

First week:

Physical Chemistry

Chapter One . (Gaseous State)

There are two types of gases

1-Ideal gases

2- Non – Ideal or real gases

1-Ideal gases : ideal gases are obeys gas laws such as BoyLes law and Charles law at all temperatures and pressure .

2- Areal gases : areal gases obeys these law only at low pressure and high temperature .

Equation state :

The state of a fluid depends on the volume , pressure ,and temperature if the effect of the gravitational and external electric and magnetic fields are neglected .

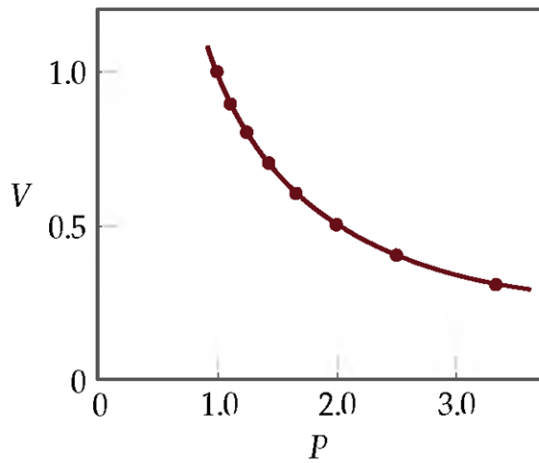
$P = f(V, T)$ equation of state

Boyles Law : this law given by Robert Boyle in 1662 at constant temperature , the volume of a given quantity of a gas varies inversely as pressure on the gas .

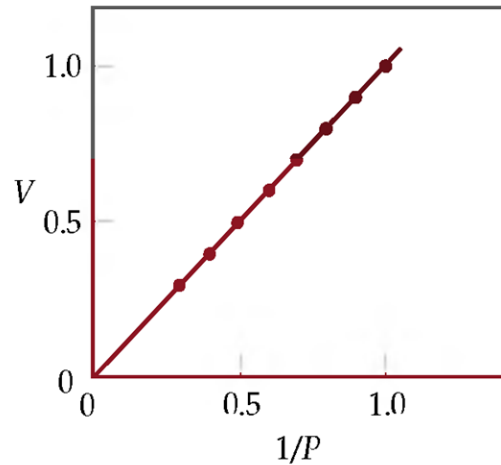
$$v \propto 1/p$$

At constant Temperature .

$$PV = \text{const.} = K$$



(a)



(b)

- At constant temperature and a quantity of gas :
- $P_1 V_1 = P_2 V_2 = K$

Charles or Gay-Lussacs Law :

Charles observed at 1787 that :

- 1- At constant pressure the volume of any gas expanded by the same fraction of its initial volume at 0 °C for every one degree centigrade rise in temperature .

$$V \propto T \quad \frac{V}{T} = \text{const.}$$

Gay –Lussac in 1802 found that for each degree rise in temperature, the volume of the gas increased by approximately $1/273$ of the volume of gas at 0°C .

2- Constant volume, the pressure of any quantity of any gas is proportional with temperature.

$$P \propto T$$

$$P / T = \text{const.}$$

- At constant pressure

$$- \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

At constant volume

$$- \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

$$- \text{Or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

-

General gas Law:

For any definite quantity of gas obeying Boyles and Charles :

$$PV \propto T$$

$$pV_m \propto T \quad pV_m / T = \text{const.} \quad V_m = \text{molar volume}$$

$$PV = nRT$$

H.W / Prove the general (ideal) gas law.

H.W / Prove that the $R = 0.082 \text{ L.atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

$$= 8.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

$$= 1.982 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

Dalton Law and Partial Pressures of gases :

- For A gas , n_A moles in V volume , according for ideal gas equation :
- $P_A = n_A (RT/V)$
- $P_B = n_B (RT/V)$
- $P_t = P_A + P_B = (n_A + n_B) (RT/V)$
- $P_j = n_j (RT/V) \dots\dots\dots(1)$
- $n_t = n_A + n_B + \dots\dots$
- $X_j = n_j / n$

The equation (1) become .

$$P_j = n_j (RT/V) = X_j (n RT/V) = X_j P.$$

H.W / Prove that the $P_j = X_j P.$

Grahames Law of Diffusion .

At constant pressure and temperature , the rate of diffusion of any gas is inversely proportional to the square of the density or the molecular weight of the gas .

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

EX: A system of gases enclosed in a steel cylinder it contains (125g) of O_2 , (52g) of nitrogen and (0.002)kg of H_2 at standard condition. Calculate :

- The volume of the cylinder .
- Partial pressure of each gas .

$$a) n_{O_2} = \frac{126}{32} = 3.93 \text{ mole}$$

$$b) n_{H_2} = \frac{2}{2} = 1 \text{ mole}$$

$$c) n_{N_2} = \frac{52}{28} = 1.85 \text{ mole}$$

$$PV = nRT \quad , \quad V = \frac{nRT}{P} = \frac{6.7 * 0.082 * 273}{1} = 151.93 \text{ L}$$

$$b) x_{O_2} = \frac{3.93}{6.78} = 0.579$$

$$x_{N_2} = \frac{1.85}{6.78} = 0.272$$

$$p_{O_2} = x_{O_2} p_t = 0.579 * 1 = 0.579 \text{ atm}$$

$$p_{N_2} = x_{N_2} p_t = 0.272 * 1 = 0.272 \text{ atm}$$

$$p_{H_2} = x_{H_2} p_t = 0.147 * 1 = 0.147 \text{ atm}$$

EX : what is the relative rate of diffusion for H_2 molecules compared to those of O_2 at the same temperature .

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{M_{H_2}}}{\sqrt{M_{O_2}}}$$

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{32}}{\sqrt{2}} = 4$$

اذن جزيئات الهيدروجين تنتشر اسرع باربعة مرات من جزيئات الاوكسجين .

second week :

The kinetic of ideal Gases :

The kinetic theory of gases , first proposed by Bernoulli (1738) and subsequently developed by Claudius , Clark , Maxwell , Boltzmann Vander Waals and others .

-The essential postulates of kinetic theory of ideal gases are :

1. Every gas consists of a very large number of tiny solid particles called molecules .
2. The molecules of gas within a container are in a state of constant rapid motion in all possible directions . They travel in straight lines until on collision with another molecule or with the walls of the container the direction of motion is changed .

3. The pressure of a gas on any surface is the result of continuous bombardment on the surface by its molecules . Pressure increase and volume decrease at constant temperature , Pressure increase and temperature decrease at constant volume .

4. The collisions of the molecules with each other and the walls of the container are perfectly elastic and there is no loss of kinetic energy resulting from their collisions .

5. The absolute temperature of a gas is measure of the average kinetic energy of all the molecules present in it and is directly proportional to it .

6. There is no effect of gravity on the motion of the molecules of a gas.

7. The molecules are very small as compared to the distances between them.

Consider a cubical vessel each side (L) with perfectly elastic wall containing a very large number of molecules (n'), (m) the mass of each molecule , (u) is the velocity . (the velocity taken here is known as the mean square velocity).

$$U^2 = U_x^2 + U_y^2 + U_z^2$$

The molecules strikes the face (A) with velocity (U_x) and momentum (mu_x) .

After striking , velocity ($-U_x$) and momentum ($-m U_x$) in the back direction .

Change in momentum is :

$$\Delta S = m U_x - (- m U_x) = 2mU_x$$

The time taken by the molecules to go to the other side and then to come back
 $= 2L / U_x$.

The number of impacts with the wall A per second is :
 $= U_x / 2L$

The force $f = \text{change in momentum} \times \text{number of impacts}$

$f_x = (2mU_x) (U_x / 2L) = mU_x^2 / L$ to the face A and

$f_x = mU_x^2 / L$ to the face A'

The $f_x = 2mU_x^2 / L$ for X - direction

The $f_y = 2mU_y^2 / L$ for Y - direction

The $f_z = 2mU_z^2 / L$ for Z - direction

The total force $f = 2mU_x^2 / L + 2mU_y^2 / L + 2mU_z^2 / L$
 $= 2m / L (U_x^2 + U_y^2 + U_z^2)$
 $= 2m U^2 / L$

For n' molecules :

$$f = 2mn' U^2 / L$$

$$P = f / A$$

$$= 2mn' U^2 / LA$$

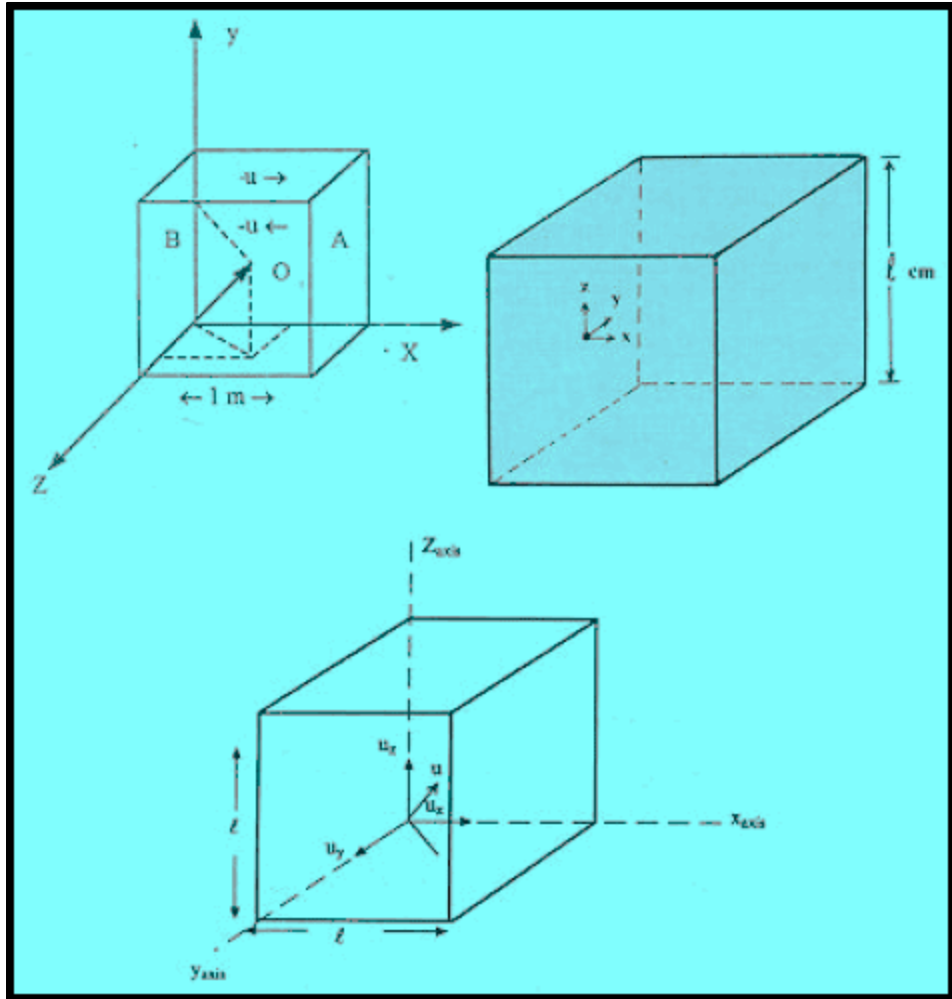
The total area the wall $= 6L^2$

$$P = m n' U^2 / 3L^3$$

The volume of the cube = L^3

$$P = m n' U^2 / 3V$$

or $PV = m n' U^2 / 3$ for cubic vessel .



Third week :

Deduction Of Gas Laws From Kinetic Theory :

1- Boyles Law :

According to postulate (5) the kinetic energy for (n') molecules ($\frac{1}{2} m n' u^2$) is directly proportional to the absolute temperature

$$\left(\frac{1}{2} m n' u^2 \propto T\right)$$

$$\left(\frac{1}{2} m n' u^2 = K T\right) \quad K = \text{constant}$$

$$\frac{3}{2} \left(\frac{1}{3} m n' u^2 = K T\right)$$

$$\frac{1}{3} (m n' u^2 = \frac{2}{3} K T)$$

$$PV = \frac{2}{3} K T = \text{constant} \quad \text{if } T \text{ constant}$$

2- Charles Law :

$$\text{From above } PV = \frac{2}{3} K T$$

$$\text{or } V = \frac{2}{3} (K / P) T$$

$$V \propto T \text{ if } p \text{ constant .}$$

3- Avogadro's Law :

Equal volume of two gases under similar conditions of temperature and pressure condition equal number of molecule

$$P_1 V_1 = \frac{1}{3} m_1 n_1' u_1^2 \quad \text{and} \quad P_2 V_2 = \frac{1}{3} m_2 n_2' u_2^2$$

if P and V of two gases are equal

$$P_1 V_1 = P_2 V_2$$

$$\frac{1}{3} m_1 n_1' u_1^2 = \frac{1}{3} m_2 n_2' u_2^2 \text{ -----(1)}$$

The two gases are at the same temperature

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2 \text{ -----(2)}$$

$$K = \frac{1}{2} m_1 U_1^2 \text{ kinetic energy .}$$

From equation (1) and (2)

$$n_1 = n_2$$

4 - Grahams Law of Diffusion .

$$PV = \frac{1}{3} m_1 n' u^2$$

$$u^2 = \frac{3PV}{m n'}$$

$$d = \frac{m n'}{V'}$$

$$u^2 = \frac{3P}{d} \text{ or } u = \sqrt{\frac{3P}{d}}$$

$$u \propto \sqrt{\frac{1}{d}} \text{ if pressure is constant}$$

For two gases at constant volume and pressure

$$\frac{1}{3} m_1 n_1' u_1^2 = \frac{1}{3} m_2 n_2' u_2^2$$

$$u_1^2 / u_2^2 = m_2 n_2' / m_1 n_1'$$

$$u_1 / u_2 = \sqrt{(m_2 n_2' / m_1 n_1')} = \sqrt{(M_2 / M_1)}$$

$$n_2' = n_1' = N \text{ (Avogadro number)}$$

at constant temperature and pressure, the two gases will have the same molar volume

$$u_1 / u_2 = \sqrt{d_2 / d_1}.$$

5- Daltons Law of Partial pressure :

$$PV = \frac{1}{3} m_1 n' u^2$$

$$P_1 = \frac{1}{3V} m_1 n_1' u_1^2$$

$$P_2 = \frac{1}{3V} m_2 n_2' u_2^2$$

$$P_3 = \frac{1}{3V} m_3 n_3' u_3^2$$

If these gases are forced together in another flask of the same volume and the same temperature, the total pressure (p) is given by .

$$P = \frac{1}{3V} m_1 n_1' u_1^2 + \frac{1}{3V} m_2 n_2' u_2^2 + \frac{1}{3V} m_3 n_3' u_3^2$$

$$P = P_1 + P_2 + P_3 \quad \text{Dalton's Law}$$

$$PV = \frac{1}{3} m n' u^2 = n RT$$

$$n' = n N$$

$$PV = \frac{1}{3} n(m N) u^2 = n RT$$

Where N = Avogadro's number

$$PV = \frac{n M u^2}{3} = n RT$$

Where M = Nm.

H.W Prove that the $u = \sqrt{\frac{3pv}{M}}$, $u = \sqrt{\frac{3p}{d}}$, $u = \sqrt{\frac{3RT}{M}}$

By using kinetic theory of gases where u = velocity of molecules .

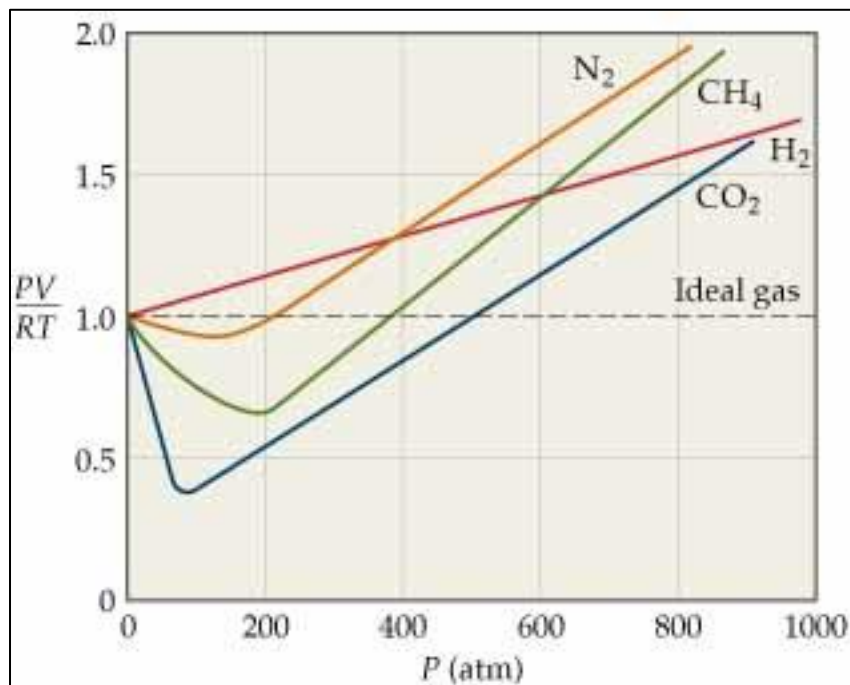
Fourth week:

Real Gases :

Deviation from ideal behaviors .

A gas is said to be an ideal gas if it obeys the various gas law , expressed in the form of equation $(PV = n RT)$. Actual behaviors of various gases , it is found that very few gases obey the ideal gas equation only at low pressures and high temperature . however , at high pressures and low temperature marked deviation from the ideal behaviour have been observed .

- To illustrate how much a gas deviates ideal gas behaviour , consider $(PV = n RT)$



Type One / The curve from the value of PV and value PV increases continually with increases pressure . this type of curve is obtained for various gases having smaller molecules , H₂, He .

Type two / The curve from the value of PV and value PV decreases in the beginning ,passes through a minimum and then begins to increase with increasing pressure . this type of curve is generally obtained for gases having Larger molecules , O₂ ,CO₂.

مقدار الانحرافات عن المثالية فيقاس بواسطة عامل الانضغاطية (compression factor)

$$Z = P V / RT$$

For ideal gas $z = 1$ and is independent of pressure and temperature .

For real gas Z is a function of both temperature and pressure and its value varies

Modification of the Ideal Gas Equation :

1 - the attraction force between the molecules give to touch them near and this the measured pressure less than the ideal pressure .

2 - the volume that occupied by a gas is b and the volume for n molecules is (nb) , and the volume in the ideal equation be $(v - nb)$.

If (v) is the volume occupied by (n) moles of the gas then both these two factors and hence the correction term (p') is directly proportional to (n^2 / v^2) .

$$p' \propto n^2 / v^2$$

$$p' = a n^2 / v^2$$

$$p_j = p + a n^2 / v^2$$

where a = constant characteristic of each gas .

p_j = ideal pressure

if $(p + a n^2 / v^2) (v - nb) = n RT$ Vander – Waals eq .

$(p + a / v^2) (v - b) = n RT$, for one mole of a gas .

Specific Heat of Gases :

The amount of heat in calories required to rise the temperature of one gram of the substance through 1°C for one mole .

Molar heat capacity = Molecular weight * specific heat

The $T \uparrow$ at constant volume $\rightarrow \uparrow$ internal energy of the gas which is due to the kinetic energy of the motion of the molecules and no work will be done . c_v

If the gas heated at constant pressure , the energy supplied not only \uparrow the internal energy of the gas molecules but also some work in the expansion of the gas against the constant external pressure . c_p

For solid and liquids , the difference between the two heat capacities is very small and negligible because the effect of heat on volume is very small . but in case of gases ,effect of heat on volume is very high .

The translational energy ($E_k = 3/2 RT$)

E_k = internal rnergy of the gas at temperature T.

If the temperature raised by 1 °C from (T) to (T + 1) .

The internal energy = $3/2 R (T+ 1)$

$$\Delta E = 3/2 R(T + 1) - 3/2 RT$$

$$\Delta E = 3/2 R = C_v$$

لان الحرارة المسلطة للغاز لمول واحد بثبوت الحجم سوف يزيد الطاقة الحركية بمقدار 1 درجة مئوية من انجاز الشغل .

Suppose one of the gas is heated at constant pressure in acy linder the heat increase E_k , but will also do external work through the expansion .

$$W = P \Delta V$$

$$C_p = C_v + W$$

$$C_p = C_v + P \Delta V$$

For one mole of an ideal gas .

$$P \Delta V = R \Delta T$$

$$\Delta T = 1$$

$$P \Delta V = R$$

$$C_P = C_V + R$$

$$C_V = 3/2 R$$

$$C_P = 5/2 R$$

$$\gamma = C_P / C_V$$

fifth week :

Phase Equilibria :

The phase rule is a generalization which seems to explain the equilibrium existing between the heterogeneous system and was theoretically deduced by Willard Gibbs in 1876 .

$$F + P = C + 2$$

F = number of degree of freedom

P = number of phases

C = number of components

Phase : is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces .

Ex:

- 1) Liq.H₂O + vap. H₂O.
- 2) Mohr's salt FeSO(NH₄)₂ SO₄ . 6 H₂O.
- 3) 2 miscible Liq. are one phase .
- 4) 2 immiscible Liq. are two phase (benzene + H₂O)

Component :

The number of components of a system at eq. is the smallest number of independently variable constituents by means of which the composition of

each phase can be expressed either directly in the form of chemical equation

.

Ex:

1) Water sys. Three phases (ice , Liq , vap) the composition .

Of each is $H_2O \rightarrow$ One component system .

2) Sulphur sys. Four phases (rhombic , monoclinic , Liq . , vap)

3) Acetic acid .

Ex/



- Three phases .
- Two components . ($CaCO_3 + CaO$, $CaCO_3 + CO_2$)
- The composition of (3) phases expressed by :
 - $CaCO_3 + CaO$,
 - $CaCO_3 + CO_2$
- Ex /
- $CuSO_4 \cdot 5H_2O \leftrightarrow CuSO_4 \cdot 3H_2O(s) + H_2O(g)$.
- Three phases
- Two components . ($CuSO_4 + H_2O$)
- Ex /
- $Fe(s) + H_2O(g) \leftrightarrow FeO(s) + H_2(g)$.
- Four phases .
- Three components . ($Fe + H_2O + H_2$, $FeO + H_2O + H_2$)

Degree of freedom (variance).:

- the number of degree of freedom or variance of a system is the number of variable factors such temp. , pressure , or conc.

Which must be specified in order to define the system completely .

Ex :

-H₂O gas (one phases sys. →to define (temp . + pressure)the system has (2) degree of freedom (bivariant)

-ice + Liq H₂O(2 phase sys.) . →to define (temp . + pressure)the system has (2) the system has (1) degree of freedom (univariant)

- ice + Liq H₂O+ vap. H₂O (3 phase sys.) . →to define (no degree of freedom) .

Because the three phases can co – exist in eq. only at particular tem . and pressure which are automatically fixed . (invariant).

Determination of degrees of freedom without phase rule :

Ex: gas system (one phase , one component) .

$$F + P = C + 2 \quad \text{or} \quad F + P = C + 2 - P$$

$$F = 1 + 2 - 1 = 2$$

$$f(P, T, C) = 0 \quad F = V - E$$

V = variables

E= equation s

$$F = 3 - 1 = 2$$

Ex : H₂O+ vap. H₂O (two phases , one component)

$$F = C + 2 - P$$

$$F = 1+2-2 = 1$$

$$f_L (P, T, C_1) = 0$$

$$f_v (P, T, C_v) = 0$$

for each phase $F = 2$

$$M^L_{H_2O} (P, T, C_v) = M^V_{H_2O} (P, T, C_v) \quad M = \text{Chemical potential}$$

$$F = V - E$$

$$F = 4 - 3 = 1$$

Ex:

- ice + Liq H_2O + vap. H_2O (3 phase, one component)

$$F = C + 2 - P$$

$$F = 1 + 2 - 3 = 0$$

$$f (P, T, C_1) = 0$$

$$f (P, T, C_1) = 0$$

$$f (P, T, C_v) = 0$$

$$M^i_{H_2O} = M^L_{H_2O}, \quad M^L_{H_2O} = M^v_{H_2O}$$

$$F = V - E$$

$$= 5 - 5 = 0$$

EX : Homogeneous solution of sugar in H_2O

$$F = C + 2 - P$$

$$= 2 + 2 - 1 = 3$$

$$f (T, P, C_{H_2O}, C_{sug.}) = 0$$

$$F = V - E$$

$$= 4 - 1 = 3$$

Sixth week :

Free energy function :

Entropy is a measure of unavailable energy . when entropy is multiplied by absolute temperature the product (TS) is equal to the amount of heat (energy) which is not free to be used for useful work . then the total heat absorbed by a system the amountless by (TS) must be the available amount of heat which can be put for useful work . thus free energy (x) can be expressed as :

$$X = q - TS$$

Then the (q) may be replaced either by (E) or (H)

The free energy would be equal to (E- TS) or (H- TS).

$$A = E - TS \quad A = \text{Helmholtz free energy}$$

$$G = H - TS \quad G = \text{Gibbs free energy}$$

$$\Delta A = nR \ln \frac{v_1}{v_2}$$

$$\Delta A = nR \ln \frac{P_2}{P_1}$$

$$\Delta G = nR \ln \frac{v_1}{v_2}$$

$$\Delta G = nR \ln \frac{P_2}{P_1}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{for isothermal and isobaric change}$$

Solution :

Type of solution .

- 1) G- G (mixture of gases , air)
- 2) G- L (NH₃ in H₂O , aerated water)
- 3) G- S (H₂ in pd)
- 4) L – G (vaporization of a liquid into a gas)
- 5) L-L (H₂O in ethanol)
- 6) L-S (liquid benzene in solid into a gas)
- 7) S – G (sublimation of a solid into a gas)
- 8) S – L (sugar in H₂O)
- 9) S – S (pb in Ag , Cu in Ni)

Modes of expressing composition (concentration) of solution s:

Ex :

B → A

1) Weight per cent $\%B = \frac{WB}{WA+WB} * 100$

2) Weight ratio $= \frac{WB}{WA}$

3) Volume percent $\%B(\text{ volume }) = \frac{vB}{v} * 100$

4) Molarity (M) $M = \frac{Wt}{M.Wt} * 100/ v(\text{mL})$

5) Normality (N) $M = \frac{Wt}{eq.Wt} * 100/ v(\text{mL})$

6) Formality (F) $M = \frac{Wt}{F.Wt} * 100/ v(\text{mL})$

7) Molarliy (L)

$$L = \frac{\text{no.moles}}{\text{solv.}(kg)}$$

8) Mole fraction (x)

$$X_A = \frac{n_A}{n_A+n_B}$$

$$X_B = \frac{n_B}{n_A+n_B}$$

$$X_A + X_B = 1$$

Solution of gases in Liquids :

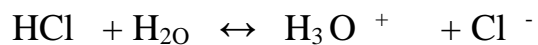
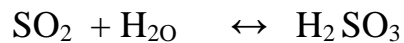
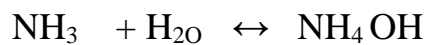
Most of gases are easily soluble in (H₂O) forming true solution .(O₂ in H₂O)

Gas in a liquid is an two component system :

$$F + P = C+2$$

$$F + 2 = 2+2$$

$$F = 2$$



seventh week :

The gases can be easily Liquefied are fairly soluble in solvent

The gases cannot be easily Liquefied are least soluble in solvent

Effect of (T) on solubility :

According to Le- Chatelier principle , solubility of a gas in a liquid will decrease with rise of temperature

(except of H₂, O₂ and the inert gases

Effect of (p) on solubility . (Henry's law)

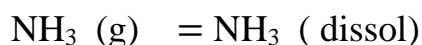
(Henry's law) At constant temperature the mass of a gas dissolved in a unit volume of a liquid is directly proportional to the pressure of the gas above the liquid at eq.

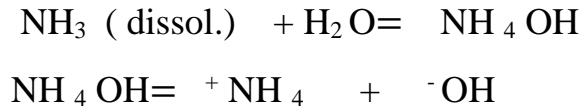
$$m \propto p$$

$$m = k p \quad k = \text{Henry's constant}$$

It has been observed that for the (strict applicability of Henry's law)

- 1) (T) should be high
- 2) (p) should be low
- 3) No chemical reaction should taken





Henry's law and Raoult's law:

$$m = kp \text{----- (1)}$$

$$m = w_2/w_1 \quad w_2/w_1 = k' p_2 \text{----- (2)}$$

$p =$ eq . pressure

$p_2 =$ vapor pressure of avolatil solute

$w_2 =$ weight of gas

$w_1 =$ weight of solvent

$$\frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}} = k' p_2 \text{----- (3)}$$

$$\frac{n_2}{n_1} = k' p_2 \text{----- (4)}$$

If the gas has very little solubility :

$$\frac{n_2}{n_1} = \frac{n_2}{n_1+n_2} \text{----- (5)}$$

$$\frac{n_2}{n_1+n_2} = x_2 = k'' p_2$$

In dilute solution , the $p_2 \propto x_1$

If p_2° is the pressure of the pure solute

$$1 = k' p_2 \quad \text{if } x_2 = 1$$

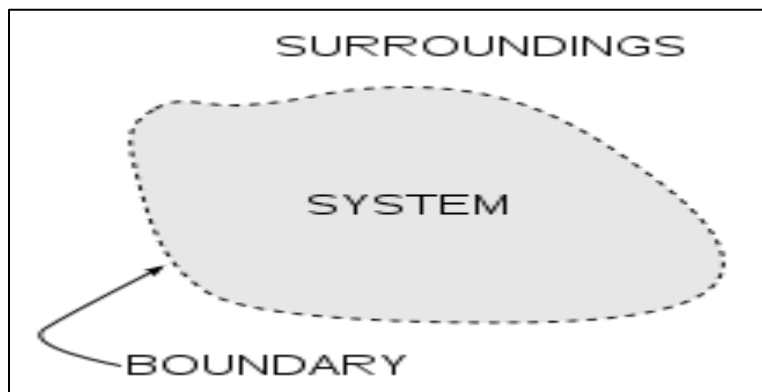
eight week :

Therodynamics :

System / a thermodynamics . sys. is the part of the physical universe to which we direct our attention for the purpose of experimental or theoretical investigation .

Surroundings / the surrounding are the remainder of the universe which can in any way effect or can be effect by the system .

Boundary / the space separating the system from the sourrounding

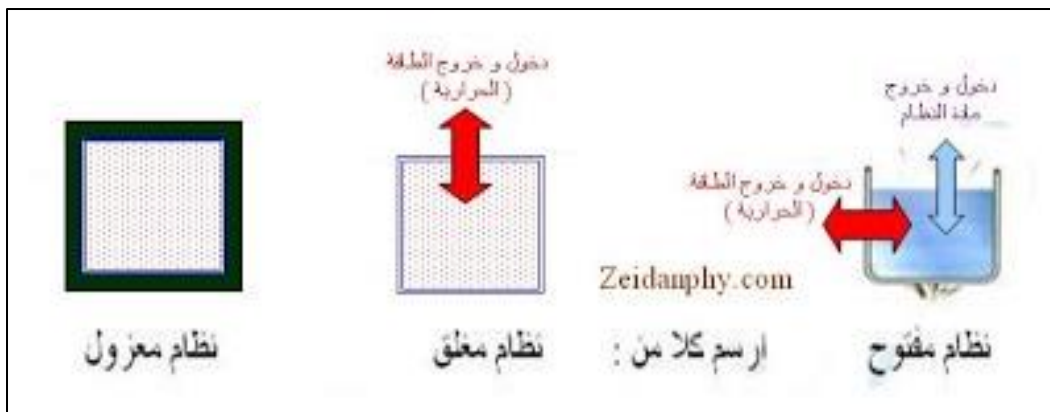


System :

Aclosed sys. : It is a sys . enclosed by impermeable walls in this sys. the mass ermaines constant but the energy may change ($dM = 0$, $d E \neq 0$) .

Anopen sys. : It is a sys . enclosed by impermeable walls that can exchange both the energy and the matter with the surrounding across the boundary ($dM \neq 0$, $dE \neq 0$) .

Anisolated sys. : It is a sys . enclosed by rigid , adiabatic walls and not acted up on by any external force field . ($dM= 0$, $dE= 0$)



Process:

Isothermal process : when the temp. of the system is kept constant during various operation then the process said to be isothermal .

Adiabatic process: there is no exchange of heat between the system and surrounding and (Q) is zero . thus in Adiabatic process there is always a change in temp.

Isobaric process : when the pressure of the system . remains constant during the period of the change .

Cyclic process : If a system having undergone a change returns to initial state then process is called cyclic process.

Reversible process: when the process occurs in such a way that the properties of the system . at every instant process is one which proceeds through a succession of eq. states, each of which is an eq. state

Irreversible process : If the change is produced rapidly and the system . does not have time to attain eq. then the process is called irreversible. All natural processes are irreversible and hence spontaneous.

ninth week :

First Law of thermodynamics :

Matter contains energy . the first law is based on the observation that energy can neither be created nor destroyed , the total energy of system is conserved .

- The change in internal energy (ΔE) in any system is the difference between the heat entering the system . (q) and the work done by system (W). the internal energy of an isolated system is constant and $q = w = 0$

$$dE = dq - dw$$

Reversible and Irreversible process(work):

- 1) $P_{int} > P_{ext}$ (expansion work against P_{ext})

- 2) $P_{\text{int}} < P_{\text{ext}}$ (expansion work against P_{int})
 3) $P_{\text{int}} = P_{\text{ext}}$ (equ. Reversible work of expan)

$$d w = F d h = (P_{\text{ext}} d v) (P_{\text{int}} - d p) d v \cong P_{\text{int}} d v$$

because $d p d v$ is very small .

Reversible work : Reversible process are of great importance because they yeild maximum amount of work which may be obtained from a given net change .

$$d w = (p - dp) d v$$

$$d w = p d v - dp d v$$

$$d w = p d v$$

$$\int d w = \int_{v_1}^{v_2} p d v$$

$$W_{\text{rev}} = \int_{v_1}^{v_2} p d v$$

$$P V = n R T$$

$$W_{\text{rev}} = \int_{v_1}^{v_2} \frac{n R T}{V} d v$$

$$W_{\text{rev}} = \int_{v_1}^{v_2} \frac{n R T}{V} d v$$

$$W_{\text{rev}} = n R T \ln \frac{V_2}{V_1} \quad \text{isothermal revrsible}$$

$$\frac{V_2}{V_1} = \frac{p_2}{p_1} \quad \text{or} \quad p_1 v_1 = p_2 v_2$$

$$W_{\text{rev}} = n R T \ln \frac{p_1}{p_2}$$

Heat contents (Enthalpy) . Heat change at constant p).

$$H = E + P V$$

$$\Delta H = \Delta E + \Delta(P V)$$

$$\Delta H = \Delta E + P \Delta V + V \Delta P$$

$\Delta H = \Delta E + P\Delta V$ because $\Delta p = 0$ (p is constant) from first Law of thermodynamic

$$\Delta H = q_p$$

Heat change at constant V.

$$\Delta E = q - w \quad (\text{from first Law})$$

$$q = \Delta E + w$$

$$q = \Delta E + p\Delta v$$

$$q_{(v)} = \Delta E \quad \text{because } \Delta V = 0$$

Heat capacity of ideal gases .

Heat capacity / is a heat required to raise the temp. of the sysytem by one degree .

$$C = \frac{\partial q}{\partial T}$$

$$C_V = \left(\frac{\partial q}{\partial T} \right)_V$$

$$q = \Delta E + p\Delta v$$

$$q_V = \Delta E \quad \text{where } v = 0 \text{ (constant)}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \quad \text{for ideal gases}$$

$$C_p = \left(\frac{\partial q}{\partial T} \right)_p$$

$$\Delta H = q_p$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad \text{for ideal gases}$$

$$C_p - C_V = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_V \quad \text{-----(1)}$$

$$H = E - PV$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \text{ -----(2)}$$

Sub . (2) in (1)

$$C_P - C_V = \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial E}{\partial T}\right)_V$$

ربط الحد الاول والاخير بعلاقة رياضية تقوم : $E = f(T, V)$

$$E = \left(\frac{\partial E}{\partial T}\right)_V dT - P \left(\frac{\partial E}{\partial V}\right)_V dv \text{ -----(4) بثبوت الضغط } dT \text{ على}$$

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial V}\right)_V \text{ ----- (5)}$$

وبتعويض 5 في 3 يعطي :

$$C_P - C_V = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \text{ ----- (6)}$$

وبنفس الطريقة اعتمادا على

$$H = f(T, P)$$

مثل $H = f(T, V)$ نكتب

$$C_P - C_V = \left(\frac{\partial P}{\partial V}\right)_V \left[\left(\frac{\partial H}{\partial T}\right)_{T-V}\right] \text{ -----(8)}$$

(الغرام مول واحد من غاز مثالي يكون

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

$$C_P - C_V = P \left(\frac{\partial V}{\partial T}\right)_P$$

One mole of ideal gas has $PV = nRT$

اشتقاق هذه المعادلة نسبة الى درجة الحرارة بثبوت الضغط يكون:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$C_p - C_v = R$$

tenth week :

Irreversible work :

$$w = \int_{v_1}^{v_2} p dv$$

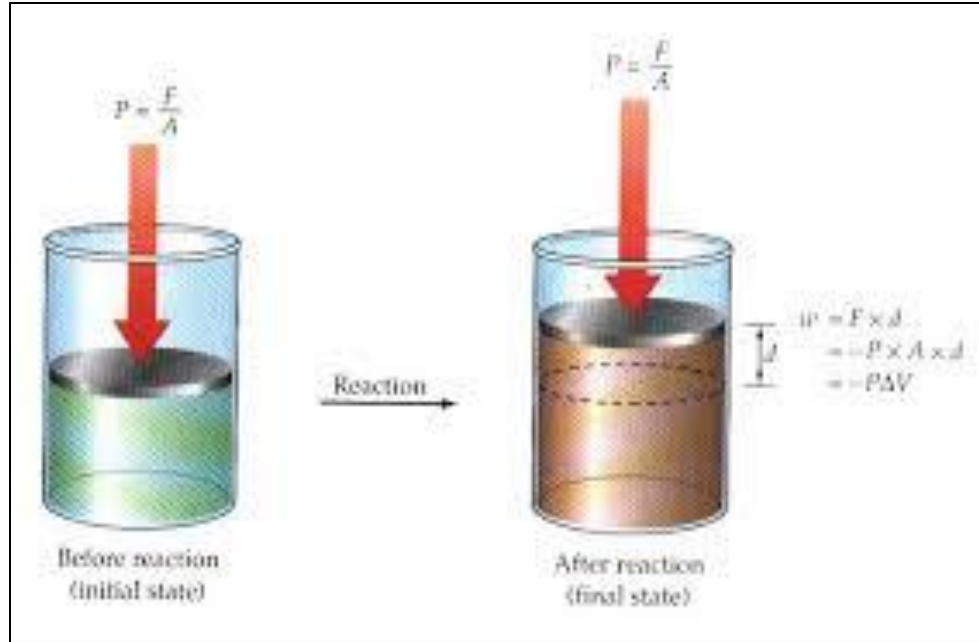
$$w = \int_{v_1}^{v_2} p_2 dv$$

$$w = p_2 \int_{v_1}^{v_2} dv$$

$$w = p_2 (v_2 - v_1) = p_2 \Delta v$$

$$w = p_2 \left[\frac{nRT}{p_2} - \frac{nRT}{p_1} \right]$$

$$w_{\text{irr}} = nRT \left[1 - \frac{p_2}{p_1} \right]$$



Comparison of W_{rev} and W_{irr} :

$$W_{\text{rev}} = nRT \left[1 - \frac{p_1}{p_2} \right]$$

من اضافة وطرح واحد يعطي :

$$W_{\text{rev}} = nRT \left[1 - 1 + \frac{p_1}{p_2} \right]$$

$$W_{\text{rev}} = nRT \left[1 - \left(1 - \frac{p_1}{p_2} \right) \right]$$

$$\{\text{Ln}(1-x) = -x - \frac{1}{2}x^2 \cong -x\}$$

$$W_{\text{rev}} = -nRT \left[\left(1 - \frac{p_1}{p_2} \right) \right]$$

$$W_{\text{rev}} = nRT \left[\left(\frac{p_1}{p_2} - 1 \right) \right]$$

$$W_{\text{irr}} = nRT \left[\left(1 - \frac{p_2}{p_1} \right) \right]$$

$$W_{\text{rev}} - W_{\text{irr}} = nRT \left[\left(\frac{p_1}{p_2} - 1 \right) \right] - nRT \left[\left(1 - \frac{p_2}{p_1} \right) \right]$$

$$W_{\text{rev}} - W_{\text{irr}} = nRT \left[\left(\frac{p_1}{p_2} - 2 + \frac{p_2}{p_1} \right) \right]$$

$$W_{\text{rev}} - W_{\text{irr}} = nRT \left[\left(\frac{p_1^2 - 2p_1p_2 + p_2^2}{p_1p_2} \right) \right]$$

$$W_{\text{rev}} - W_{\text{irr}} = nRT / p_1p_2 (p_1p_2)^2$$

Adiabatic expansion :

In Adiabatic $q=0$

$$\Delta E = q - w \quad (\text{from first Law})$$

$$\Delta E = -w$$

$$w = -\Delta E, \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}, \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}, \quad \frac{P_2}{P_1} = \left(\frac{T_1}{T_2} \right)^{\gamma/\gamma-1}$$

Adiabatic reversible expansion:

$$dE = n C_V dT$$

$$\int_{E_1}^{E_2} dE = n \int_{T_1}^{T_2} C_V dT$$

$$\Delta E = E_2 - E_1 = n C_V (T_2 - T_1)$$

$$\Delta E = n C_V (T_2 - T_1) = -w$$

$$W_{ad} = -n C_V (T_2 - T_1) \quad , \quad W_{ad} = C_V T_1 \left[\left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma} \right]$$

$$W_{ad} = R (T_2 - T_1) / 1 - \gamma$$

Enthalpy change (ΔH):

$$\Delta H = H_2 - H_1 = (E_2 + p_2 v_2) - (E_1 + p_1 v_1)$$

$$\Delta H = (E_2 - E_1) + (p_2 v_2 - p_1 v_1)$$

$$\Delta H = \Delta E + n R (T_2 - T_1)$$

$$\Delta H = n C_V (T_2 - T_1) + n R (T_2 - T_1)$$

$$\Delta H = n (T_2 - T_1) (C_V + R)$$

$$\Delta H = n C_p (T_2 - T_1)$$

a) Rrlation between (T) and (V):

$$dE = n C_V dT$$

$$dw = pdv$$

for adiabatic $q = 0$

$$dE = -pdv = n C_V dT$$

$$n C_V dT = \frac{-nRT}{V} dv \quad \quad P = \frac{nRT}{V}$$

$$\frac{C_V dT}{R T} = \frac{-dv}{V}$$

$$\frac{C_V}{R} \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\frac{C_V}{R} \ln \frac{T_2}{T_1} = - \ln \frac{v_2}{v_1}$$

$$\frac{C_V}{R} \ln \frac{T_2}{T_1} = \ln \frac{v_1}{v_2}$$

$$\ln\left(\frac{T_2}{T_1}\right)^{Cv/R} = \left(\ln \frac{v_1}{v_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \left(\ln \frac{v_1}{v_2}\right)^{Cv/R}$$

$$C_p - C_v = R$$

$$\ln \frac{T_2}{T_1} = \left(\ln \frac{v_1}{v_2}\right)^{C_p - C_v / C_V}$$

$$\ln \frac{T_2}{T_1} = \left(\ln \frac{v_1}{v_2}\right) \left(\frac{C_p}{C_V}\right) - 1$$

$$\ln \frac{T_2}{T_1} = \left(\ln \frac{v_1}{v_2}\right)^{\gamma-1} \quad \frac{C_p}{C_v} = \gamma$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

eleventh week :

b) Relation between (p) and (v):

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

$$T_2 v_2^{\gamma-1} = T_1 v_1^{\gamma-1}$$

$$p_2 v_2 / R v_2^{\gamma-1} = p_1 v_1 / R v_1^{\gamma-1}$$

$$P_2 v_2^\gamma = P_1 v_1^\gamma$$

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^\gamma$$

C) Relation between (P) and (T):

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{\gamma-1}$$

$$\text{Ln} \frac{T_2}{T_1} = \text{Ln} \left(\frac{v_1}{v_2} \right)^{\gamma-1}$$

$$1/\gamma-1 \text{ Ln} \frac{T_2}{T_1} = \text{Ln} \left(\frac{v_1}{v_2} \right)$$

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^{\gamma}$$

$$\text{Ln} \frac{P_2}{P_1} = \text{Ln} \left(\frac{v_1}{v_2} \right)^{\gamma}$$

$$1/\gamma \text{ Ln} \frac{P_2}{P_1} = \text{Ln} \left(\frac{v_1}{v_2} \right)$$

$$1/\gamma \text{ Ln} \frac{P_2}{P_1} = 1/\gamma-1 \text{ Ln} \frac{T_2}{T_1}$$

$$\text{Ln} \frac{P_2}{P_1} = \gamma/\gamma-1 \text{ Ln} \frac{T_2}{T_1}$$

$$\text{Ln} \frac{P_2}{P_1} = \text{Ln} \left(\frac{T_2}{T_1} \right)^{\gamma/\gamma-1}$$

$$\text{Ln} \frac{P_2}{P_1} = \text{Ln} \left(\frac{T_2}{T_1} \right)^{c_p/R}$$

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1} \right)^{c_p/R}$$

$$\gamma/\gamma-1 = \frac{c_p}{c_v-1}$$

$$\begin{aligned}
 &= \frac{\frac{C_p}{C_v}}{\frac{C_p - C_v}{C_v}} \\
 &= \frac{C_p}{R}
 \end{aligned}$$

Adiabatic irreversible expansion (Free expansion):

$$q = 0$$

the gas expands into vacuum where there is no pressure therefore the work = zero

$$\Delta E = q - w \quad 0 - 0 = 0$$

$$\Delta E = n C_v (T_2 - T_1) = 0$$

$$T_2 = T_1$$

$$\Delta H = C_p (T_2 - T_1) = 0$$

W , q , ΔE , ΔH are zero for free expansion .

Adiabatic irreversible expansion:

$$\begin{aligned}
 W_{\text{irr}} &= \int_{v_1}^{v_2} p_2 dv \\
 &= p_2 (v_2 - v_1)
 \end{aligned}$$

Real gases . (Non ideal gases)

$$(p + a n^2 / v^2) (v - nb) = n RT$$

Twelvth week:

Reversible isothermal expansion :

$$dw = pdv$$

$$= \int_{v_1}^{v_2} pdv$$

$$P = \frac{nRT}{V-nb} - \frac{an^2}{v^2}$$

$$P = \int_{v_1}^{v_2} \frac{nRT}{V-nb} dv - \int_{v_1}^{v_2} \frac{an^2}{v^2} dv$$

$$W = nRT \ln \left(\frac{v_2-nb}{v_1-nb} \right) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$dE = \frac{an^2}{v^2} dv$$

$$\int_{E_1}^{E_2} dE = \int_{V_1}^{V_2} \frac{an^2}{v^2} dv$$

$$E_2 - E_1 = \Delta E = -an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\Delta E = -an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\Delta H = H_2 - H_1$$

$$= (E_2 + p_2 v_2) - (E_1 + p_1 v_1)$$

$$\Delta H = (E_2 - E_1) + (p_2 v_2 - p_1 v_1)$$

$$\Delta H = \Delta E + (p_2 v_2 - p_1 v_1)$$

$$P = \frac{nRT}{V-nb} - \frac{an^2}{v^2}$$

$$\Delta H = \Delta E + n RT \left(\frac{v_2}{v_2-nb} - \frac{v_1}{v_1-nb} \right) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\frac{v_2}{v_2-nb} - \frac{v_1}{v_1-nb} = \frac{v_2(v_2-nb) - v_1(v_1-nb)}{(v_2-nb)(v_1-nb)}$$

$$= \frac{nb(v_1-v_2)}{(v_2-nb)(v_1-nb)}$$

$$\Delta H = \Delta E + n RT \left(\frac{nb}{v_2-nb} - \frac{nb}{v_1-nb} \right) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\Delta E = -an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right) + n RT \left(\frac{nb}{v_2-nb} - \frac{nb}{v_1-nb} \right) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\Delta H = nb^2 RT \left(\frac{nb}{v_2-nb} - \frac{nb}{v_1-nb} \right) + 2an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$q = \Delta E + w$$

$$q = -an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right) + n RT \left(\frac{nb}{v_2-nb} - \frac{nb}{v_1-nb} \right) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$q = n RT \ln \left(\frac{v_2-nb}{v_1-nb} \right)$$

Adiabatic reversible expansion :

$$q = 0$$

$$\Delta E = -w$$

$$E = E(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT - P \left(\frac{\partial E}{\partial V}\right)_T dv$$

$$\left(\frac{\partial E}{\partial T}\right)_V = n C_V, \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{an^2}{v^2}$$

$$dE = n C_V dT + \frac{an^2}{v^2} dv$$

$$\int_{E_1}^{E_2} dE = n C_V \int_{T_1}^{T_2} dT + an^2 \int_{V_1}^{V_2} \frac{dv}{v^2}$$

$$\Delta H = (E_2 - E_1) = \Delta E = n C_V (T_2 - T_1) - an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$W = -n C_V (T_2 - T_1) + an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

Thirteen weak :

step (1):

the gas cylinder is placed in a constant temperature bath maintained at temperature (T_2) and the gas is expanded isothermally at a temperature (T_2) from an initial volume (v_1) to a volume (v_2) the gas will absorb heat (q_2) and perform work on its surrounding

$$\Delta E = 0$$

$$q_2 = w_1 = RT_2 \ln \frac{v_2}{v_1}$$

step (2):

the cylinder is then insulated the gas allowed to expand reversibly and adiabatically to volume (v_2) since no heat is transferred ($q=0$) the temperature of the gas will fall from T_2 to T_1

$$W = -\Delta E = -n C_V (T_2 - T_1) = C_V (T_2 - T_1)$$

step (3):

the gas cylinder is now placed in a constant temperature bath maintained at temperature (T_1) and the gas is compressed isothermally and reversibly at a temperature (T_1) from volume (v_3) to a volume (v_4) the gas will absorb heat (q_1) is given out to the cold reservoir. since the gas ideal and the temperature is constant

$$q_1 = w_3 = n R T_1 \ln \frac{v_4}{v_3}$$

v_4 less than v_3

$\ln \frac{v_4}{v_3}$ is negative

q_1, w_3 are negative and correspond to the heat being given off from the gas and the work the being done the gas

step (4):

the gas finally compressed reversibly and adiabatically from volume (v_4) to a volume (v_1) the gas performs amount of work (w_4) and temperature of the system rises from (T_1) to (T_2) and returns to its original state.

$$q = 0$$

$$W_4 = -\Delta E_4 = -n C_V (T_2 - T_1)$$

$$W = q_2 - q_1$$

$$W = w_1 + w_2 + w_3 + w_4$$

$$W = n RT_1 \ln \frac{v_2}{v_1} + n C_V (T_2 - T_1) - n RT_1 \ln \frac{v_3}{v_4} - n C_V (T_2 - T_1)$$

$$W = n RT_1 \ln \frac{v_2}{v_1} - n RT_1 \ln \frac{v_3}{v_4}$$

$$\frac{v_2}{v_1} = \frac{v_3}{v_4}$$

$$W = n RT_1 \ln \frac{v_2}{v_1} - n RT_1 \ln \frac{v_3}{v_4}$$

$$W = n R (T_2 - T_1) \ln \frac{v_2}{v_1}$$

Fourteen week:

Efficiency of Carnot cycle :

$$\varepsilon = \frac{w}{q_2} = \frac{n R (T_2 - T_1) \ln \frac{v_2}{v_1}}{RT_2 \ln \frac{v_2}{v_1}}$$

$$\varepsilon = \frac{T_2 - T_1}{T_2}$$

$$\varepsilon = \frac{q_2 - q_1}{q_2}$$

$$\varepsilon = 1 - \frac{q_1}{q_2}$$

- 1) Heat cannot spontaneously pass from a colder to a hotter body .
- 2) The mechanical work can completely be converted into heat , but on the contrary heat cannot completely be converted into work without making other change either in the system or the surrounding in a cyclic process.

a) q is the amount of heat supplied to the gas , the gas will expand and the piston will be pushed , the work done by the gas is ($w = pdv$) due the expansion .

b) if the work equivalent to the above amount of heat work is done on the gas ,the gas would be compressed and heat will be evolved .

$$q_2 < q_1$$

- this clearly indicates that the whole of the heat absorbed in process (A) has been converted into work .
- when heat is absorbed the gas ,the kinetic energy of the gas molecules will move faster and collide with
 - 1) each other
 - 2) the container
 - 3) the face of the piston
- Only the third type of collision will bring about the expansion of the gas . shown in (b)
- The work due to expansion is not exactly equivalent to the amount of heat absorbed
- The heat goes waste only due the random motion of the gas molecules . so we can correlate the randomness with the unavailable work that is (entropy)

- Under ideal situation if all the gas molecules were striking the piston perpendicularly, the whole of the heat will be converted into work as in (a).

Entropy : is the measure of randomness of a molecular system

$$dq_{rev} = dE + d w_{rev}$$

$$= d E + Pd v$$

$$dE = n C_V d T$$

$$P = \frac{nRT}{V}$$

$$dq_{rev} = n C_V d T + n RT \frac{dv}{v}$$

$$\frac{dq_{rev}}{T} = n C_V \frac{dT}{T} + nR \frac{dv}{v} \quad \text{dividing the equation by } T$$

$$\int_1^2 \frac{dq_{rev}}{T} = n C_V \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1}$$

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

$$\frac{v_2}{v_1} = \frac{p_1 T_2}{p_2 T_1}$$

$$\Delta S = C_V \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= (C_V + R) \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$C_p - C_V = R$$

$$C_p = C_V + R$$

$$\int_1^2 \frac{dq_{rev}}{T} = n C_p \frac{T_2}{T_1} - nR \ln \frac{v_2}{v_1}$$

$$S_2 - S_1 = \Delta S = \int_1^2 \frac{dq_{rev}}{T} = n C_p \frac{T_2}{T_1} - nR \ln \frac{v_2}{v_1}$$

$$ds = \frac{dq_{rev}}{T}$$

fifteen week :

combine of first and second Law of thermodynamics:

$$\begin{aligned} dq_{rev} &= dE + d w_{rev} \\ &= dE + Pd v \end{aligned}$$

$$ds = \frac{dq_{rev}}{T}$$

$$dq = T ds$$

$$T ds = dE + pdv$$

$$dE = T ds - pdv$$

Enthalpy and entropy :

$$H = E + Pv$$

$$dH = dE + Pd v + v dp$$

$$dE = T ds - pdv$$

$$dH = dE + Pd v + Pd v + v dp$$

$$\Delta H = T ds - vdp$$

Entropy change at constant pressure for heating or cooling

$$\Delta S = \int_{T_1}^{T_2} n C_p \frac{dT}{T} = n C_p \frac{T_2}{T_1}$$

Entropy for reversible isothermal process:

$$d q_{\text{rev}} = d w_{\text{rev}} = p d v = n R T \frac{d v}{v}$$

$$\Delta S = \int_1^2 \frac{d q_{\text{rev}}}{T} = \int_{v_1}^{v_2} n R \frac{d v}{v}$$

$$\Delta S = n R \ln \frac{v_2}{v_1}$$

$$p_1 v_1 = p_2 v_2$$

$$\Delta S = n R \ln \frac{p_2}{p_1}$$

Entropy for reversible adiabatic process:

$d q_{\text{rev}} = 0$ at all stages of the process.

$$\Delta S = 0$$

Entropy change on heating or cooling of the substance (change of state):

$$\Delta S = \int_{T_1}^{T_2} \frac{dq}{T} = \int_{T_1}^{T_2} n C_V \frac{dT}{T}$$

$$\Delta S = n C_V \ln \frac{T_2}{T_1} \text{ (at temperature change)}$$

$$ds = \frac{dq_{rev}}{T} = \frac{\Delta H}{T} \text{ (at state change)}$$