the behavior of gases, thermodynamics (laws governing energy and spontaneity), chemical equilibrium, and molecular structure. They will explore quantum theory, atomic and molecular spectra, and how molecular symmetry affects chemical properties. Students will also learn about solid-state chemistry, processes at solid surfaces, and the motion of molecules, providing them with a comprehensive foundation in physical chemistry.

ألاهداف الخاصة

- Ideal and Real Gases: Understand the differences between ideal and real gases. Study the behavior of real gases and how to describe them using equations of state.
- Mixture of Gases: Learn how to handle multiple gases in a system and calculate properties like pressure, volume, and temperature in a gas mixture.
- Basic Thermodynamic Concepts: Understand the different types of systems in thermodynamics (closed, open, and isolated systems). Comprehend thermodynamic processes and how energy and heat transfer in systems.
- First Law of Thermodynamics: Study the concepts of internal energy, work, and heat in systems. Apply the first law to calculate changes in energy for various systems.
- Second Law of Thermodynamics: Study the concept of entropy and its applications in thermodynamic systems. Understand the direction of natural processes in closed systems.
- Third and Zeroth Laws of Thermodynamics: Explain the laws that govern the thermal behavior of systems at low temperatures. Study the impact of the Zeroth Law on thermal equilibrium.
- Helmholtz and Gibbs Free Energy: Study the importance of Helmholtz and Gibbs free energies in determining the feasibility of thermodynamic processes.

- Electrochemistry and its Applications: Understand the concepts of electrochemistry and its applications in industrial processes such as batteries, fuel cells, and water treatment. Study electrochemical reactions and their applications in energy conversion.
- Types of Electrochemical Cells: Understand the different types of electrochemical cells (galvanic cells, electrolytic cells, fuel cells) and their applications. Study the role of electrochemical cells in electrolysis and energy generation.

ألهداف السلوكيةاونواتج التعلم

- **Ideal and Real Gases:**
  Identify the behavior of ideal and real gases using equations of state.
  Apply the Van der Waals equation for real gases in practical calculations.
- **Mixture of Gases:**
  Calculate the composition of a gas mixture using Dalton's Law of Partial Pressures.
  Apply gas laws to determine the composition of gases under specific conditions.
- **Thermodynamics:**
  Distinguish between different thermodynamic systems and identify the type of process (expansion or compression) in a given system.
  Solve thermodynamic problems using fundamental laws and principles.
- **First Law of Thermodynamics:**
  Apply the first law to calculate changes in internal energy in closed systems.
  Solve problems related to work and heat in thermodynamic systems.
- **Second Law of Thermodynamics:**
  Explain the concept of entropy and calculate its change during natural processes.
  Analyze natural processes using the second law to determine the feasibility of processes.
- **Third and Zeroth Laws of Thermodynamics:**
  Calculate entropy changes at low temperatures and understand the third law's impact on systems.
  Apply the Zeroth Law to understand thermal equilibrium.
- **Helmholtz and Gibbs Free Energy:**
  Interpret and study the roles of Helmholtz and Gibbs free energies in determining the direction of processes.
  Apply these energies to understand chemical reactions and transformations in systems.
- **Electrochemistry:**
  Analyze electrochemical reactions using equations like the Nernst equation.
  Design and apply electrochemical cells for various applications such as batteries.
- **Types of Electrochemical Cells:**
  Classify and explain the different types of electrochemical cells.
  Apply the principles of electrochemical cells in practical applications like electrolysis and energy production.

المتطلبات السابقة

- Student should know basic chemistry and physics with simple Algebra.

أساليب التدريس

الاسلوب او الطريقة	مبررات الاختيار
1. التفاعل على السبورة أو على الورقة	إشراك الطالب في شرح المفاهيم الفيزيائية المعقدة وتنظيم الأفكار، مما يتيح لهم التفاعل المباشر مع المحتوى وحل المسائل الرياضية والتطبيقية المتعلقة بالكيمياء الفيزيائية.
2. استخدام الأنشطة العملية والتطبيقية	يساهم في ربط المفاهيم النظرية في الكيمياء الفيزيائية بالتطبيقات العملية، مثل دراسة التفاعلات الحرارية أو قياس خواص المواد في المختبر، مما يعزز الفهم العميق للقوانين الفيزيائية والكيميائية.
3. عرض فيديو توضيحي للتفاعلات الكيميائية	يساعد في تبسيط المفاهيم المعقدة مثل الديناميكا الحرارية أو السكونية الكيميائية، ويوضح كيفية تطبيق هذه المفاهيم في التجارب المعملية والصناعية.
4. العمل الجماعي والنقاشات الصفية	يعزز قدرة الطالب على التعاون وحل المشكلات الفيزيائية والكيميائية معًا، ويشجع على تبادل الأفكار ومناقشة تطبيقات المفاهيم مثل التوازن الكيميائي أو الديناميكا الحرارية.
5. العروض التقديمية والأنشطة التفاعلية باستخدام وسائل التعليم الحديثة	تدعم تقديم المفاهيم الفيزيائية في الكيمياء بطرق مبتكرة وتفاعلية، مما يسهم في تعزيز استيعاب الطالب ويساعدهم في تطبيق المفاهيم بشكل عملي وحل المسائل المعقدة.

عنوان الفصل	الوقت					
التوزيع الزمني	النظري	العملي	العنوان الفرعي	طريقة التدريس	التقنيات	طرق القياس
ألسبوع 1	2	2	Introduction of Physical Chemistry and basis	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	PowerPoint، سبورة تفاعلية	اسالة عامة لمعرفة مستوى الطلبه
ألسبوع 2	2	2	Behavior of gases (Properties of gases)	شرح مفصل، أمثلة عملية	سبورة تفاعلية، فيديوهات توضيحية	أسئلة تفاعلية
ألسبوع 3	2	2	Behavior of gases (Perfect Gas)	شرح، مناقشة تفاعلية	PowerPoint، سبورة تفاعلية	اختبار صغير
السبوع 4	2	2	Behavior of gases (Real Gas)	شرح، مناقشة تفاعلية، عرض تجارب معملية	سبورة تفاعلية، حل اساله تطبيقية	ختبار عملي، تقييم أدائي
ألسبوع 5	2	2	Thermodynamics Basis (System, Boundaries, Surroundings)	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	سبورة تفاعلية، حل اساله تطبيقية	تفاعل على السبورة
ألسبوع 6	2	2	Thermodynamic Processes	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	سبورة تفاعلية، حل اساله تطبيقية	تفاعل على السبورة
ألسبوع 7	2	2	First Law of Thermodynamics	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	سبورة تفاعلية، حل اساله تطبيقية	اسالة شفه
ألسبوع 8	2	2	Second Law of Thermodynamics	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	PowerPoint، سبورة تفاعلية	اساله عن المحاضره السابقه
ألسبوع 9	2	2	Third Law of Thermodynamics	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	PowerPoint، سبورة تفاعلية	اساله عن المحاضره السابقه
ألسبوع 10	2	2	The Helmholtz and Gibbs	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	عمل مجاميع داخل المحاضرة لحل اساله ونشاطات	تصحيح الإجابات لهم

الأسبوع 11	2	2	Applications of Laws of Thermodynamic	شرح، مناقشة تفاعلية	PowerPoint، سبورة تفاعلية	تقييم شفوي
الأسبوع 12	2	2	Maxwell Relations	شرح، مناقشة تفاعلية	PowerPoint، سبورة تفاعلية	تقييم شفوي
الأسبوع 13	2	2	Electrochemical Cells	شرح، مناقشة تفاعلية	سبورة تفاعلية، فيديوهات توضيحية	تقييم شفوي
الأسبوع 14	2	2	Types of Electrochemical Cells (Galvanic Cells & Electrolytic Cells)	شرح، مناقشة تفاعلية، عرض تجارب معملية	عمل مجاميع داخل المحاضرة لحل اساله ونشاطات	تصحيح الإجابات لهم
الأسبوع 15	2	2	Applications of Electrochemical Cells	عرض تقديمي، شرح، أسئلة وأجوبة، مناقشة	PowerPoint، سبورة تفاعلية	تقييم شفوي
الأسبوع 16	2	2	preparatory week before the final exam	مراجعة المواد	PowerPoint، سبورة تفاعلية	حل اساله للطلبه

المحتوى العلمي

Chapter 1

Introduction to Physical Chemistry Basis

Physical chemistry deals with the principles of physics involved in chemical interactions. It examines:

- How matter behaves on a molecular and atomic level
- How chemical reactions occur

Physical chemists are focused on understanding the physical properties of atoms and molecules, the way chemical reactions work, and what these properties reveal. Their discoveries are based on understanding chemical properties and describing their behavior using theories of physics and mathematical computations.

1.0 Measurement in physical chemistry: Unit is a scientific way of quantifying substances or parameters. It is used to give insight about the magnitude or dimension of matter. **SI UNITS** means international system of units. It is a means or system that is used to provide a set of internationally accepted standard units of measurement. Basically, there are seven primary SI units. The remaining units are derived from the primary units and they are referred to as secondary units or derived units.

= m x m x m

= m^3

1.1 PRIMARY UNITS

These are the units of measurement that take their origin from the base quantity.

Table 1: Primary Units and their symbol:

S/No	Symbol	Name of Units	Base Parameter
1	S	Second	Time
2	Kg	Kilogram	Mass
3	M	Meter	Distance/Length
4	K	Kelvin	Temperature
5	A	Ampere	Electric current
6	Mol	Mole	Amount of substance
7	Cd	Candela	Luminous intensity

1.2 DERIVED UNITS

These are secondary units that are derived or obtained by combination of two or more primary units. The unit of Area is a derived unit because it is a combination of two primary units.

Area = Length x breadth

= m x m

= m^2

Similarly, the unit of volume is a derived unit;

Volume = length x breadth x height

= m x m x m

= m^3

Other derived units are given in table 2

Table 2: Secondary units and their quantity

S/No	Parameter	Derivation	Unit
1	Force	Mass x acceleration	Kg x m/S^2 = Kgm/S^2 = N
2	Work	Force x distance	Kgm/S^2 x m = Kgm^2/S^2 = J
3	Density	Mass/Volume	Kg/m^3.
4	Pressure	Force/Area	Kgm/S^2 ÷ m^2 = Kg/S^2m = Kg/mS^2.
5	Power	Work/time = force x distance/time	Kgm/S^2 x m/S = Kgm^2/S^3 = J/S
6	Electric charge	Current x time = q = It	A x s = As = Coulomb = C

1.3 Unit Equivalent

There is always a conversion factor when charging from one unit to another

1.3.1 Length

Unit	Equivalent
1cm	10^{-2}m
1dm	10^{-1}m ≡ 10cm
1mm	10^{-3}m
1nm	10^{-9}m
Å	10^{-8}cm ≡ 10^{-10}m

1.3.2 Mass

Unit	Equivalent
1Kg	10^3g
1mg	10^{-3}g
1µg	10^{-6}g
1ng	10^{-9}g

1.3.3 Volume

Unit	Equivalent
$1mm^3$	1µL≡ $10^{-9}m^3$
$1cm^3$	1mL≡$10^{-6}m^3$
$1dm^3$	1L = $10^{-3}m^3$
1L	1000ml
1ml	1cc (cc= cubic centimeter)

1.3.4 Pressure

Unit	Equivalent
1atm	760mmHg = 760torr = 14.692psi
1mmHg	1 torr
1 pa	$1N/m^2$
1barr	$10^5N/m^2$

1.3.5 Energy

Unit	Equivalent
1cal	4.184J
1erg	10^{-7}J
1 eV	1.602×10^{-19}J

1.3.6 Time

Unit	Equivalent
1min	60 seconds
1 hr	60 mins
1 day	24 hr
1 week	7 days
1 year	52 weeks = 365 days

Exercise 1

1 Convert the following

(a) 50.3km to nm

(b) 1.60 x 10^{-2}μg to kg

(c) 15.66psi to bar

(d) 185μL to dm^3

(e) 7.865cal to J

(f) 3.5 weeks to seconds

(g) -10^0C to Kelvin

(h) 2.5yrs to seconds

(i) 1.75N/m^2 to atm

(j) 9.26atm to mmHg

Chapter 2

Behavior of Gases

GASES

Properties, Behavior and Equations of state

Gases are the least dense and the most mobile among the three states of matter. A ***gas*** molecule moves at very high velocities and has high kinetic energy.

General Characteristics of Gases

1. Expansibility

Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.

2. Compressibility

Gases are easily compressed by application of pressure to a movable piston fitted in the container.

3. Diffusibility

Gases can diffuse rapidly through each other to form a homogeneous mixture.

4. Pressure

Gases exert pressure on the walls of the container in all directions.

5. Effect of Heat

The Perfect Gas

Firstly: The Perfect Gas law

The equation of state of a gas at low pressure was established by combining a series of empirical laws. The volume of a given sample of a gas depends on the temperature and pressure applied to it. Any change in temperature or pressure will affect the volume of the gas. As results of experimental studies from 17th to 19th century, scientists derived the relationships among the pressure, temperature and volume of a given mass of gas. These relationships, which describe the general behavior of gases, are called the **gas laws.**

Parameters of a gas:

A gas sample can be described in terms of four parameters (measurable properties):

(1) the volume, V of the gas

(2) its pressure, P

(3) its temperature, T

(4) the number of moles, n, of gas in the container

Boyle's law:

Through a series of experiments, Robert Boyle (1627–1691) determined the relationship between the pressure (P) and volume (V) of a particular quantity of a gas. This relationship of P and V is known as Boyle's law:

At constant temperature (T), the volume (V) of a fixed mass of a gas is inversely proportional to the pressure (P), which may be expressed as:

$$\boldsymbol{V \propto \frac{1}{P}} \qquad \boldsymbol{P_1V_1 = P_2V_2} \quad (\boldsymbol{for\ different\ condiotions})$$

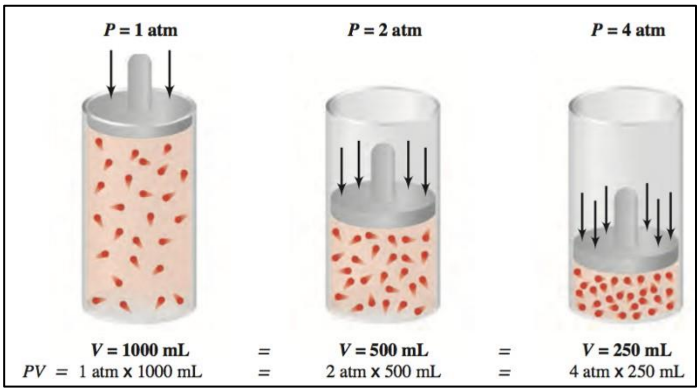


Figure 1

Charles' law:

In 1787 the French Physicist J. A. C. Charles observed the effect of temperature on the volume of a gas. As we see in the figure below, the net result is an increase in volume due to an increase in temperature.

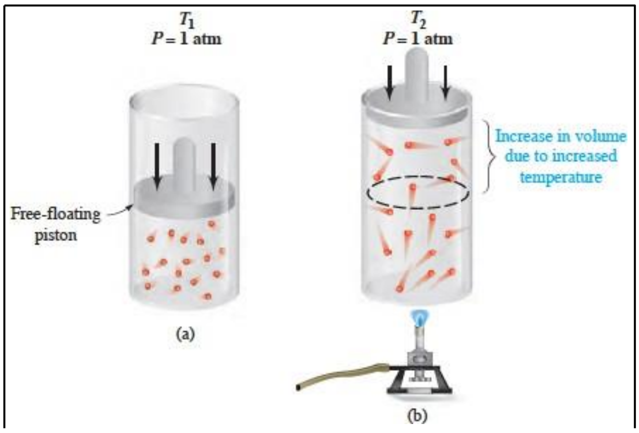


Figure 2

At constant pressure, the volume of a fixed mass of any gas is directly proportional to the absolute temperature, which may be expressed as

$$\boldsymbol{V} \propto \boldsymbol{T} \qquad , \qquad \frac{\boldsymbol{V_1}}{\boldsymbol{T_1}} = \frac{\boldsymbol{V_2}}{\boldsymbol{T_2}} \quad (\boldsymbol{for\ different\ condiotions})$$

Avogadro’s law:

The volume of a gas depends on the temperature, the pressure, and the number of gas molecules. Different gases at the same temperature have the same average kinetic energy. Hence, if two different gases are at the same temperature, occupy equal volumes, and exhibit equal pressures, each gas must contain the same number of molecules. This statement is true because systems with identical ***PVT*** properties can be produced only by equal numbers of molecules having the same average kinetic energy.

Equal volumes of different gases at the same temperature and pressure contain the same number of molecules.

$$\boldsymbol{V} \propto \boldsymbol{n} \qquad , \qquad \frac{\boldsymbol{V_1}}{\boldsymbol{n_1}} = \frac{\boldsymbol{V_2}}{\boldsymbol{n_2}} (\boldsymbol{for\ different\ condiotions})$$

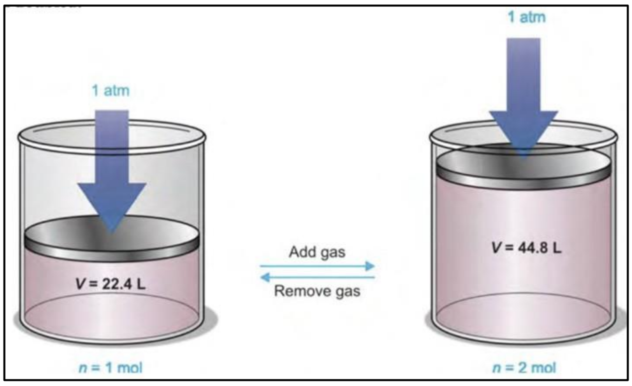


Figure 3

Combined Gas laws:

Boyle's Law and Charles' Law can be combined into a single relationship called the ***Combined Gas Law***

Boyle's law $\boldsymbol{V \propto \frac{1}{P}}$ (T, n constant)

Charles' law $\boldsymbol{V \propto T}$ (P, n constant)

Therefore, $\boldsymbol{V \propto \frac{T}{P}}$ (n constant)

For a fixed mass of gas, the volume is directly proportional to kelvin temperature and inversely proportional to the pressure.

$$\boldsymbol{\frac{PV}{T} = k \quad (n\ constat)}$$

If the pressure, volume and temperature of a gas be changed from P_1, V_1 and T_1 to P_2, T_2 and V_2, then

$$\boldsymbol{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

Gay-Lussac's law

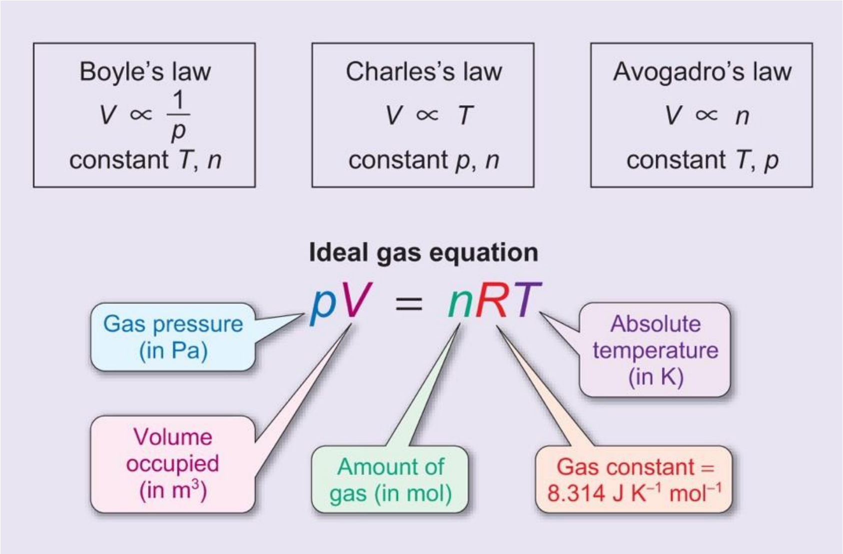
In 1802 Joseph *Gay-Lussac* as a result of his experiments established a general relation between the pressure and temperature of a gas. This is known as **Gay-Lussac's Law or Pressure-Temperature Law.** It states that:

At constant volume, the pressure of a fixed mass of gas is directly proportional to the Kelvin temperature or absolute temperature.

$$\boldsymbol{P \propto T \qquad or \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

Ideal Gas law:

Now we can summarize the whole above relationships that used in gas calculations by combining them in a single equation:



Where ***V*** is the volume, ***P*** is the pressure, ***T*** is the temperature, ***n*** is the number of molecules of moles, and ***R*** as known is the ideal gas constant. The units of ***R*** depend on the units of ***P, V*** and ***T***. In addition, we can calculate ***R*** by taking ***1 mole*** of a gas at ***STP*** conditions:

$$\boxed{\boldsymbol{R = \frac{PV}{nT} = \frac{(1\,atm)(22.4\,L)}{(1\,mol)(237\,K)} = 0.0821\ \frac{L.atm}{mol.K}}}$$

Values of gas constant, R

- 8.314 $JK^{-1}mol^{-1}$
- 0.0821 L.atm/ mol. K
- 8.314 Pa m^3 K^{-1} mol^{-1}
- 62.3 mmHg L K^{-1} mol^{-1}

Secondly: Mixtures of Gases

Dalton's Law of Partial Pressures:

There is plenty of space between the molecules in a gas. This means that, when gases mix together, the molecules can easily intermingle (mix).

The figure below shows three containers of equal volume. The first one contains a gas exerting a pressure ***P_A***, the second one contains a different gas exerting a pressure ***P_B***. While in the third container, the two gases occupy the same volume together.

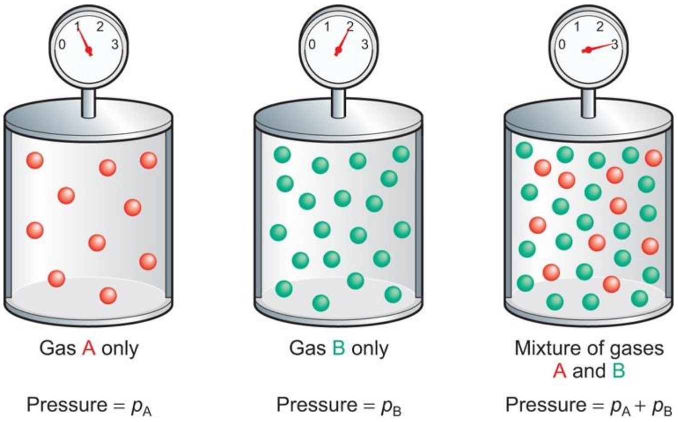


Figure 4

Therefore, the total pressure is simply the sum of the two individual pressures. This is expressed in ***Dalton's law***:

The total pressure of a mixture of gases is the sum of the partial pressures exerted by each individual gas.

The ***partial pressure***: is the pressure that can be exerted if the gas was alone in the container.

In general, for a mixture of gases, A, B, C, …….

$$P_{total} = P_A + P_B + P_C + \dots\dots\dots = \sum_i Pi$$

To describe the proportion of each component in a mixture, the mole fraction, ***X***, of the component is used. This is given by:

Mole fraction of gas A: $$X_A = \frac{number\ of\ moles\ of\ A}{total\ number\ of\ moles} = \frac{n_A}{n_{total}}$$

Note:

- The sum of the mole fractions for all the components in a mixture is equal to (1).
- The mole fraction has no units because it is a ratio.

For an ideal gas, at constant ***V*** and ***T***, $P_A \propto n_A$
So, for a component A in a mixture of gases

$$\frac{P_A}{P_{total}} = \frac{n_A}{n_{total}} = X_A, \quad So, \quad \frac{P_A}{P_{total}} = X_A$$

then the partial pressure: $\boxed{P_A = X_A P_{total}}$

The Real Gases

For many gases (such as N_2, O_2, and He) at around atmospheric pressure, the ideal gas equation describes their bahaviour very well. However, these gases are termed nonideal or real gases. The behavior of other gases (such as CO_2 and butane) deviates slightly from the ideal model behavior even at atmospheric pressure. So how might ideal gas equation be tested?

An ideal gas obeys Boyle's law under all conditions. If the volume of a fixed amount of a gas is measured as a function of pressure at constant temperature, a plot of ***P*** versus ***1/V*** will give a straight line of the gas obeys Boyle's law. As shown in Figure 5, there is a very good agreement between Boyle's law and experimental data at low pressures but deviations from ideal behavior occur when the pressure increases.

An alternative approach is to plot P versus V. Plots of pressure versus volume at fixed temperatures are called ***p-V isotherms***. Examples for three temperatures are shown in the figure below, where the solids lines are predicted from the ideal gas equation and the points are experimental measurements. There is a good fit of the experimental results to ideal behavior, particularly at higher temperatures and lower pressures. However, at low temperatures or high pressures, there are marked deviations from ideal behavior.

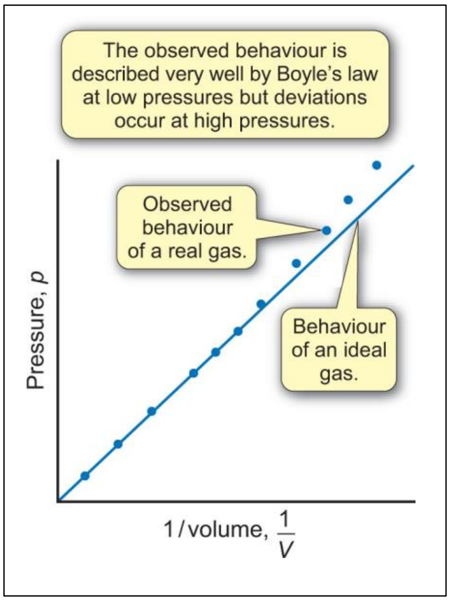


Figure 5

Comparison of the behavior of a real gas with that of an ideal gas (the straight line)

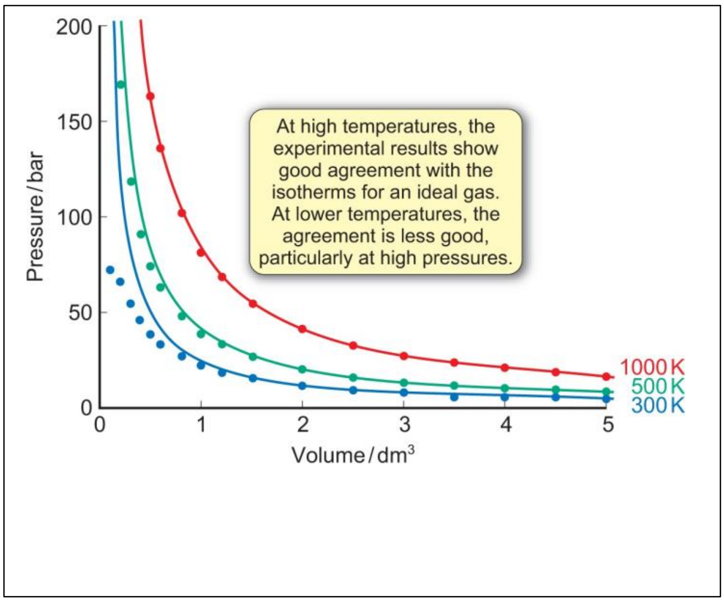


Figure 6

P-V isotherms for gases. The points show experimental measurements; the solid lines show the behavior of an ideal gas

The plots in Figure 5 and 6 Suggest that pressure of a sample of a gas can be increased indefinitely with little change in gas behavior. However, this does not happen in reality because, if the pressure is increased enough, especially at low temperatures, the gas will start liquefy, as shown in Figure 7.

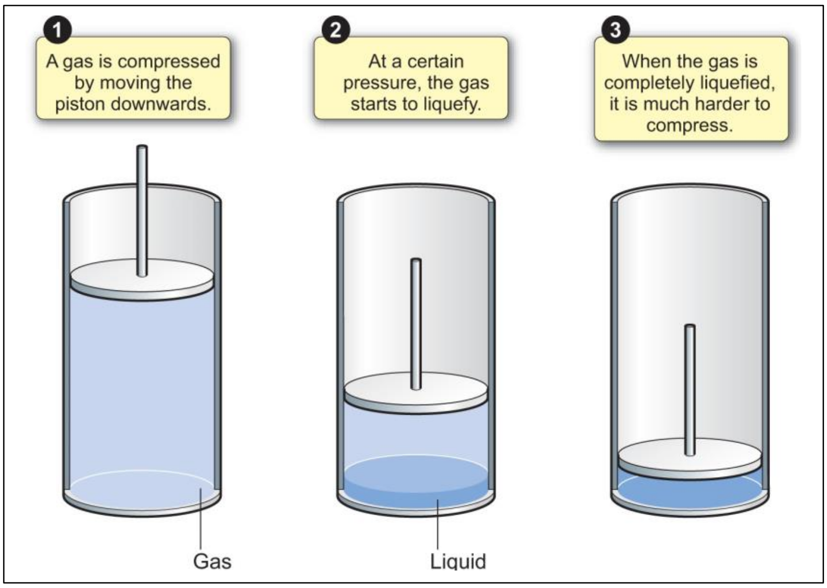


Figure 7

In Figure …. , at low pressures, the isotherm looks like that for an ideal gas. However, as the pressure increases, a value is reached where the gas starts to liquefy and noticeable decrease in volume occurs with no change in gas pressure (the flat step in the graph). When all the gas has turned to liquid, the curve is much steeper since it takes very large pressure changes to significantly change the volume of a liquid -it is much less compressible.

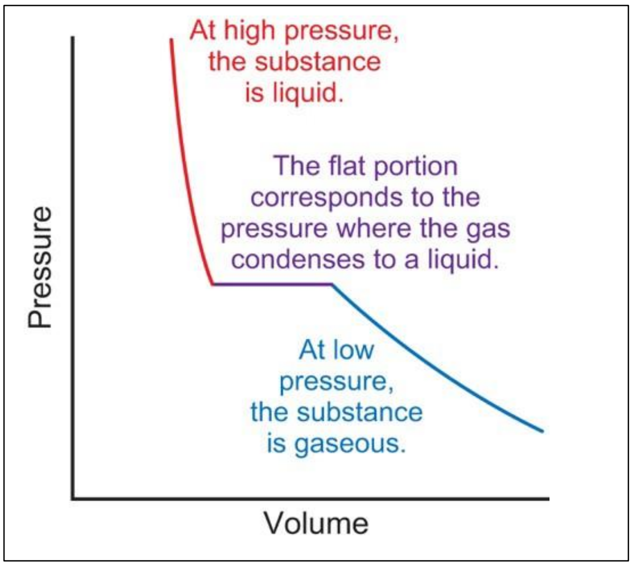
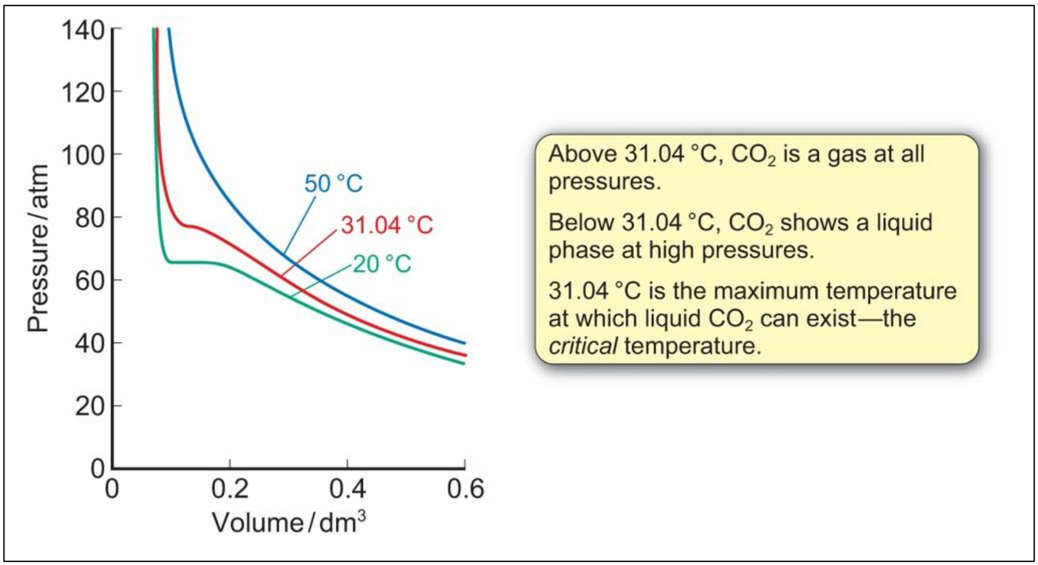


Figure 8: A p – V isotherm showing condensation of a real gas.

Some experimental data for the isotherms of carbon dioxide CO_2, Figure …, demonstrate the behavior of a real gas at different temperatures. At 50 °C, the isotherms looks like that for an ideal gas. At this T, the compound exists as a gas at any pressure. While at low temperature of 20 °C , the isotherm shows that liquefaction occurs when the pressure reached about 60 atm.



Above 31.04 °C, CO_2 is a gas at all pressures.

Below 31.04 °C, CO_2 shows a liquid phase at high pressures.

31.04 °C is the maximum temperature at which liquid CO_2 can exist—the *critical* temperature.

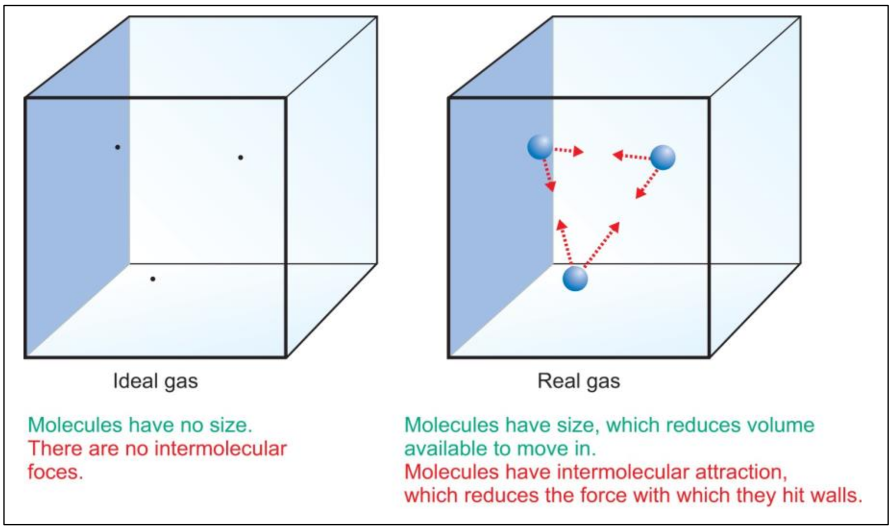
Figure 9: Experimental p – V isotherms for 1 mol of carbon dioxide, CO_2.

At 31.4 ℃, the behavior is different and the isotherm shows a point of inflection. 31.4℃ is the highest temperature at which the liquid CO_2 can exist and known as the critical temperature Tc. Above Tc, the gas cannot be liquified simply by increasing the pressure. Liquid CO_2 can only exist below ***T_c***.

To summarize, real gases show deviations from the perfect gas law because molecules interact with one another. A point to keep in mind is that ***repulsive forces*** between molecules assist expansion and ***attractive forces*** assist compression.

Two assumptions that are defining an ideal gas:

1. The size of the molecules is negligible.
2. There are no intermolecular interactions.



Molecules have no size.
There are no intermolecular foces.

Molecules have size, which reduces volume available to move in.
Molecules have intermolecular attraction, which reduces the force with which they hit walls.

Figure 10

(a) The compression factor

The compression factor, Z, of a gas is the ratio of its measured molar volume, $V_{m(r)} = V/n$, to the molar volume of a perfect gas, $V_{m(i)}$, at the same pressure and temperature:

$$\boxed{Z = \frac{V_m}{V_m^{\circ}}}$$

Because the molar volume of a perfect gas for ***1 mol*** is equal to: $V^{\circ}_m = RT/P$, an equivalent expression is

$$\boxed{Z = \frac{PV_m}{RT}}$$

Because for a perfect gas *Z* =1 under all conditions, deviation of *Z* from 1 is a measure of departure from perfect behaviour. Some experimental values of *Z* are plotted in Fig. 11 At very low pressures, all the gases shown have $Z \approx 1$ and behave nearly perfectly. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

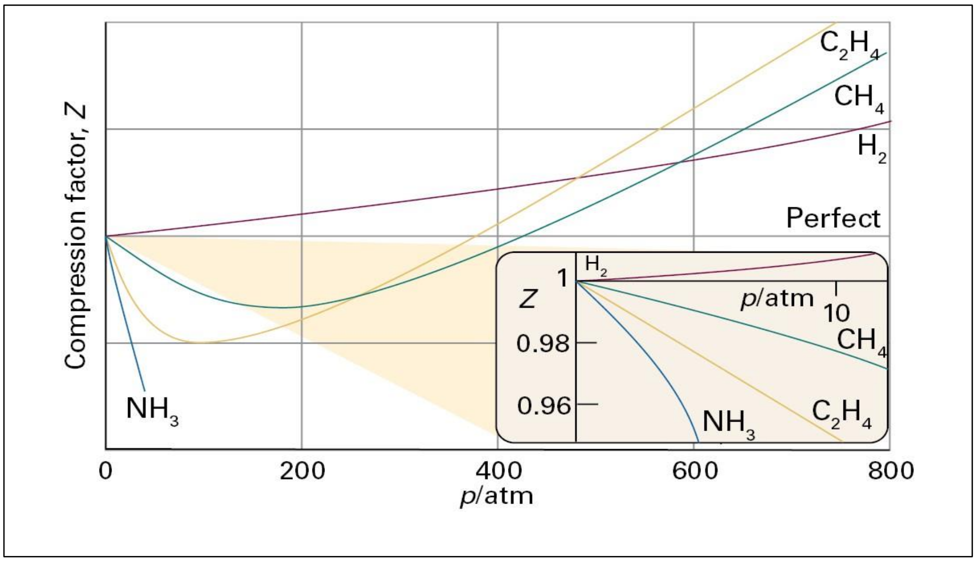


Figure 11: The variation of the compression factor Z, with pressure for several gases at 0°C

(b) The van der Waals equation for gases:

The first successful attempt to account for the behavior of real gases was introduced by the Dutch physicist Johannes van der Waals in 1873. He started from the ideal gas equation and introduced some additional terms to account for the behavior of real gases.

1. The first correction accounts for the attractions between the molecules. These mean that, in a real gas, the pressure is somewhat less than in the ideal case. Thus, van der Waals suggested that a correction factor should be added to the actual value of (***P)*** to make up for the slightly reduced pressure, and so obtain the ideal value:

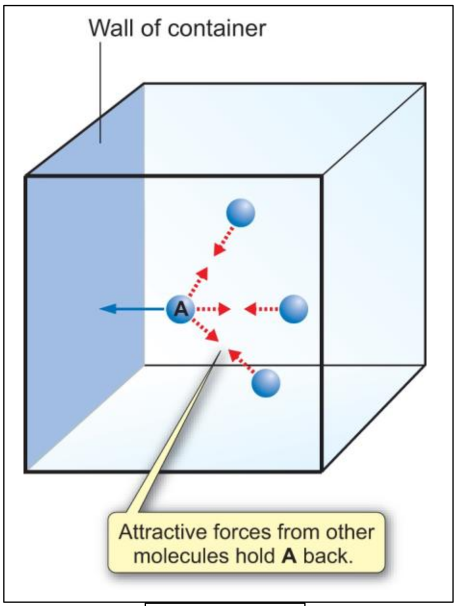
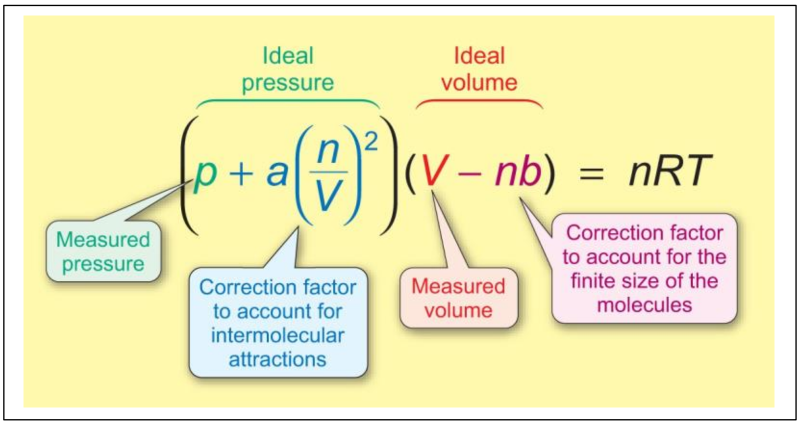


Figure 12

2. The second correction concerns the finite size of the molecules. Because the molecules have a small volume of their own, the volume in which molecules can move is less than the total volume of the container. So, van der Waals subtracted a correction factor from the actual value of V to allow for this reduction. This takes the form (***V – nb***), where the value of ***(b)*** is a constant related to the volume of the molecules.



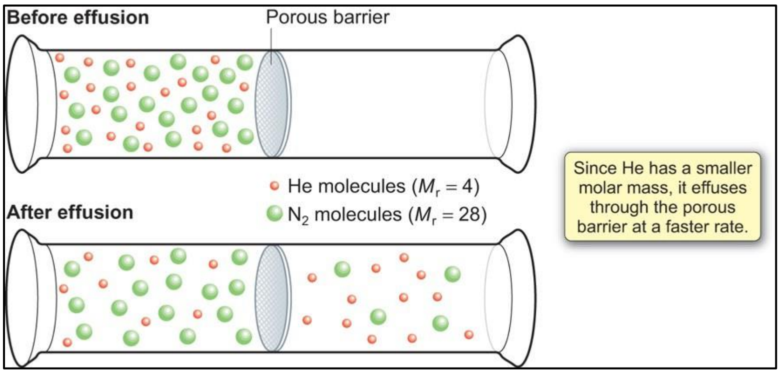
The constants ***a*** and ***b*** are called the ***van der Waals*** coefficients. Therefore, a represents the strength of attractions interactions between the molecules. They are characteristic of each gas but independent of the temperature.

Effusion and Diffusion

In 1833, Thomas Graham studied the effusion of a range of gases and found that:

At a given temperature and gas pressure, the rate of effusion (the number of molecules passing through the hole per second) is inversely proportional to the square root of the molar mass. **Rate of effusion** $\propto \frac{\mathbf{1}}{\sqrt{\boldsymbol{M}}}$

The effusion process in which gas molecules pass through a small hole such as a pore in a membrane, as shown in the figure below. Therefore, effusion can be defined as the process when gas molecules escape through a tiny hole into an evacuated space.



Since He has a smaller molar mass, it effuses through the porous barrier at a faster rate.

Figure 13

For a mixture of two gases, ***A*** and ***B***, with molar masses, $\boldsymbol{M_A}$ and $\boldsymbol{M_B}$, the ***Graham's law*** of effusion can be written as:

$$\frac{Rate\ of\ effusion\ of\ \boldsymbol{A}}{Rate\ of\ effusion\ of\ \boldsymbol{B}} = \mathbf{c}\,\frac{\overline{M_{\mathrm{e}}}}{\boldsymbol{M}_{\mathrm{f}}}$$

Gases with different molar masses will effuse at different rates. A gas with a low molar mass (such as helium) effuses faster than a gas with higher molar mass (such as Nitrogen). This explains why a balloon filled with helium collapses faster than if filled with air.

The process of ***Diffusion*** also depends on the movement of molecules. The figure below illustrates how ***diffusion*** differs from ***effusion***. Diffusion occurs when two (or more) gases come into contact and mix. There are large spaces between molecules, so they can easily mix.

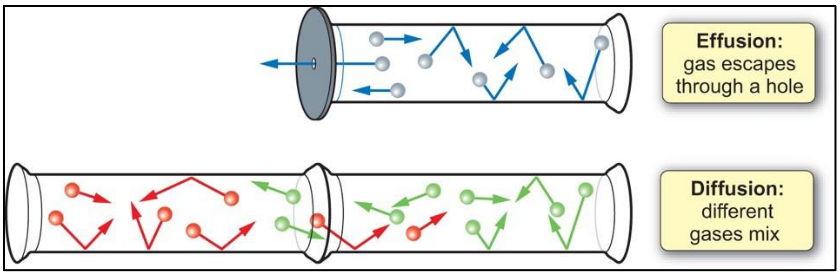


Figure 14

Diffusion is the random motion or movement of gas molecules from a region of high concentration to a region of lower concentration.

Chapter 3

Thermodynamics

THERMODYNAMICS

Thermodynamics is the branch of science that deals with the transformations of energy as heat or work. Thermodynamics is concerned with the study of ***macroscopic*** systems, those consisting of large, measurable amounts of matter. It does not deal with the properties of individual molecules.

Thermodynamics terms and basic concepts

An important part of the study of thermodynamics is a few terms and definitions that must be understood clearly:

► ***System, Boundary, Surroundings***

- ***A system*** is any part of the Universe that is of interest (chosen for studying).
- ***Surrounding*** is the rest of the universe.
- ***A boundary*** is the actual or notional surface that separates the system from its surrounding.

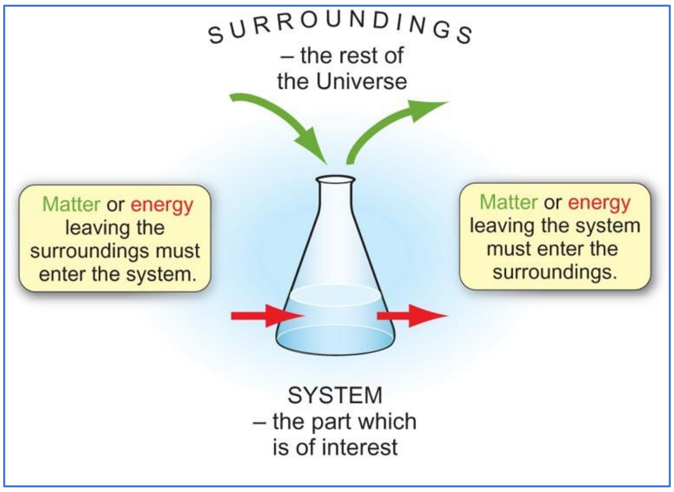


Figure 1: The system and surroundings. A change for the system causes a change with the same magnitude (size) but with opposite sign in the surroundings.

► Types of Thermodynamic systems

There are three types of thermodynamic systems depending on the nature of the boundary:

1. ***An open system:*** is a system in which both matter and energy can be exchanged with the surroundings.

   Hot water contained in a beaker placed on laboratory table is an open system. The water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

2. ***A closed system:*** is a system that can exchange only energy with the surroundings.

   A specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapor can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

3. ***An isolated system:*** is a system that can be no exchange energy and matter with the surroundings.

   Let us consider a system 100 ml of water in contact with its vapor in a closed vessel which is insulated. Since the vessel is sealed, no water vapor (matter) can escape from it. Also, because the vessel is insulated, no heat (energy) can be exchanged with the surroundings.

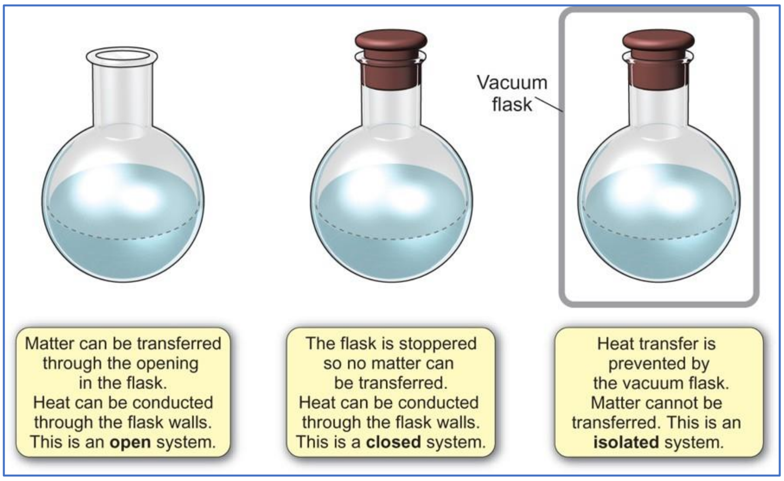


Figure 2: Types of Thermodynamic systems

► ***Properties of a system: Intensive and Extensive properties***

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:

(a) Intensive properties
(b) Extensive properties

Intensive Properties

A property which does not depend on the quantity of matter present in the system, is known as an intensive Property.

Some examples of intensive properties are *pressure, temperature, density*, and *concentration*. If the overall temperature of a glass of water (our system) is 20°C, then any drop of water in that glass has a temperature of 20°C. Similarly, if the concentration of salt, NaCl, in the glass of water is 0.1 mole/litre, then any drop of water from the glass also has a salt concentration of 0.1 mole/litre.

Extensive Properties

A property that does depend on the quantity of matter present in the system, is called an Extensive Property.

Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy*. Some of these properties are unfamiliar to you but these will be defined and illustrated later.

Intensive properties	Extensive properties
Temperature	**Mass**
Pressure	**Length**
Density	**Volume**
Specific heat capacity	**Amount of substance**
Molar heat capacity	**Enthalpy**
Concentration	**Entropy**
All molar properties	**Gibbs free energy**

► State of a system

The fundamental properties which determine the state of a system are pressure (*P*), temperature (*T*), volume (*V*), mass and composition. Since a change in the magnitude of such properties alters the state of the system, these are referred to as **State functions.**

A state function is a property that its values depend only on the current state of the system.

The most important thing to remember about a state function is that the change in value of the function depends only on the final and initial conditions. It is independent on the path between them. For example, internal energy, entropy, enthalpy, Gibbs free energy, mass, pressure, volume, temperature, …. etc. Therefore, for any state function**, *X***

$$\boxed{\Delta X = X_{final\ state} - X_{initial\ state}}$$

► Thermodynamic Processes

When a thermodynamic system changes from one state to another, the operation is called a Process. These processes involve the change of conditions (temperature, pressure and volume). The various types of thermodynamic processes are:

(1) Isothermal Processes

Those processes in which the temperature remains fixed, are termed isothermal processes. This is often achieved by placing the system in a thermostat (a constant temperature bath).

(2) Adiabatic Processes

Those processes in which no heat can flow into or out of the system, are called adiabatic processes. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle. High vacuum and highly polished surfaces help to achieve thermal insulation.

(3) Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes. For example, heating of water to its boiling point and its vaporization take place at the same atmospheric pressure.

(4) Isochoric Processes

Those processes in which the volume remains constant are known as isochoric processes. The heating of a substance in a non-expanding chamber is an example of isochoric process.

(5) Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

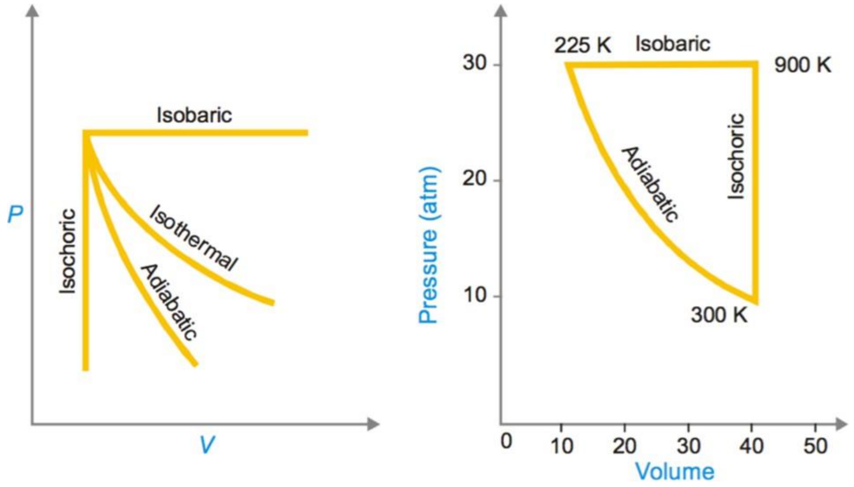


Figure 3:Types of Thermodynamic Processes

Work, Heat & Energy

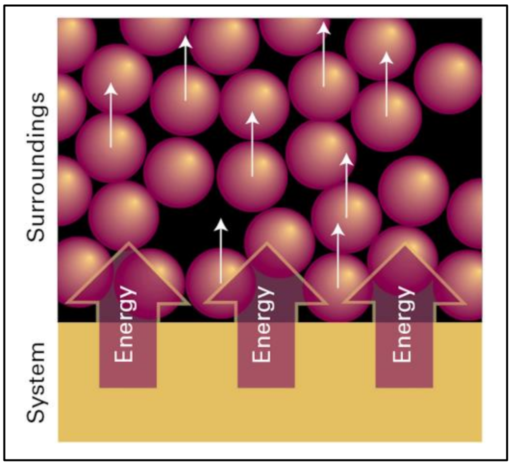
- ### Work

Mechanical work:

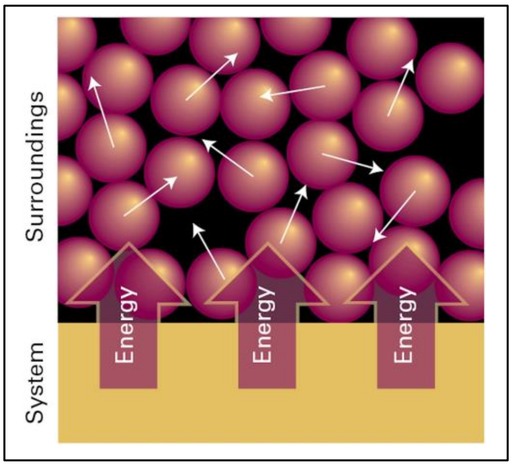
The fundamental physical property in thermodynamics is work: ***work*** is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

$$dw = F\,dz \quad \text{(definition of work)}$$

The state of a system is changed by the supply or removal of energy in the form of heat or work. In molecular terms, heating is the transfer of energy that makes use of disorderly, apparently random, molecular motion in the surroundings. In contrast, work is the transfer of energy that makes use of organized motion in the surroundings.



Work

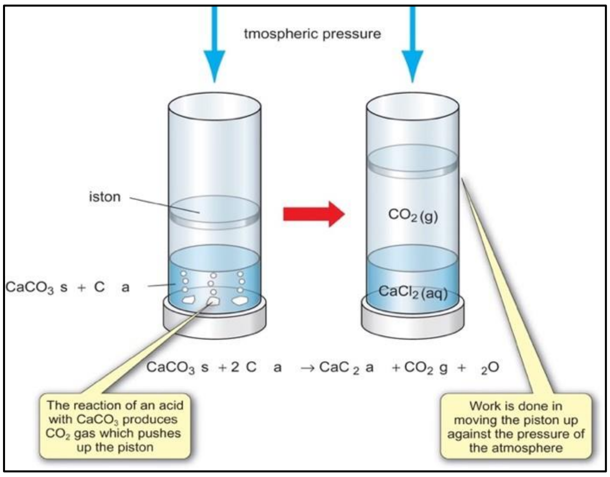


Heat

Therefore, when energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. On the other hand, when a system does work, it stimulates orderly motion in the surroundings.

Expansion Work

Expansion work is the work that arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation of gases or consumption of gases (for instance, the thermal decomposition of calcium carbonate as illustrated in Figure), and the thermodynamic characteristics of a reaction depend on the work it can do. The term 'expansion work' also includes work associated with negative changes of volume.



The reaction of an acid with $CaCO_3$ produces CO_2 gas which pushes up the piston

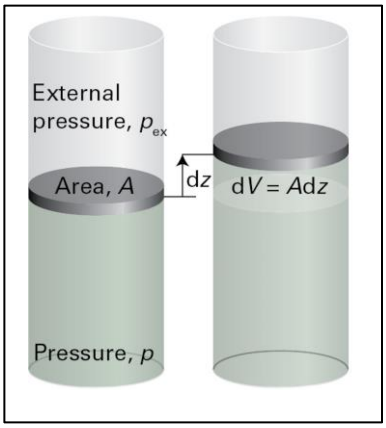
Work is done in moving the piston up against the pressure of the atmosphere

(a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance ***ds (dz)*** *against an opposing force.*

$$w = -\int_{v_i}^{v_f} P_{ex}\, dv$$

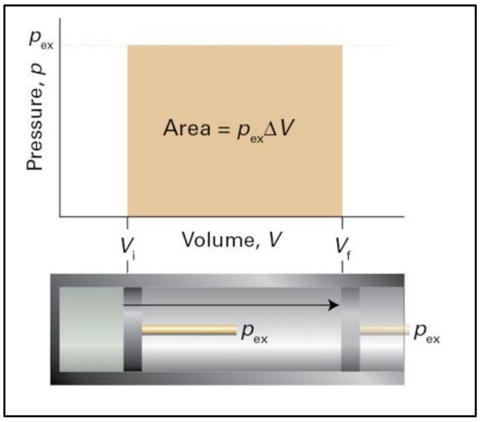
The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease.



(b) Expansion against constant pressure

Suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion.

$$w = -P_{ex}\,\Delta v$$



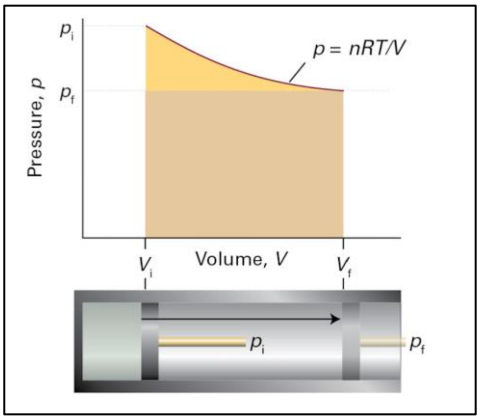
(c) Reversible expansion:

A reversible change or process means that a process which can be reversed in direction at any stage. The main idea of reversible expansion work is the system in equilibrium. $P = P_{ex}$

(d) Isothermal reversible expansion

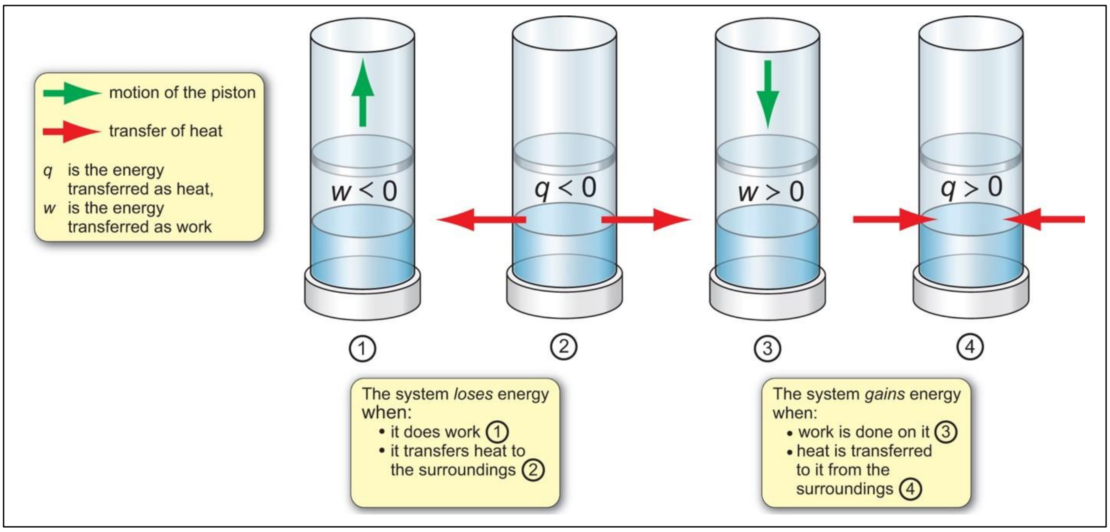
The expansion is made isothermal by keeping the system in thermal contact with its surroundings (a constant temperature bath).

$$w = -nRT\ \ln\frac{v_f}{v_i}$$



Note:

- **Energy gained (heat absorbed by or work done on) a system is *positive*;**
- **Energy lost (heat released from or work done by) a system is *negative*.**



► Energy is the capacity to do work.

SI Units: Joule, J which is equal to 1Nm = 1 Kg.m^2. s^{-2}

Power is the rate of supplying energy. Its unit is the ***Watt*, 1W = 1 J. s^{-1}**

There are many forms that energy can take. Some of these forms are thermal, mechanical, kinetic, potential, electric, magnetic, chemical, and nuclear. When you sum all of the forms of energy acting within a system you will obtain the system's total energy.

There are two types of energy that make up the energy of a system:

1. **Macroscopic forms**: are those which can be influenced by external effects such as gravity, magnetism electricity and surface tension.

   a. ***Kinetic Energy, K$_E$***: is the energy that the body possesses as a result of its motion.

   $K_o = \frac{1}{2}mv^2$ where, ***m*** = mass, ***v*** = velocity Unit: Joule

   b. ***Potential Energy, PE***: is the energy that body possesses as a result of its position.

   $P_o = mgh$ where m:mass, g: acceleration of gravity, h: height

2. **Microscopic forms**: are those related to the molecular structure of a system. The sum of microscopic energies is called ***internal energy.***

► **Heat** is the energy that transferred from on system to another as a result of thermal interactions.

There are two main processes in the energy transferring as heat:

1. ***An exothermic process*** is a process that releases energy as heat into the surroundings. All combustion reactions are exothermic.

2. ***An endothermic process*** is a process in which energy taken in from the surroundings.

Question:

1. Calculate the energy transferred as work, when **1 mol** of a gas expands from a volume of **5 dm^3** to **10 dm^3** against a constant pressure of **760 torr**.

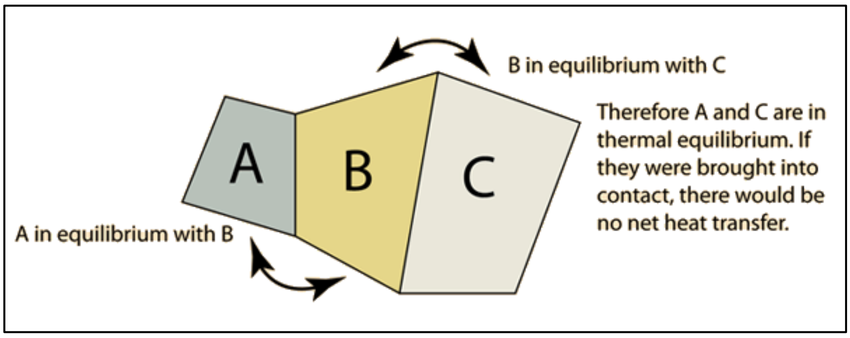
2. When a sample of 1.0 mol of Ar, regarded as a perfect gas, undergoes an isothermal reversible expansion at 20.0°C from 10.0 dm^3 to 30 dm^3. Calculate the work done.

3. A chemical reaction takes place in a container of cross-section area 75.0 cm2. As a result of the reaction, a piston is pushed out through 25.0 cm against an external pressure of 150 kPa. Calculate the work done by the system.

THERMODYNAMICS

Laws of Thermodynamics

1. **Zeroth law of thermodynamics**
   If two bodies are in thermal equilibrium with a third body, they are in thermal (thermodynamics) equilibrium with each other.



2. **First law of Thermodynamics**
   the first law can be state as '' Energy can be transferred or transformed but cannot be created or destroyed".

   The internal energy of an isolated system is constant.

   Mathematical formula: $\boxed{\Delta \boldsymbol{U} = \boldsymbol{q} + \boldsymbol{w}}$

   where $\Delta \boldsymbol{U}$: *the change in internal energy*
   $\boldsymbol{q}$: *energy transferred as heat*
   $\boldsymbol{w}$: *work done on/by the system*

- **Internal Energy**

The internal energy is the total energy of a system. It is the sum of potential and kinetic energy of the atoms, ions or molecules of the system.

The internal energy is a state function, so it depends only on the initial and final states of a system.

$\Delta \boldsymbol{U} = \boldsymbol{U}_f - \boldsymbol{U}_i$ Unit: Joule, **J = Kg.m^2.m^{-2}**

The internal energy of a system is an extensive property (depends on the amount of a substance). While the Molar Internal energy is an intensive property. The Molar internal energy is the internal energy divided by the amount of substance in a system. I

$$\boxed{U_m = \frac{U}{n}}$$

Unit: kJ/mol

► **There are two ways that the value of expansion work can be zero:**

1. **Free expansion: free expansion work when** ***P = 0*** **, so** ***w = 0***

   No expansion work is done because the gases expand into a vacuum. From the first law of thermodynamics

   $$\Delta U = q + w$$

   Therefore, $\Delta U = q_P$ Heat supplied to the system at constant pressure

2. **Reactions at constant volume:**

   $w = -P_{ex}\,\Delta v$ **because of at constant volume** $\Delta v = 0$

   so, $w = 0$

   $$\Delta U = q + w$$

   Therefore, $\Delta U = q_V$ Heat supplied to the system at constant volume

► **Enthalpy**

Enthalpy can be defined as a thermodynamic property, its value is the sum of internal energy plus the product of the pressure and volume of the system.

$$\boxed{H = U + pv}$$

The Enthalpy change, ΔH: is the heat transferred at constant pressure by a chemical reaction or a process.

Because of the internal energy, pressure and volume are state function, therefore the enthalpy is a state function. In addition, it depends on the amount of a substance, so it is an extensive property.

Q/ How to prove that enthalpy change is equal to the transferred heat at constant pressure?

$$\boxed{\Delta H = q_P}$$

► Heat capacities

Heat capacity is the heat needed to raise the temperature of a substance by 1K.
Unit: J/K
Mathematical formula:

$$\boxed{C = \frac{q}{\Delta T}}$$

where c: the heat capacity
q: quantity of heat supplied
ΔT: change in temperature

Heat capacity is an extensive property but can be an intensive property when:

1. ***Specific heat capacity***, Cs, which is the heat capacity of a sample divided by the mass.

$$\boxed{C_s = \frac{C}{m}\ , \qquad so\ , \quad C_s = \frac{q}{m\,\Delta T} \qquad Unit\colon \frac{J}{K.kg}}$$

2. ***Molar heat capacity***, **C_m**, which is the heat capacity of a sample divided by the amount of substance.

$$\boxed{C_m = \frac{C}{n} \qquad so\ , \quad C_m = \frac{q}{n\,\Delta T} \qquad Unit\colon \frac{J}{K.mol}}$$

► Isochoric and Isobaric Heat Capacities:

1. Heat capacity at constant pressure (isobaric): is the heat capacity that recorded at constant pressure.

$$C_P = \frac{q_P}{\Delta T} \qquad so, \quad q_P = C_P \, \Delta T$$

The heat capacity at constant pressure is used to relate the change in enthalpy to the change in temperature. Therefore, from the definition of the change in enthalpy, we proved that $\Delta H = q_{\}}$

So,

$$\Delta H = C_P \, \Delta T \qquad C_P = \frac{\Delta H}{\Delta T}$$

The heat capacity at constant pressure is the analogue of heat capacity at constant volume, and both of them are *extensive properties*. ***The molar heat capacity at constant pressure***, $C_{p,m}$, *is the heat capacity per mole pf substance; it is an intensive property.*

2. Heat capacity at constant volume (Isochoric heat capacity): is the heat capacity that recorded at constant volume

$$C_v = \frac{q_v}{\Delta T} \qquad so, \quad q_v = C_v \, \Delta T$$

From the first law of thermodynamic we proved that there is no expansion work is done at constant volume, therefore: $\Delta U = q_v$

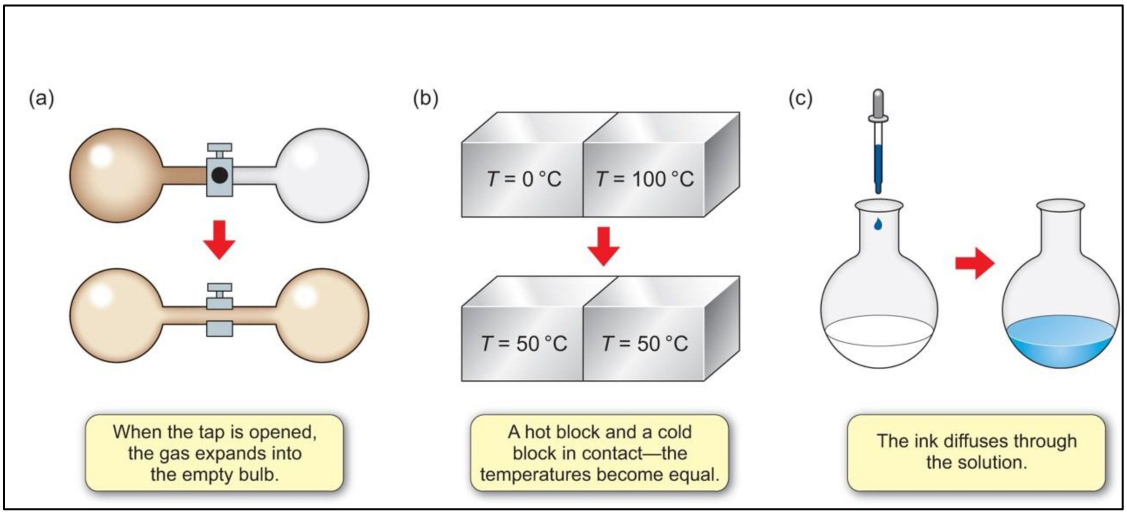
$$C_v = \frac{\Delta U}{\Delta T}$$

The molar heat capacity at constant volume, $C_{v,m}$, is the heat capacity per mole of substance.

Laws of Thermodynamics

3. The Second law of thermodynamics: what are spontaneous processes

A spontaneous process is a process that occurs naturally without any external intervention. As shown in the figures below, when the tap in figure (a) is opened, gas flows into an evacuated vessel until the pressure is equal on both sides. The same thing that happens when a block of hot metal is placed against a cold one, as in figure (b), it very unlikely that it will get hotter while cold one cools down. Heat will be transferred until both blocks are the same temperature.



► Entropy and the second law of Thermodynamics

The main use of Entropy is in predicting the direction of chemical (or any other) change. This is summarized in the Second Law of Thermodynamic. The second law can be stated in a number of ways, but the most straightforward is:

Spontaneous processes are those that increase the total entropy of the Universe

Since the entropy is related to disorder, the second law shows that spontaneous processes are those that lead to an increase in disorder of the Universe. The total entropy change for a process is made up of the changes for the system and the surroundings. The Second law can therefore be expressed as:

$$\boxed{\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}}$$

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$ ***spontaneous process***

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} < 0$ ***non- spontaneous process***

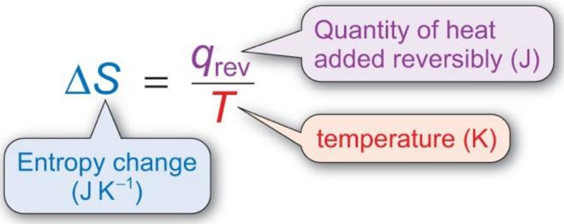
$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$ ***process is at equilibrium***

► The definitions of Entropy

Entropy is a measure of the randomness or disorder in a system. There are two approaches, one classical and one molecular. They turn out to be equivalent, but each one enriches the other:

a. The thermodynamics definitions of entropy

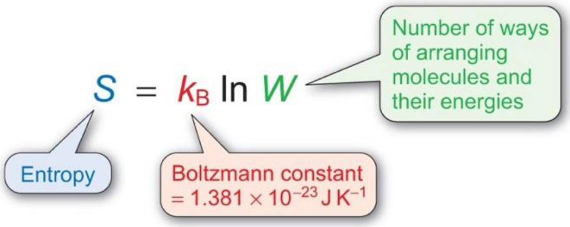
The thermodynamic definition of entropy concentrates on the change in entropy, ΔS, that occurs as a result of a physical or chemical change. As illustrated before, heat stimulates random motion in the surroundings. On the other hand, work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.



according to the above equation, when the energy transferred as heat is expressed in joules, J, and the temperature in kelvin, so the units of entropy are (J/K). entropy is an extensive property. Molar entropy is the entropy divided by the amount of substance, Sm = S/n, units are J/K.mol.

b. The statistical definitions of entropy

The entry point into the molecular interpretation of the Second law of thermodynamics is Boltzmann's formula.



W is the number of ways (microstates) of arranging the molecules and their energy in the system. The larger the number of arrangements, the less ordered the system, the larger the entropy.

► **The Entropy as a state function**

Entropy is a state function

A. The first step is to prove that Entropy is a state function and $\Delta S = \mathbf{q_{rev}} \mathbf{/ T}$ is independent on the path that taken between the initial and final states by Carnot Cycle. It is the most efficient heat engine cycle. It's a theoretical thermodynamic cycle named by the French engineer Carnot.

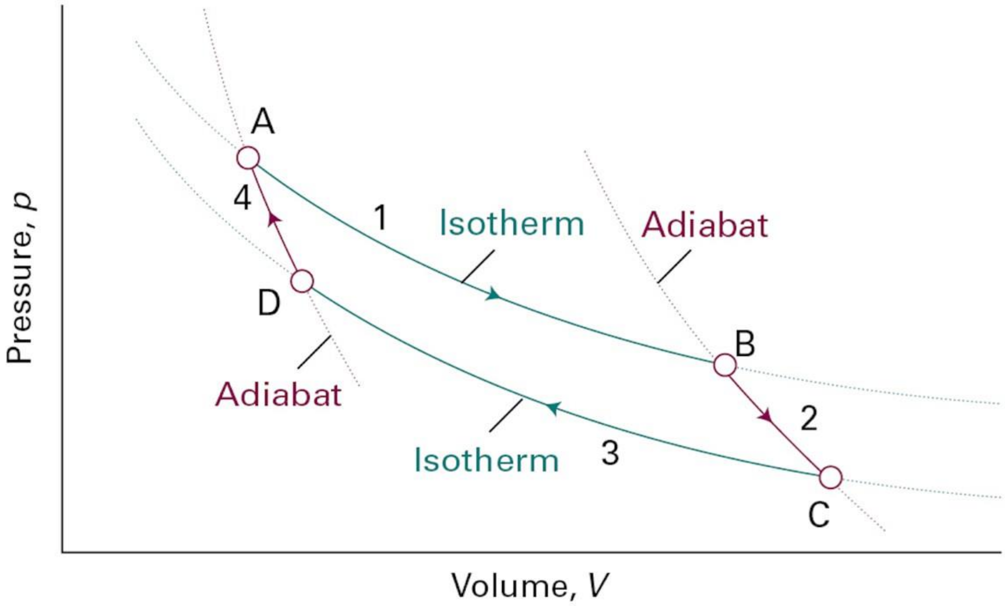
Carnot cycle consists of four reversible stages or processes:

1. Reversible isothermal expansion from A to B at $\mathbf{T_h}$; the entropy change is $\mathbf{q_h/T_h}$, where $\mathbf{q_h}$ is the energy supplied to the system as heat from the hot source.

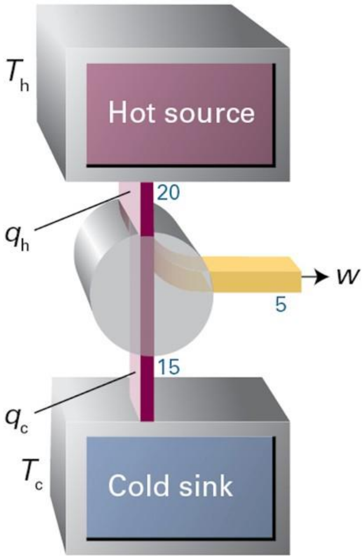
2. Reversible adiabatic expansion from B to C. no energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from $\mathbf{T_h}$ to Tc the temperature of the cold sink.

3. Reversible isothermal compression from C to D at $\mathbf{T_c}$. Energy is released as heat to the cold sink; the change in entropy of the system is $\mathbf{q_c/T_c}$; in this expression $\mathbf{q_c}$ is negative.

4. Reversible adiabatic compression from D to A. no energy enters the system as heat, so the change in entropy is zero. The temperature rises from $\mathbf{T_c}$ to $\mathbf{T_h}$.



B. The second step is to show that $\Delta S = q_{rev} / T$ can be applied to any material, not just a perfect gas. And this will be by finding the ***Efficiency*** of the heat engine. The efficiency of a heat engine relates how much useful work is output for a given amount of heat energy input.



Heat engine is basically a device that converts heat energy into mechanical work. Heat naturally flows from hot to cold reservoir. The system can absorb some of the heat energy and use it to convert it to mechanical work.

$$\boxed{\eta = \frac{\textit{work performed}}{\textit{heat absorbed from hot source}} = \frac{|w|}{|q_h|}}$$

The work in this case is equal to the difference between the heat energy of hot source and cold source.

$$\boldsymbol{w = |q_h| - |q_c|}$$

While the efficiency of Carnot cycle will be

$$\boldsymbol{\eta_c = 1 - \frac{T_c}{T_h}}$$

► **Entropy changes accompanying specific processes:**

We now see how to calculate the entropy changes that accompanying a variety of basic processes:

(a) Expansion

The change in Entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\boldsymbol{\Delta S = nR \ln \frac{V_f}{V_i}}$$

Entropy change for the isothermal expansion of a perfect gas

Because S is a state function, the value of ΔS is independent of the path between the initial and final states, so this expression applies whether the change of state occurs reversible or irreversible.

(b) Phase transitions

Entropy changes during of phase-fusion (melting), vaporization, sublimation provide straightforward applications of of equation ΔS = q/T. At the normal temperature of phase change, the reversible heat change at constant pressure is the enthalpy change so that $\boldsymbol{q_{rev} = \Delta H}$

$$\boldsymbol{\Delta_{vap}S = S_{(vapour)} - S_{(liquid)}} \quad \textbf{and} \quad \boldsymbol{q_{rev} = \Delta_{vap}H}$$

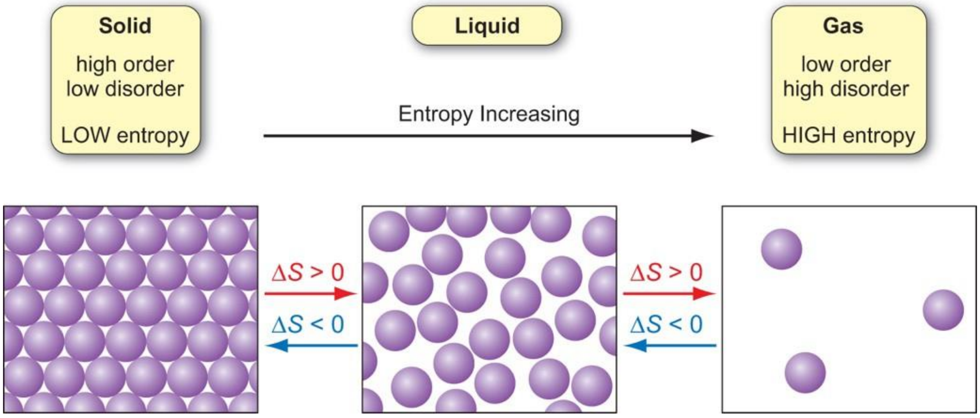
$$\boldsymbol{\Delta_{fus}S = S_{(liquid)} - S_{(solid)}} \quad \textbf{and} \quad \boldsymbol{q_{rev} = \Delta_{fus}H}$$

therefore,

$$\Delta_{vap}S = \frac{\Delta_{vap}H^\circ}{T_b} \qquad \Delta_{fus}S = \frac{\Delta_{fus}H^\circ}{T_m}$$

where $\Delta_{vap}H^\circ$ and $\Delta_{fus}H^\circ$ are the standard enthalpy changes of vaporization and fusion at the boiling point and melting point, T_b and T_m, respectively. The entropy changes for the reverse processes- condensation and freezing- have the opposite sign but the same magnitude as those for vaporization and fusion.

$\Delta_{vap}H^\circ$ and $\Delta_{fus}H$ have positive values since vaporization and fusion are endothermic processes and an input of energy required. This is consistent with the idea of entropy as a measure of disorder. A vapor is more disordered- and so has higher entropy than liquid as illustrated in the figure below:

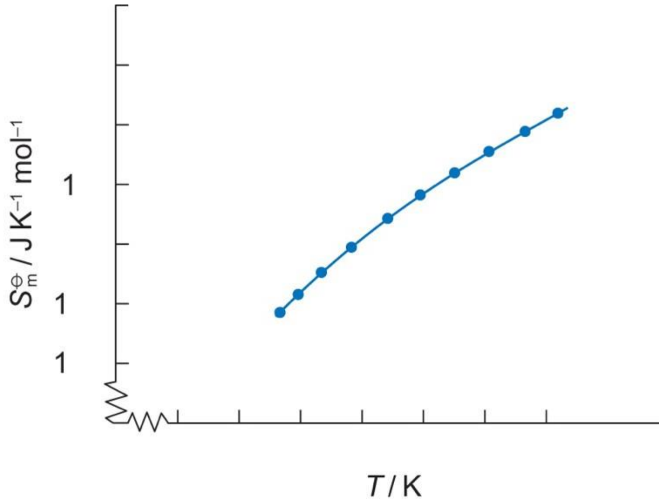


(c) Heating – how the entropy of a system changes with temperature:

As the temperature increases, matter generally becomes more disordered. The entropy of a system will increase with temperature**.**

The difference between the entropy of 1 mol of a substance (its molar entropy) at two temperatures is given by the equation below. When S_{Ti} is the molar entropy of a substance at an initial temperature T_i and S_{Tf}, is the molar entropy at the final temperature T_f.

$$S_{Tf} = S_{Ti} + C_P \ln \frac{T_f}{T_i}$$



Questions

1. A heat engine absorbs 2500J of heat and discards 2100J of heat. Calculate the work performed by this engine and its thermal efficiency.

2. A jet engine releases 5000 J of energy per cycle and performs 800J of work. (a) how much heat is absorbed by this engine per cycle? (b) what is the thermal efficiency? (c) how much work can this engine perform in 50 cycles? (d) if the engine completes each cycle in 0.20 seconds, what is the power rating of this engine?

3. 8000 J of heat energy is absorbed per cycle by a diesel engine that is 15% efficient. (a) How much work does it perform per cycle? (b) how much energy does it expel to the environment per cycle?

4. An engine has a heat input of 175 kW and a work output of 21 kW. (a) what is the thermal efficiency? (b) at what rate is heat discarded into the environment?

5. A Carnot engine takes in 4500J of heat energy from a reservoir at 800K. (a) how much energy will be released to a cold reservoir at 300K? (b) how much work is performed by this engine? (c) what is the efficiency?

Laws of Thermodynamics

4. The Third law of Thermodynamics

Entropy is related to disorder, so a perfectly ordered system has zero entropy. Such a system would be a perfect solid crystal at absolute zero of temperature so that there is no disorder of any type. A perfect crystal is one with all the atoms, ions, or molecules aligned perfectly and with no defects. At 0K, all molecules will be in their ground state. There is only one way of arranging the molecules, so ***W= 1*** in the Boltzmann formula and hence ***S = 0***.

(a) The Nernst heat theorem

The experimental observation that turn out to be consistent with the view that entropy of a regular array of molecules is zero at T = 0. So, it is summarized as "*The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero:* $\Delta S \to 0$ *as* $T \to 0$ *provided all the substances involved are perfectly ordered*. This conclusion is summarized by the ***Third law of Thermodynamics:***

The entropy of all perfect crystalline substances at zero kelvin is zero.

(b) Third-law entropies

Entropies reported on the basis that S (0) = 0 are called Third-law entropies (and commonly just 'entropies'). When the substance is in its standard state at the temperature T, the standard (Third-law) entropy is denoted S^0. The standard entropy S^0_{298}, of a substance is the entropy of 1 mol at 298K and 1 bar pressure. The units are $J\ K^{-1} mol^{-}.^{1}$

► Standard entropy change of reaction

The standard entropy change of a reaction is defined as the difference between the molar entropies of the pure, separated products and pure, separated reactants. For values at 298K

$$\Delta_r S^{\ominus}_{298} = \underbrace{\sum \nu_i S^{\ominus}_{298}\,(\text{products})} - \underbrace{\sum \nu_i S^{\ominus}_{298}\,(\text{reactants})}$$

Since S^{0}_{298} refers to one mole of a substance, it must be multiplied by the stoichiometric coefficient, ν_i, in the balanced equation for the reaction.

Example

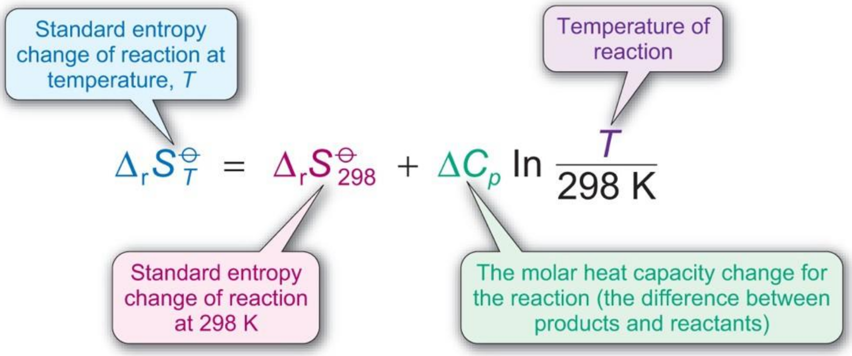
Calculate the standard entropy change of a reaction at 298K for each of the following reactions:

a. $C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$

b. $C_2H_5OH_{(l)} + CH_3CO_2H_{(l)} \rightarrow CH_3CO_2C_2H_{5(l)} + H_2O_{(l)}$

► Reactions at other temperatures

The entropy change at other temperature can be calculated by using the equation below to find the standard entropies of the reactants and products at other temperatures. The standard entropy change of reaction at temperature T, given by:



$$\Delta_r S^{\ominus}_T = \Delta_r S^{\ominus}_{298} + \Delta C_p \ln \frac{T}{298\ \text{K}}$$

The above equation enables the calculation of entropy changes for reactions at any temperature as long as heat capacity data are available. **ΔC_p** is the difference in molar heat capacities of the products and reactants given by this equation:

$$\Delta C_p = \text{à}\, v_i C_p\,(\mathbf{products}) - \text{à}\, v_i C_p\,(\mathbf{reactants})$$

Example

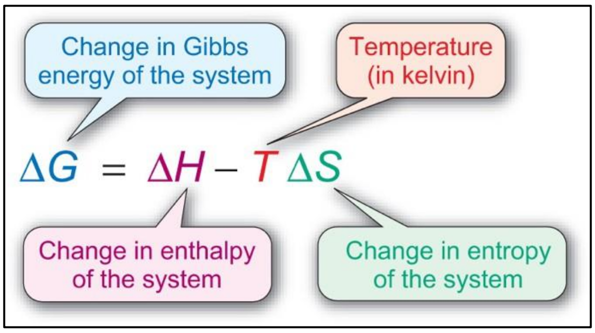
The entropy changes at 298K for the following reactions are as shown. Calculate $\Delta_{\text{å}} S$ for each reaction at 1023 K.

- **a.** $C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta_{\text{å}} S°_{\text{äää}}$ = +2.96 $JK^{-1}mol^{-1}$
- **b.** $N_{2(g)} + 3H_2 \rightarrow 2NH_{3(g)}$ $\Delta_{\text{å}} S°_{\text{äãå}}$ = - 198.7 $JK^{-1}mol^{-1}$

► Gibbs free energy

Total entropy change and Gibbs energy change

The sign of total entropy change for a reaction indicates whether or not it will be spontaneous. The Gibbs energy change, ΔG, combines changes in enthalpy and entropy into a single state function that describes the spontaneity of a process at constant temperature and pressure and uses only properties of the system.



Since the enthalpy and entropy are state functions, Gibbs energy must also be a state function. The requirement for a change to be spontaneous is $\Delta S > 0$. Since ΔG = $-\,T\Delta S$. Therefore, the key relationships are summarized as follows:

- If $\Delta G < 0$ *the reaction or process is spontaneous*
- If $\Delta G > 0$ *the reaction or process is non- spontaneous*
- If $\Delta G = 0$ *the reaction or process is at equilibrium*

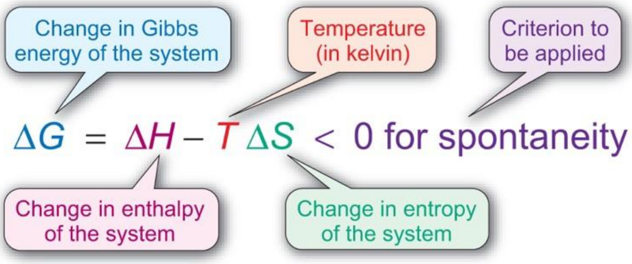
Processes that have $\Delta G < 0$ are spontaneous because they increase the entropy of the Universe and thus obey the Second law. The Gibbs energy just gives a convenient way of applying the Second Law while considering properties only of the system.

Example

Calculate the change in Gibbs energy when 1.00 mol of ice melts at: (**a**) 0℃ (**b**) 10 ℃ (**c**) -10 ℃. Comment on the results of each temperature.
($\Delta_{éèê}H°$ (H_2O) = +6.01 kJ mol^{-1} and $\Delta_{éèê}S°$ (H_2O) = +22.0 J K^{-1} mol^{-1})

► **Gibbs energy: the balance between enthalpy change and entropy change**

If we look again in detail to the equation of the definition of Gibbs energy, as below,

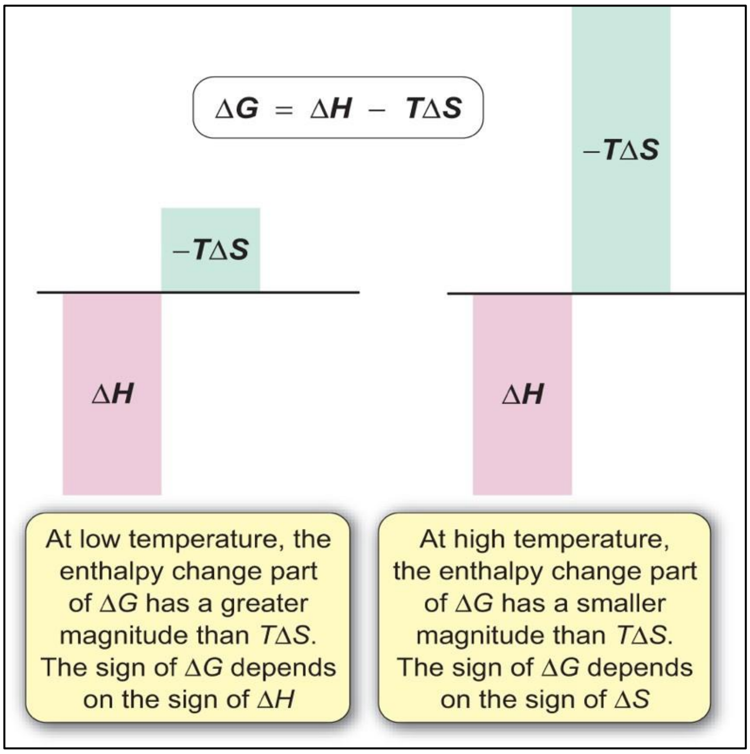


the Gibbs energy change must be negative for a process to be spontaneous at constant temperature and pressure. But for the contributions of enthalpy and entropy changes:

- ΔH < 0 *(negative, exothermic change) makes a favorable contribution to spontaneity.*
- ΔH > 0 *(positive, endothermic change) makes an unfavorable contribution to spontaneity.*

- ΔS < 0 *(negative, entropy decreases) makes an unfavorable contribution to spontaneity.*
- ΔS > 0 *(positive, entropy increases) makes a favorable contribution to spontaneity.*

The contribution of ΔS *works* in the opposite way to that of ΔH because of the minus sign in the $(-T\Delta S)$ term. The temperature determines the relative importance of these two contributions.



An exothermic reaction that also has an increase in entropy will be spontaneous at all temperatures, since both contributions lead to a negative value for ΔG. An endothermic reaction that also has a decrease of entropy will be non-spontaneous at all temperatures, since both contributions lead to a positive value for ΔG. As illustrated in the table below:

Reaction	**Value of ΔH**	**Value of ΔS**	**Value of ΔG**	**Spontaneity**
Endothermic	Positive, > 0	Negative, < 0	Positive for all T	Never spontaneous
Endothermic	Positive, > 0	Positive, > 0	Positive at low T, Negative at high T	Becomes spontaneous on heating
Exothermic	Negative, < 0	Positive, > 0	Negative for all T	Always spontaneous
Exothermic	Negative, < 0	Negative, < 0	Positive at high T; Negative at low T	Becomes spontaneous on cooling

Helmholtz Free Energy

Helmholtz energy, *A*, is a thermodynamics property that determine the the criteria of spontaneous change.

$$\boxed{dA_{T,v} \leq 0 \ \text{= spontaneous}}$$

Helmholtz energy is independent on the path of the reaction or the process, so it's a state function. Moreover, it is an extensive property.

The Helmholtz and Gibbs energies

Consider a system in thermal equilibrium with its surroundings at a temperature *T*. When a change in the systems occurs and there is a transfer of energy as heat between the system and the surroundings, the ***Clausius inequality*** (the expression ***Clausius inequality*** proves to be of great importance for the discussion of the spontaneity of chemical reactions) reads

$$dS - \frac{dq}{T} \geq 0$$

we can develop this inequality in two ways according to the conditions (of constant volume or constant pressure)

(a) Consider heating at constant volume and temperature. Then in the absence of additional (non-expansion) work, we can write $dq_v = dU$, consequently

$$dS - \frac{dU}{T} \geq 0 \qquad \boxed{dA_{T,v} \leq 0 \ \text{= spontaneous}}$$

(b) Consider heating at constant pressure and temperature. When energy transferred as heat at constant pressure, and there is no work other than expansion work, we can write $dq_p = dH$, consequently

$$dS - \frac{dH}{T} \geq 0$$

$$\boxed{dG_{T,p} \leq 0 \ \text{= spontaneous}}$$

Maximum work

The change in the Helmholtz function is equal to the maximum work accompanying a process at constant temperature:

$$\boxed{dw_{max} = dA \qquad \textbf{Maximum work (constant T)}}$$

As a result, A is sometimes called the 'maximum work function' or the 'work function'.

► Maximum non-expansion work

The analogue of the maximum work interpretation of ΔA, and the origin of the name 'free energy' can be found for ΔG. In the following equation, we show that at constant temperature and pressure, the maximum additional (non-expansion) work, $w_{add,max}$ is given by the change in Gibbs energy:

$$\boxed{w_{add,max} = \Delta G \qquad \textbf{Maximum non-expansion work } (\textit{constant } T \textit{ and } p)}$$

This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells.

Chapter 4

Electrochemistry

Electro chemistry

2- ELECTROCHEMICAL CELLS

Let us consider the reaction

$2\ Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$

It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na+ ion. At the same time, Cl gains an electron and is reduced to Cl^- ion. Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction** in brief.

2-1 Types of electrodes

1- Metal-Metal ion electrodes

A metal rode that dipped in an electrolyte solution containing metal ions. Ther is a potential difference between these two phases and this electrode can act as a cathode or anode

Anode: $M \longrightarrow M^{n+} + ne^-$

The potential of a single electrode in a half-cell is called the **Single electrode potential.** So the Nernst eq. takes the form:

$$E = E^{\ominus} - \frac{RT}{zF} \ln a_{M^{+n}}$$

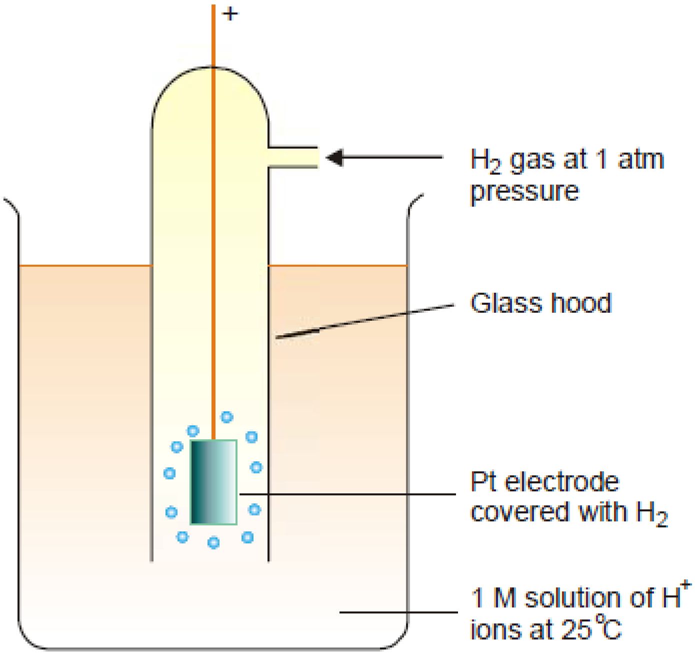
2--Gas electrode (Standard Hydrogen Electrode (SHE)

Electrode gases like H_2, Cl_2....etc. are used with their respective ions , for example: H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

This electrode is also used to measure other potentials **(emf)**. Its own potential is est to 0v as a reference , the Con. Of HCl is 1M and the electrode is called ***Standard Hydrogen Electrode (SHE)*** ,(fig.6)



Standard Hydrogen Electrode (SHE)

The emf of the unknown half-cell, E°, can then be calculated from the expression

$$\mathbf{E_{measured} = E_R - E_L}$$

where ER and EL are the **reduction potentials** of the right-hand and left-hand electrodes respectively, The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE),** is selected for coupling with the unknown half-cell.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So,SHE can be used as a standard for other electrodes.

Example/ it is desired to determine the emf of the zinc electrode, Zn | Zn^{2+}. It is connected with the hydrogen electrode and the emf ofthe complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

$$\mathbf{Ecell = E_R - E_L}$$

$$= -0.76 - 0 = -0.76\ V$$

– 0.76 V is the emf for Zn

3- *Metal- insoluble salt electrode*

The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled.Metal- insoluble salt electrode system whose potential has been determined relative to the SHE can also be used as Secondary standard electrode.

a-The Standard Silver-Silver chloride Electrode:

In this electrode system, silver wire is covered with silver chloride (a highly insoluble substance). It is dipped in potassium chloride solution in which the concentration of Cl^- ion is 1 M This electrode can be represented as

The corresponding half-reactions can be presented as follows:

$$\mathrm{Ag^+ + e^- \rightleftharpoons Ag(s)}$$
$$\mathrm{AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-}$$

or can be written together:

$$\mathrm{AgCl(s) + Ag(s) + e^- \rightleftharpoons Ag(s) + e^- + Cl^- + Ag^+}$$

which can be simplified:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+ + Cl^-}$$

The Nernst equation below shows the dependence of the potential of the silver-silver(I) chloride electrode on the activity or effective concentration of chloride-ions:

$$E = E^0 - \frac{RT}{F} \ln a_{\mathrm{Cl^-}}$$

The standard electrode potential E^0 against standard hydrogen electrode (SHE) is 0.230 V

b- The Calomel Electrode

It is the most commonly used secondary standard reference electrode. The standard calomel electrode, **SCE,**

The calomel electrode is represented as

Cl^- (1M) | Hg_2Cl_2, Hg

and the half-cell reaction is:

$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

4- *Glass Electrode*

A commonly used secondary standard electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 7) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode.

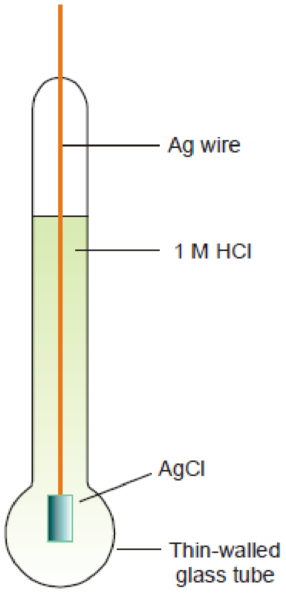


Fig. 7:glass electrode

The glass electrode represented as

$$\text{Ag, AgCl} \mid \text{1 M HCl} \,\vdots\, \text{H}^{+} \text{ (Test Solution)}$$

When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential Equation of a glass electrode can be determined :

$$E = E^\circ + \frac{2.303RT}{nF} \ \mathbf{PH}$$

2-2ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

1- Galvanic Cells

A **galvanic cell,** also known as a is **Voltaic cell** one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown in Fig. 5. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the ***anode*** compartment.

$Zn \longrightarrow Zn^{2+} + 2e^-$

The reduction half-reaction takes place in the ***cathode*** compartment.

$Cu^{2+} + 2e^{-} \longrightarrow Cu$

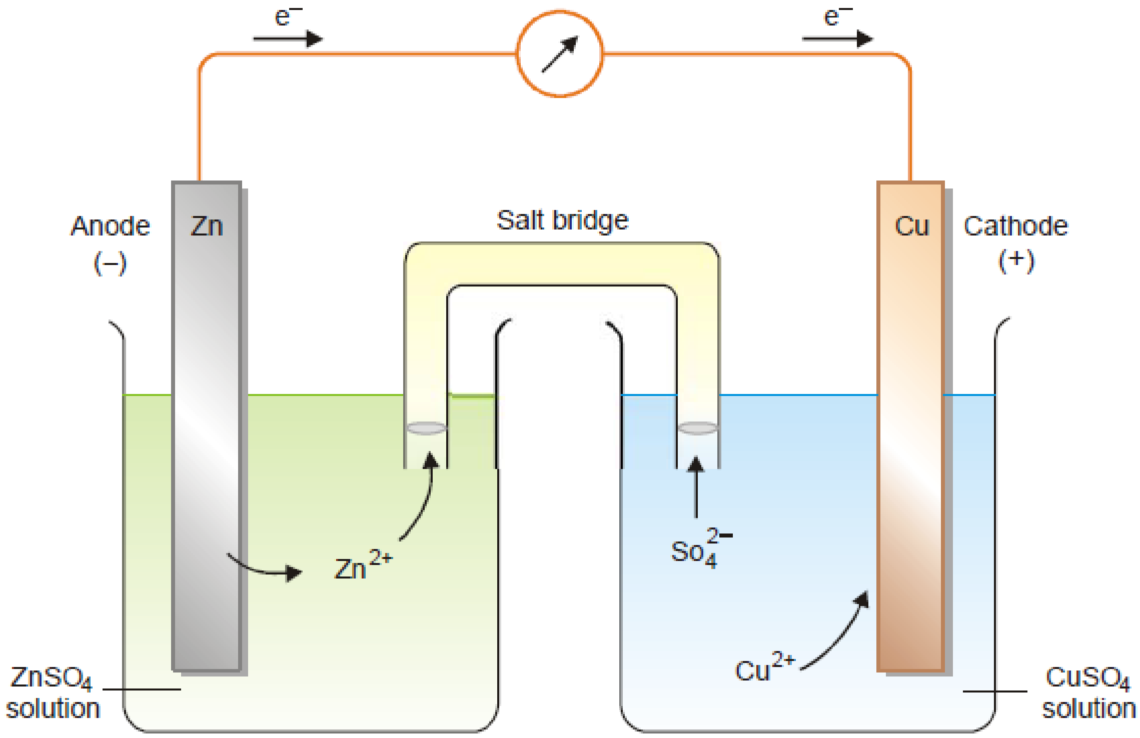


Fig. 5: A **simple galvanic cell**

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn2+ ions. The Cu2+ ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, $SO4^{2-}$ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensure continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up

Cell reaction:

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(a) Half-reactions :

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$ *Anode*

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ Cathode

(b) Cell reaction(cell over all reaction) by adding up the half-reactions

Zn(*s*) + Cu2+ (*aq*) ——→ Zn2+ (*aq*) + Cu(*s*)

Cell diagram or Representation of a Cell

In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line** (**|**) represents a phase boundary between metal electrode and ion solution (electrolyte).

(2) A **double vertical line** (**||**) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as

$$\underset{\substack{\text{Anode}\\ \text{Half-Cell}}}{Zn \mid Zn^{2+}} \parallel \underset{\substack{\text{Cathode}\\ \text{Half-Cell}}}{Cu^{2+} \mid Cu}$$

Calculating the emf (electromotive force) of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$\mathbf{E_{cell} = E_{cathode} - E_{anode}}$$

$$\mathbf{= E_R - E_L}$$

Let us predict the emf of the cell

$$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag$$

by using the E° values from the Table

$$\begin{aligned} E^\circ_{cell} &= E^\circ_R - E^\circ_L \\ &= 0.80 - (-0.763) \\ &= 0.80 + 0.763 \\ &= 1.563\ V \end{aligned}$$

The answer is so clear from Fig. 29.12.

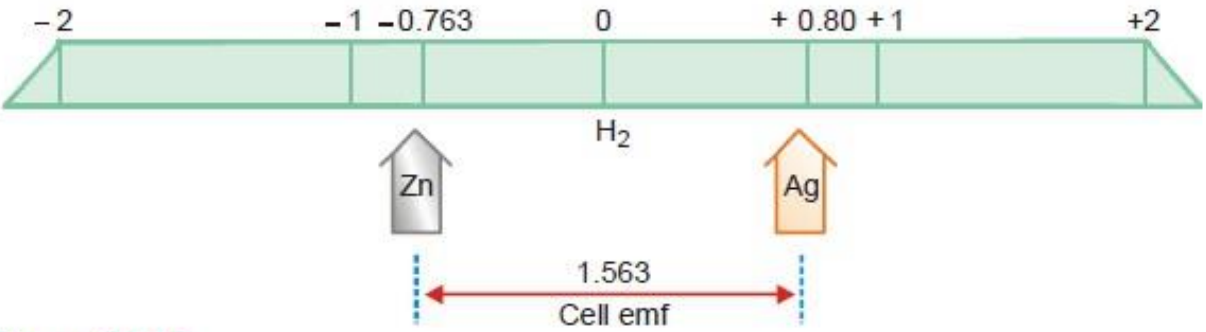
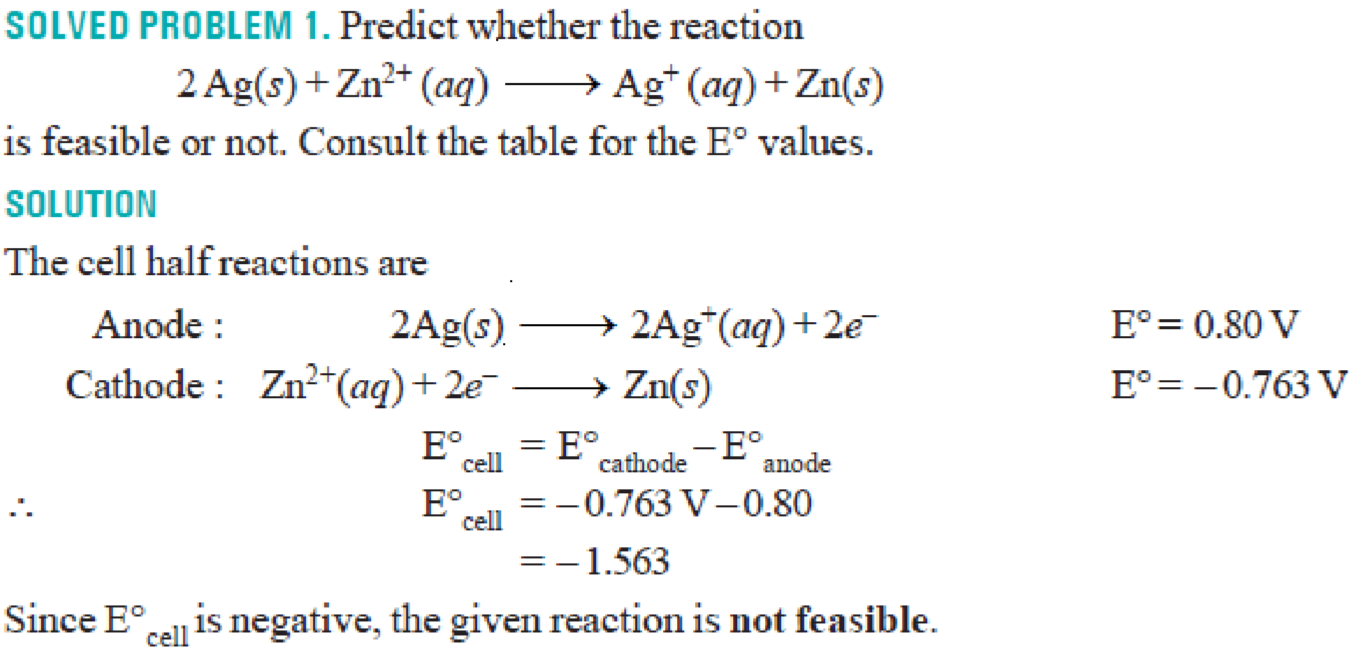


Figure 29.12
Diagrammatic representation of Cell emf.



SOLVED PROBLEM 1. Predict whether the reaction

$$2\,Ag(s) + Zn^{2+}(aq) \longrightarrow Ag^{+}(aq) + Zn(s)$$

is feasible or not. Consult the table for the E° values.

SOLUTION

The cell half reactions are

$$\text{Anode}: \quad 2Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-} \qquad E^\circ = 0.80\ V$$

$$\text{Cathode}: \quad Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s) \qquad E^\circ = -0.763\ V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$\therefore \quad E^\circ_{cell} = -0.763\ V - 0.80$$

$$= -1.563$$

Since E°_{cell} is negative, the given reaction is **not feasible.**

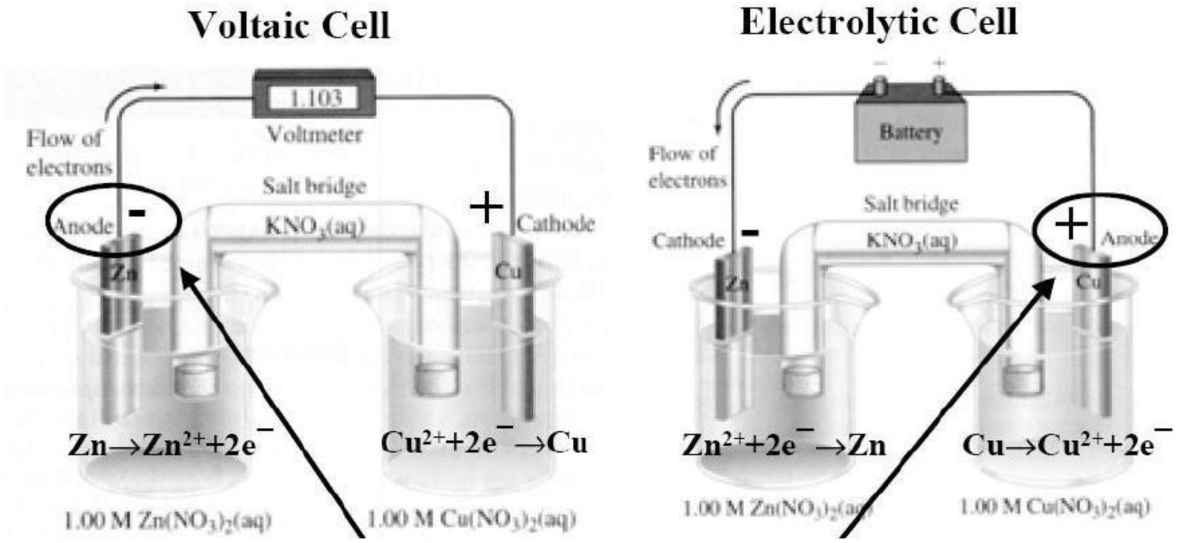
2-1 Electrolytic Cell

Electrolysis: The decomposition of some substance by means of an electric current.

Electrolytic Cell: A cell that requires electrical energy to cause nonspontaneous oxidation-reduction reactions to occur.

1- It utilizes an external source of electrical energy.
2- It forces electrons to flow in the opposite direction by applying a voltage greater than the cell potential.
3- It converts electrical energy into chemical energy
4- A salt bridge can be used in the Electrolytic Cell or not used

Voltaic Cell	Electrolytic Cell
Spontaneous redox reaction releases energy	**Nonspontaneous redox reaction absorbs energy to drive it**



Anode = oxidation = negative
(negative charge supplied by *reaction*)
Cathode = reduction = positive
$E_{cell} > 0$

Anode = oxidation = positive
Cathode = reduction = negative
(negative charge supplied *externally*)
$E_{cell} < 0$

Another Example of electrolytic cells :

Electrolysis of water: is the decomposition of water into oxygen and hydrogen gas due to the passage of an electric current(fig. 6).. This technique can be used to make hydrogen gas, a main component of hydrogen fuel, and breathable oxygen gas,

the base-balanced reactions predominate in basic (high pH) solutions.

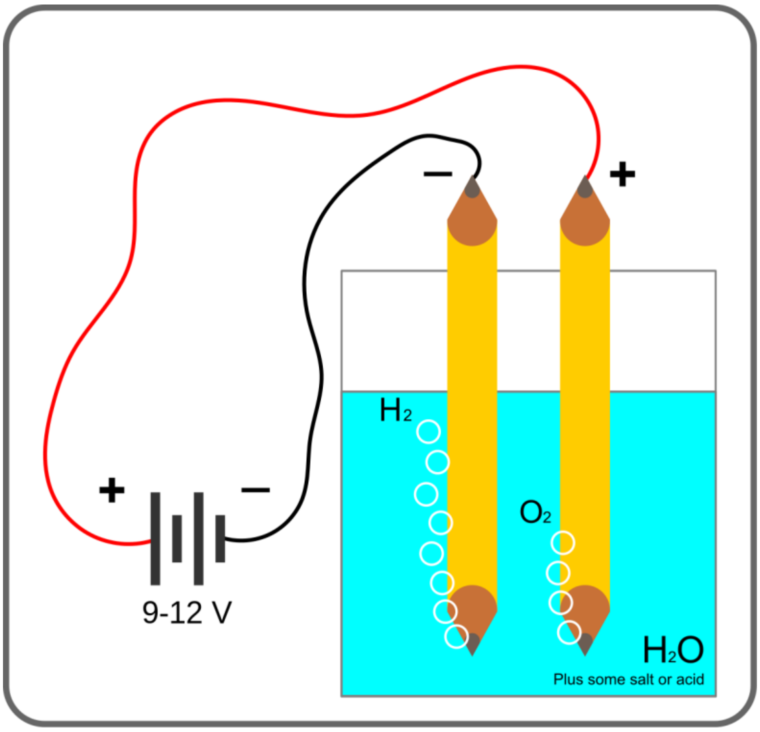
Cathode (reduction): $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

Anode (oxidation): $2\ OH^-(aq) \rightarrow 1/2\ O_2(g) + H_2O(l) + 2\ e^-$

Combining either half reaction pair yields the overall decomposition of water into oxygen and hydrogen:

Overall reaction: $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

The number of hydrogen molecules produced is thus twice the number of oxygen molecules.



Electrolysis of water

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