CONTENTS

CHEMICAL EQUILIBRIUM

Recap of Early Classes

In chemical equilibrium, we study about reactions which do not go to completion, ie. reach equilibrium state. This type of reactions are called reversible reactions. In this chapter we also study about spontaneity, ie. whether a chemical reaction is feasible or not.

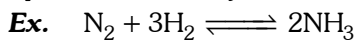## *Index*

CHEMICAL EQUILIBRIUM

1.0 INTRODUCTION

Chemical reaction : Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.   ***Ex.*** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

1.1 Types of Chemical Reactions 🆂🅻 🅰🅻

On the basis of physical state	
Homogeneous reaction	***Heterogeneous reaction***
All reactants and products are in same phase	Reactants and products are in more than one phase
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$
On the basis of direction	
Reversible reaction	***Irreversible reaction***
(i) Chemical reaction in which products can be converted back into reactants $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$ $H_2 + I_2 \rightleftharpoons 2HI$ $2KClO_3 \longrightarrow 2KCl + 3O_2$	(i) Chemical reaction in which products cannot be converted back into reactants. $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$ $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$ $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
(ii) Proceed in forward as well as backward direction.	(ii) Proceed only in one direction (forward).
(iii) To obtain reverisible reactions, if anyone of the reactant or product is in gaseous state, then the reaction should be carried out in closed vessel. $CaCO_3 (s) \longrightarrow CaO (s) + CO_2 (g)$	(iii) Generally possible in open container.
(iv) These attain equilibrium.	(iv) These do not attain equilibrium.
(v) Reactants are never completely converted into products.	(v) Reactants are completely converted into products.
On the basis of speed.	
Fast reactions	***Slow reactions***
(i) Generally these reactions are ionic reactions. $HCl + NaOH \rightarrow NaCl + H_2O$ Acid Base Salt Water	(i) Generally these reactions are molecular reactions. $H_2 + I_2 \rightarrow 2HI$
On the basis of heat	
Exothermic reaction	***Endothermic reaction***
(i) Heat is evolved in these chemical reaction $R \rightarrow P + x$ kcal	(i) Heat is absorbed in these chemical reaction $R + x$ kcal $\rightarrow P$
(ii) Change in heat energy $\Delta Q = (+)$ ve	(ii) Change in heat energy $\Delta Q = (-)$ ve
(iii) Change in enthalpy $\Delta H = (-)$ ve	(iii) Change in enthalpy $\Delta H = (+)$ ve
$\boxed{\Delta H = -\Delta Q}$ Eg. : Formation reaction Exception $N_2 + O_2 \rightarrow 2NO/N_2O/NO_2$ $O_2 + F_2 \rightarrow O_2F_2/OF_2$	Eg. : Dissociation reaction

1.2 Active Mass

SL AL

Active mass is approximately equal to molarlity for solutions.

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}}$$

$$= \frac{\text{grams}(w)}{\text{mol.wt.}(M_w) \times \text{Volume in litres}(V)} = \frac{w \times 1000}{M_w \times V(mL)}$$

The active mass of solids and pure liquids is a constant quantity (unity) and solvent (excess) is considered as one. Because there is no change in activity with the change in quantity or volume of vessel. (Actually active mass is a number only so it is dimensionless).

$$\text{Molar concentration} = \frac{w}{M_w \times V_{\text{lit.}}} = \frac{\rho}{M_w} \ (\rho = \text{density in g/lit}) = \frac{\text{density of the substance}}{\text{molecular mass of the substance}}$$

as density of pure solids and liquids is constant and molecular mass is also constant.

But this is not applicable to the substance in aqueous solution or gaseous state because their amount in a given volume can vary.

Following other names of active mass can also be use :

(i)	mole/lit.	(ii)	gram mole/lit.	(iii)	gram molecules/lit.
(iv)	molarity	(v)	Concentration	(vi)	Effective concentration
(vii)	active quantity	(viii)	n/v	(ix)	C
(x)	M	(xi)	[ ]		

● **Examples**

(a) 25.4 g of iodine is present in 2 litres of solution

then $[I_2] = \dfrac{25.4}{254 \times 2} = 0.05 \text{ mole/litre}$

(b) 8.5 g ammonia is present in a vessel of 0.5 litre capacity then

$[NH_3] = \dfrac{8.5}{17 \times 0.5} = 1 \text{ mole / litre}$

(c) Active mass of C (s) or S(s) or Zn(s) is equal to 1.

2.0 CHEMICAL EQUILIBRIUM

SL AL

The state of the reversible chemical reaction at which rate of forward reaction becomes equal to rate of backward reaction.

$$A + B \underset{R_b}{\overset{R_f}{\rightleftharpoons}} C + D \quad \begin{array}{l} R_f = \text{forward rate of reaction} \\ R_b = \text{backward rate of reaction} \end{array}$$
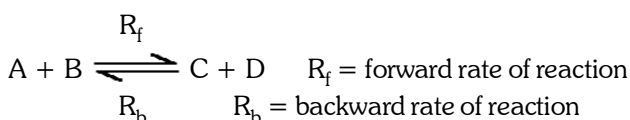
i.e. $R_f = R_b$

or The state of the reversible chemical reaction at which the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the given set of conditions is said to be chemical equilibrium conditions. Rate of forward reaction decreases as the concentration of products increases, rate of backward reaction also starts increasing.

At a certain stage, rate of forward reaction becomes equal to rate of backward reaction called equilibrium state.
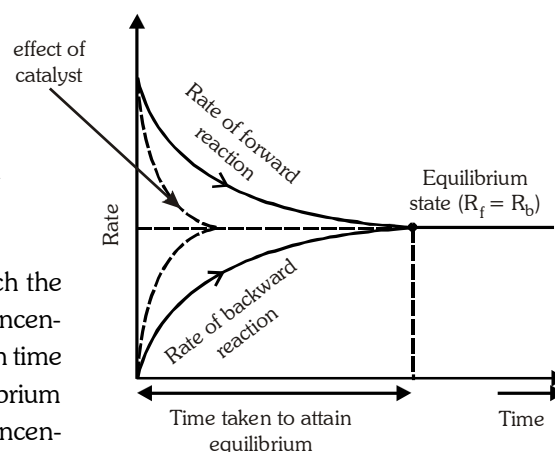
2.1 At Equilibrium State

SL AL

Rate of forward reaction = Rate of backward reaction

- At this state of equilibrium forward and backward reactions proceeds with same speed.
- The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.
- The equilibrium state is dynamic in nature.
- The reaction does not stop, but both the opposing reactions are going on continously with same speeds.

2.2 Characteristics of Equilibrium

SL AL

(a) Chemical equilibrium is dynamic in nature means the reaction, although appears to be stopped, but actually takes place in both the directions with the same speed.

*(b)* To obtain equilibrium, if anyone of the reactant or product is in gaseous state then the reaction should be carried out in closed vessel.

(c) At a given temperature and pressure of equilibrium the properties like concentration, colour, density remains constant.

(d) In a reversible chemical reaction the equilibrium state can be attained in lesser time by the use of positive catalyst.

A catalyst doesn't change the equilibrium state becuase it increases the rate of both forward and backward reaction simaltaneously by changing the path or activation energy of reaction and it helps in attaining equilibrium rapidly.

(e) Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.
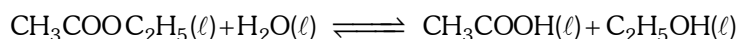
$$CH_3COOC_2H_5(\ell) + H_2O(\ell) \rightleftharpoons CH_3COOH(\ell) + C_2H_5OH(\ell)$$

(f) Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

$$Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$$
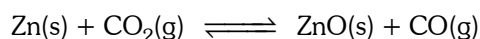
Note : *(i)* *Whenever question doesn't ask about direction, then we take forward direction only.*

(ii) *In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic or vice versa.*

3.0 TYPES OF EQUILIBRIA

3.1 Physical Equilibria

SL

If in a system only physical state (phase) is changed and then equilibrium is established, (i.e. there is no chemical change) the equilibrium is called physical equilibrium.

e.g. Fusion of ice, evaporation of water, dissolution of salts and absorption of gases in liquid etc.

Following are the types of common physical equilibria :-

(i) ***Liquid-Vapour equilibria :*** In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.

Ex. H_2O (l) $\rightleftharpoons$ H_2O (g)
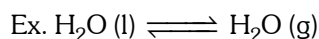
(ii) ***Solid-Liquid equilibria :*** This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.

Ex. H_2O (s) $\rightleftharpoons$ H_2O (l) at melting point
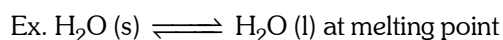
(iii) ***(Solute-Solvent), Saturated solution equilibria :*** If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.

Ex. NaI (s) $\xrightarrow{H_2O}$ Na^+ (aq.) + I^- (aq.)
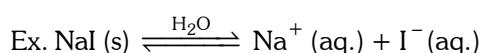
Note: *Above example is of solubility of sparingly soluble salt, which only depends on temperature.*

(iv) (Gas + Solvent), Saturated solution equilibria : In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature.

Ex. Dissolved CO_2 in cold drinks. Dissolved O_2 in water etc.

Note: (i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

(ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

$$C_g \propto P_g \quad \text{or} \quad C_g = k\, P_g$$

where k = Henry's constant

C_g = Solubility of gas in the solution (mol L^{-1})

P_g = Pressure of the gas

(iii) One should not compare it with liquid vapour equilibria.

3.2 Chemical Equilibria

SL

When chemical change occur in a reversible reaction i.e. reactants convert into products and products also convert into reactants under similar conditions of pressure and temperature, the reaction is said to be in chemical equilibria.

(i) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ (formation of HI)

(ii) $SO_2\,(g) + Cl_2\,(g) \rightleftharpoons SO_2Cl_2\,(g)$ (formation of SO_2Cl_2)

(iii) $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$ (formation of PCl_5)

(iv) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ (Decomposition of NH_3)

─────────────────────── Illustrations ───────────────────────

Illustration 1.   Chemical equilibrium is a condition :

(A) where all species have same concentration

(B) where all species have constant concentration with respect to time.

(C) where all species have concentration = 1

(D) all of above

Solution   **(B)**

Chemical equilibrium defined as when all species have constant concentration with respect to time.

Illustration 2.   Example of physical equilibria, is :

(A) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ (B) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2(g)$

(C) $H_2O\,(s) \rightleftharpoons H_2O\,(l)$ (D) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$

Solution   **(C)**

Physical equilibria does not include any chemical change.

Illustration 3*.   At equilibrium :

(A) the free energy of system is minimum   (B) the entropy of system is maximum

(C) the free energy of system is maximum   (D) the entropy of system is minimum

Solution   **(A,B)**

It is the compromising stage of minimum free energy and maximum entropy.

# 4.0 LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM

SL AL

The law of mass action is given by **Guldberg** and **Waage**.

According to them, at a given temperature, rate of reaction is proportional to product of active masses of reactants at that instant raised to the powers which are numerically equal to the number of their respective molecule in the stoichiometric equation describing the reaction.

- **Derivation of equilibrium constant :**
  Consider a reversible homogeneous reaction which has attained equilibrium state at particular temperature :
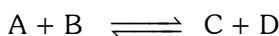
  A + B $\rightleftharpoons$ C + D

  Let the active masses of A, B, C and D be [A] [B] [C] & [D] are respectively.

- **According to law of mass action :**
  rate of forward reaction $\propto$ [A] [B]
  rate of backward reaction $\propto$ [C] [D]
  $R_f = K_f$ [A] [B] $R_b = K_b$ [C] [D]
  Where K_f and K_b are forward and backward rate constants respectively.
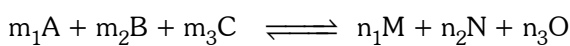 At equilibrium
  $R_f = R_b$
  K_f [A] [B] $= K_b$ [C] [D]

  $$\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

  $$K_c = \frac{[C][D]}{[A][B]}$$

  $$K_c = \frac{K_f}{K_b}$$

  K_c is known as equilibrium constant K_c has a definite value for every chemical reaction at particular temperature. For a general reaction

  $m_1 A + m_2 B + m_3 C \rightleftharpoons n_1 M + n_2 N + n_3 O$

  $r_f \propto [A]^{m_1}[B]^{m_2}[C]^{m_3}$

  $r_f = K_f [A]^{m_1}[B]^{m_2}[C]^{m_3}$ [K_f = forward rate (velocity) constant]

  $r_b \propto [M]^{n_1}[N]^{n_2}[O]^{n_3}$

  $r_b = K_b [M]^{n_1}[N]^{n_2}[O]^{n_3}$ [K_b = backward rate (velocity) constant]

  At equilibrium $r_f = r_b$

  $K_f [A]^{m_1}[B]^{m_2}[C]^{m_3} = K_b [M]^{n_1}[N]^{n_2}[O]^{n_3}$

  $$K_c = \frac{K_f}{K_b} = \frac{[M]^{n_1}[N]^{n_2}[O]^{n_3}}{[A]^{m_1}[B]^{m_2}[C]^{m_3}}$$

  The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

BEGINNER'S BOX–1

Basic Introduction of Equilibrium & Active Mass

1*. x $\rightleftharpoons$ y reaction is said to be in equilibrium, when :-
(A) Only 10% conversion x to y is just
(B) Complete conversion of x to y has taken place
(C) Conversion of x to y is only 50% complete
(D) The rate of change of x to y is just equal to the rate of change of y to x in the system

2. The role of catalyst in a chemical reaction is :-
(A) To help attain equilibrium in a shorter time.
(B) To lower the activation energy.
(C) To shift the equilibrium in such a way as to increase the concentration of the product
(D) Both A & B

3*. Ratio of active masses of 22g CO_2, 3g H_2 and 7g N_2 in a gaseous mixture :-
(A) 22 : 3 : 7   (B) 0.5 : 3 : 7   (C) 1 : 3 : 1   (D) 1 : 3 : 0.5

4. When rate of forward reaction becomes equal to backward reaction, this state is termed as:-
(A) Irreversible state   (B) Reversible state   (C) Equilibrium   (D) All of these

5. Amongst the following chemical reactions the irreversible reaction is :-
(A) $H_2 + I_2 \rightleftharpoons 2HI$ (B) $AgNO_3 + NaCl \rightleftharpoons AgCl + NaNO_3$

(C) $CaCO_3 \rightleftharpoons CaO + CO_2$ (D) $O_2 + 2SO_2 \rightleftharpoons 2SO_3$

6. The active mass of 64 g of HI in a two litre flask would be
(A) 2   (B) 1   (C) 5   (D) 0.25

7. A reversible reaction is one which:-
(A) Proceeds in one direction   (B) Proceeds in both direction
(C) Proceeds spontaneously   (D) All the statements are wrong

4.1 Forms of Equilibrium Constant

SL AL

There are two forms.
(i) Concentration form (K_C) (ii) Partial pressure form (K_P)

- ***Partial pressure :*** The individual pressure exerted by the gaseous substance of the total pressure is called partial pressure of the gases substance.

<div align="center">Closed vessel</div>

Gaseous moles	A $n_1$mol	B $n_2$mol	C $n_3$mol	D $n_4$mol	$\Rightarrow P_{Total}$

$$\text{Partial pressure} = \frac{\text{Moles of substance}}{\text{Total moles}} \times P_{total} \Rightarrow \left[\frac{\text{Moles of substance}}{\text{Total moles}} = \text{Mole fraction} \right]$$

$$= \text{mole fraction} \times P_{total}$$

let $n_1 + n_2 + n_3 + n_4 = N$

$$P_A = \frac{n_1}{N} P_t \qquad P_B = \frac{n_2}{N} P_t, \qquad P_C = \frac{n_3}{N} P_t, \qquad P_D = \frac{n_4}{N} P_t$$

$$P_A + P_B + P_C + P_D = P_{total}$$

Illustrations

Illustration 4. A vessel contains 5 mole of A & 10 moles of B. If total pressure is 18 atm. Find out partial pressure of gases.

Solution $P_A = \dfrac{5}{15} \times 18 = 6$ atm

                    $P_B = \dfrac{10}{15} \times 18 = 12$ atm

When the reactants and products are in gaseous state then partial pressure can be used instead of concentration. At a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

$$m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D$$
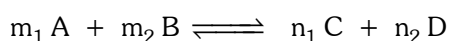
If partial pressure of A, B, C and D at equilibrium are P_A, P_B, P_C and P_D respectively, then

$$K_P = \frac{(P_c)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}}$$

4.2 Relation Between K_P and K_C

[SL] [AL]

This relation can be established for reaction not involving liquids because K_p is not defined for liquids.
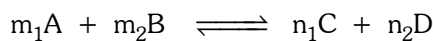Consider a reversible reaction

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

$$K_C = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

For an ideal gas $\quad PV = nRT$

$$P = \frac{n}{V}RT = \text{active mass} \times RT$$

∵ $\quad$ n = number of mole and V = Volume in litre

So $\quad \dfrac{n}{V}$ = molar concentration or active mass

$P = [\ ]RT$

at constant temperature $P \propto [\ ]$

$P_A = [A]RT, P_B = [B]RT, P_C = [C]RT, P_D = [D]RT$

So $\quad K_p = \dfrac{[C]^{n_1}(RT)^{n_1}[D]^{n_2}(RT)^{n_2}}{[A]^{m_1}(RT)^{m_1} \times [B]^{m_2}(RT)^{m_2}}$

$$K_p = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$
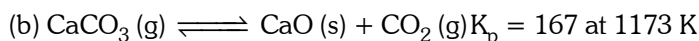
$$K_P = K_C(RT)^{(n_1+n_2)-(m_1+m_2)}$$

$\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$
$\quad$ = total number of gaseous molecules of products – total number of gaseous molecules of reactants.

$$K_P = K_C(RT)^{\Delta n_g}$$

―――――――――――― Illustrations ――――――――――――

Illustration 5. $\quad$ Find the values of K_c for each of the following equilibria from the value of K_p.

(a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$ $\quad K_p = 1.8 \times 10^{-2}$ at 600 K

(b) $CaCO_3\,(g) \rightleftharpoons CaO\,(s) + CO_2\,(g)$ $K_p = 167$ at 1173 K

Solution $\quad$ (a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$
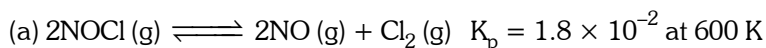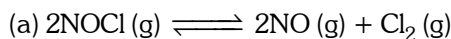
$\quad K_p = 1.8 \times 10^{-2}$

$\quad \Delta n_g = 3 - 2 = 1$

$\quad K_p = K_c(RT)^{\Delta n_g}$

∴ $\quad K_c = \dfrac{K_p}{RT} = \dfrac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4}$

(b) $\quad K_p = 167$

$\quad \Delta n_g = 1$

$\quad K_p = K_c(RT)^{\Delta n_g} = K_c \times (RT)$

∴ $\quad K_c = \dfrac{K_p}{RT} = \dfrac{167}{0.0821 \times 1173} = 1.734$

Illustration 6*. At 540 K, 0.10 moles of PCl_5 are heated in 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Solution

$$PCl_5 \text{ (g)} \rightleftharpoons PCl_3 \text{ (g)} + Cl_2 \text{ (g)}$$

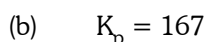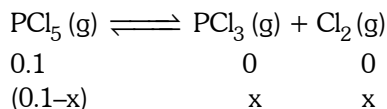| 0.1	0	0
$(0.1-x)$	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{8} \times \frac{x}{8}}{\left(\frac{0.1-x}{8}\right)} = \frac{x^2}{8(0.1-x)} \quad ....(i)$$

From gas law

$$PV = nRT$$

$$\Rightarrow \quad 1 \times 8 = (0.1 + x) \times 0.082 \times 540$$

$$\therefore \quad x = 0.08 \quad\quad\quad ....(ii)$$

From eqs. (i) and (ii)

$$K_c = \frac{0.08 \times 0.08}{8 \times (0.1 - 0.08)} = 4 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_p = K_c (RT)^{\Delta n_g} \quad (\Delta n_g = +1)$$
$$= 4 \times 10^{-2} \times (0.082 \times 540) = 1.77 \text{ atm}$$

Illustration 7*. At a given temperature and a total pressure of 1.0 atm for the homogeneous gaseous reaction,

$$N_2O_4 \rightleftharpoons 2NO_2, \text{ the partial pressure of } NO_2 \text{ is 0.5 atm.}$$

(a) Calculate the value of K_p.

(b) If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture ?

Solution For equilibrium system, $N_2O_4 \rightleftharpoons 2NO_2$, the total pressure is 1.0 atm

$$\Rightarrow \quad \text{The total pressure} = P_{N_2O_4} + P_{NO_2} = 1$$

$$\Rightarrow \quad P_{N_2O_4} = 0.5 \text{ atm and } P_{NO_2} = 0.5 \text{ atm}$$

(i) $K_p = \dfrac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}} = \dfrac{(0.5)^2}{0.5} = 0.5 \text{ atm}$

(ii) As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are

$$P_{N_2O_4} = 1.0 \text{ atm and } P_{NO_2} = 1.0 \text{ atm}$$

According to Le Chatelier's principal, when volume is decreased, the system moves in that direction where there is decrease in number of moles. Hence, the system (here moves in reverse direction, as there is a decrease in mole ($\Delta n = 2 - 1 = 1$), i.e. NO_2 will be converted into N_2O_4.
Let, the decrease in pressure of NO_2 be x atm.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial pressure (atm)	1.0		1.0
At equilibrium	1+x/2		1–x
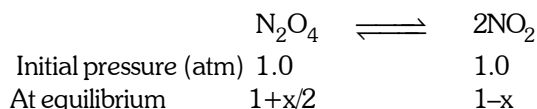
$$\Rightarrow \quad K_p = \frac{(1-x)^2}{(1+x/2)} = 0.5 \Rightarrow 4x^2 - 9x + 2 = 0$$

$$\Rightarrow \quad x = 2 \text{ or } 0.25 \text{ (x } \ne 2 \text{ as initial pressure } = 1.0) \Rightarrow x = 0.25$$

$$P_{N_2O_4} = 1 + \frac{x}{2} = 1.125 \text{ atm and } P_{NO_2} = 1 - x = 0.75 \text{ atm}$$

- The K_C is expressed by the units $(\text{mole lit}^{-1})^{\Delta n}$ and K_P by $(\text{atm})^{\Delta n}$.
  In terms of mole fraction, equilibrium constant is denoted by K_X.

For general reaction $aA + bB \rightleftharpoons mC + nD$
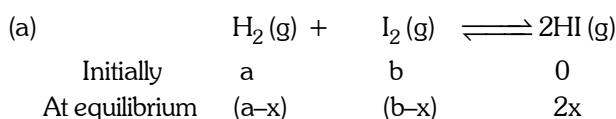
$$K_X = \frac{(X_C)^m (X_D)^n}{(X_A)^a (X_B)^b}$$

$$K_p = K_x (RT)^{\Delta n_g} \qquad \qquad ...(i)$$

$$\Delta n_g = (m + n) - (a + b)$$

When $\Delta n_g = 0$, $K_p = K_C = K_X$

4.3 Some General Equilibrium Expressions

AL

(a) $\qquad H_2\,(g) + \quad I_2\,(g) \rightleftharpoons 2HI\,(g)$

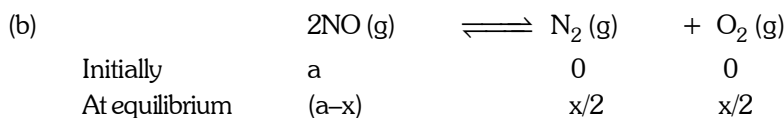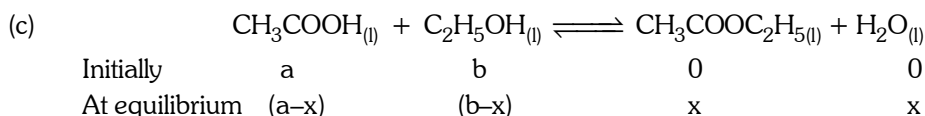| Initially | a | b | 0 |
| At equilibrium | (a–x) | (b–x) | 2x |

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{[HI]^2}{[H_2][I_2]} = \frac{\dfrac{(2x)^2}{(a+b)^2}P^2}{\left(\dfrac{a-x}{a+b}.P\right)\left(\dfrac{b-x}{a+b}.P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So $\quad K_c = K_p \qquad (\Delta n_g = 0)$

(b) $\qquad 2NO\,(g) \rightleftharpoons N_2\,(g) + O_2\,(g)$

| Initially | a | 0 | 0 |
| At equilibrium | (a–x) | x/2 | x/2 |

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_P \qquad (\Delta n = 0)$$

(c) $\qquad CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

| Initially | a | b | 0 | 0 |
| At equilibrium | (a–x) | (b–x) | x | x |

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$

K_p should not be given for this reaction

(d) $\qquad PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

Initially	a	0	0
At equilibrium	(a–x)	x	x
Active mass	$\dfrac{(a-x)}{v}$	$\dfrac{x}{v}$	$\dfrac{x}{v}$
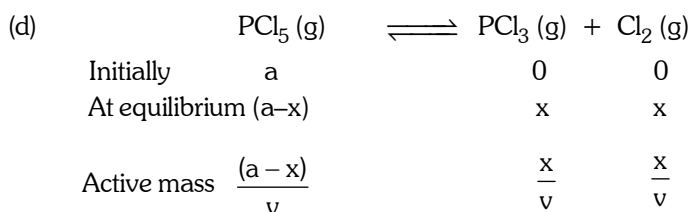
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\dfrac{x}{v} \times \dfrac{x}{v}}{\dfrac{(a-x)}{v}} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{x}{a+x}.P\right) \times \left(\frac{x}{a+x}.P\right)}{\left(\frac{a-x}{a+x}\right)P} = \frac{x^2 P}{(a+x)(a-x)} = \frac{x^2 P}{a^2 - x^2}$$

(e)

	N_2 (g) +	$3H_2$ (g) $\rightleftharpoons$	$2NH_3$ (g)
Initially	a	b	0
At equilibrium	(a–x)	(b–3x)	2x
Active mass	$\frac{(a-x)}{v}$	$\left(\frac{b-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$
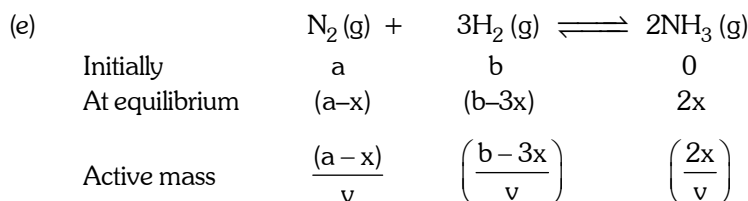
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$
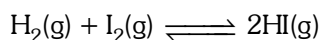
$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{(a+b-2x)}\right]\left[\frac{(b-3x)P}{(a+b-2x)}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

— Illustrations —

Illustration 8. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

(A) 30.61   (B) 13.066   (C) 29.40   (D) 20.90

Solution **(B)**

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Given
$$[H_2] = 10 \text{ mol L}^{-1}$$
$$[I_2] = 6.0 \text{ mol L}^{-1}$$
$$[HI] = 28.0 \text{ mol L}^{-1}$$

So,
$$K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066$$

Illustration 9. For a gas phase reaction at equilibrium, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of K_P if all the pressures are given in atmosphere ?

(A) 32 atm^{-2} (B) 20 atm^{-2} (C) 28.125 atm^{-2} (D) 80 atm^{-2}

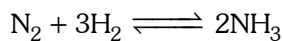**Solution** **(C)**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$,
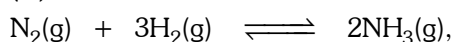
Partial pressures at equilibrium

0.8   0.4   [2.4 – (0.8 + 0.4) = 1.2]

Applying law of mass action,

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4 \times 0.4} \Rightarrow K_P = 28.125 \text{ atm}^{-2}$$

Illustration 10*. Starting with 3 : 1 mixture of H_2 and N_2 at 450°C, the equilibrium mixture is found to be 9.6% NH_3; 22.6% N_2 and 67.8 % H_2 by volume. The total pressure is 50 atm. What will be the value of K_P. The reaction is -

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
   (A) 3.25×10^{-5} atm^{-2} (B) 5.23×10^{-5} atm^{-2}
   (C) 6.23×10^{-5} atm^{-2} (D) 8×10^{-5} atm^{-2}

Solution   **(B)**

The ratio of number of moles will be the same as the ratio of volume. According to Dalton's law, the partial pressure of a gas in a mixture is given by the product of its volume fraction and the total pressure. Therefore, the equilibrium pressure of each gas is,

$$P_{NH_3} = \frac{9.6}{100} \times 50 \text{ atm } = 4.8 \text{ atm}$$

$$P_{N_2} = \frac{22.6}{100} \times 50 \text{ atm } = 11.3 \text{ atm}$$

$$P_{H_2} = \frac{67.6}{100} \times 50 \text{ atm } = 33.9 \text{ atm}$$

Total pressure = 50 atm

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} \text{ ; Substituting the values of partial pressures,}$$

$$K_P = \frac{(4.80 \text{ atm})^2}{(11.3 \text{ atm})(33.9 \text{ atm})^3} = 5.23 \times 10^{-5} \text{ atm}^{-2}$$
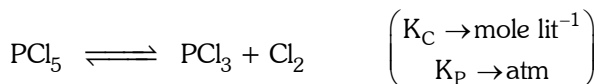
- **Three cases may arise :**
(a)   When $\Delta n_g = 0$
       $K_P = K_C (RT)^0 = K_C$
       For example :

       $N_2 + O_2 \rightleftharpoons 2NO$ $H_2 + I_2 \rightleftharpoons 2HI$
       K_C and K_P are unit less in this case.
(b)   When $\Delta n = +ve$
       $K_P > K_C$
       For example :

       $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\begin{pmatrix} K_C \rightarrow \text{mole lit}^{-1} \\ K_P \rightarrow \text{atm} \end{pmatrix}$

       $(\Delta n = 1)$

       $2NH_3 \rightleftharpoons N_2 + 3H_2$ $\begin{pmatrix} K_C \rightarrow \text{mole}^2 \text{ lit}^{-2} \\ K_P \rightarrow \text{atm}^2 \end{pmatrix}$

       $(\Delta n = 2)$

(c)   When $\Delta n = -ve$
       $K_P < K_C$

       $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\begin{pmatrix} K_C \rightarrow \text{mole}^{-2} \text{ lit}^2 \\ K_P \rightarrow \text{atm}^{-2} \end{pmatrix}$
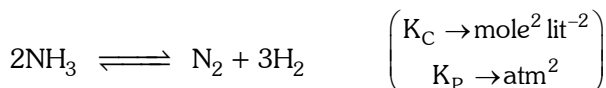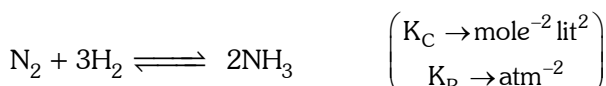
       $(\Delta n = -2)$

BEGINNER'S BOX–2

Equilibrium Constant

1. The equilibrium concentration of B $[(B)_e]$ for the reversible reaction $A \rightleftharpoons B$ can be evaluated by the expression:-

(A) $K_C [A]_e^{-1}$
(B) $\dfrac{k_f}{k_b}[A]_e^{-1}$
(C) $k_f k_b^{-1} [A]_e$
(D) $k_f k_b [A]^{-1}$

2. In a chemical equilibrium, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. The rate constant for the forward reaction is:-
(A) 2×10^{-3}
(B) 5×10^{-4}
(C) 1.12×10^{-3}
(D) 9.0×10^{-4}

3. For which reaction is $K_p = K_c$:-
(A) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
(B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(C) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

4. For the reaction
$CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)}$
Which one is correct representation :–
(A) $K_p = (P_{(H_2O)})^2$
(B) $K_c = [H_2O]^2$
(C) $K_p = K_c(RT)^2$
(D) All

5*. $\log \dfrac{K_p}{K_c} + \log RT = 0$ is true relationship for the following reaction:-

(A) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(B) $2SO_2 + O_2 \rightleftharpoons 2SO_3$
(C) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(D) (B) and (C) both

6*. What should be the value of K_c for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, if the amount are $SO_3 = 48$ g, $SO_2 = 12.8$ g and $O_2 = 9.6$ g at equilibrium and the volume of the container is one litre?
(A) 64
(B) 30
(C) 42
(D) 8.5

7. In the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the amount of each PCl_5, PCl_3 and Cl_2 is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of K_p will be
(A) 1.0 atm.
(B) 3.0 atm.
(C) 2.9 atm.
(D) 6.0 atm.

8*. At $227°$ C, 60% of 2 moles of PCl_5 gets dissociated in a two-litre container. The value of K_p will be
(A) 450 R
(B) 400 R
(C) 50 R
(D) 100 R

9*. At 1000 K, the value of K_P for the reaction : $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$ is 0.05 atmosphere. The value of K_C in terms of R would be :-
(A) 20000 R
(B) 0.02 R
(C) 5×10^{-5} R
(D) $5 \times 10^{-5} \times R^{-1}$

10. For which reaction at 298 K, the value of $\dfrac{K_p}{K_c}$ is maximum and minimum respectively:-

(a) $N_2O_4 \rightleftharpoons 2NO_2$
(b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$
(c) $X + Y \rightleftharpoons 4Z$
(d) $A + 3B \rightleftharpoons 7C$
(A) d, c
(B) d, b
(C) c, b
(D) d, a

11. The equilibrium constant (K_p) for the reaction $PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one-half its original volume, the value of K_P for the reaction at the same temperature will be :-
(A) 32
(B) 64
(C) 16
(D) 4

12. In a chemical equilibrium $A + B \rightleftharpoons C + D$ when one mole each of the two reactants are mixed, 0.4 mole each of the products are formed. The equilibrium constant calculated is :-

(A) 1   (B) 0.36   (C) 2.25   (D) $\dfrac{4}{9}$

13. 4.5 moles each of hydrogen and iodine heated in a sealed ten litre vessel. At equilibrium, 3 moles of HI were found. The equilibrium constant for $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is:-

(A) 1   (B) 10   (C) 5   (D) 0.33

5.0 FACTORS AFFECTING EQUILIBRIUM CONSTANT
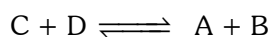
5.1 Mode of representation of the reaction
SL AL
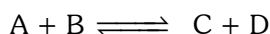
$A + B \rightleftharpoons C + D$

The equilibrium constant for the reaction

$$K_C = \frac{[C][D]}{[A][B]}$$

If the reaction is reversed

$C + D \rightleftharpoons A + B$

then, $K_c' = \dfrac{[A][B]}{[C][D]}$

The two equilibrium constant related as $\rightarrow K_C' = \dfrac{1}{K_C}$

For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ if $K_C = 5$ then K_C' for reverse reaction will be
$K_C' = 1/5 = 0.2$

5.2 Stoichiometry of the reaction
SL AL

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

For reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$

$$K_C = \frac{[N_2][O_2]^2}{[NO_2]^2}$$

For reaction $NO_2 \rightleftharpoons \dfrac{1}{2}N_2 + O_2$

$$K_c^1 = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$$ The two constants are related as $K_c^1 = \sqrt{K_C}$

5.3 Temperature
SL AL

The value of equilibrium constant changes with the change of temperature.

If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 and ΔH is the heat of reaction at constant volume, then :

$$\frac{d(\ell nk)}{dT} = \frac{\Delta H}{RT^2}$$

$$\log \frac{K_2}{K_1} = \log K_2 - \log K_1 = \frac{-\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ (According to Vant Hoff equation)}$$

(i) $\Delta H = 0$ (neither heat is absorbed or evolved)

$\log K_2 - \log K_1 = 0$

$\log K_1 = \log K_2$

$K_1 = K_2$

Thus, equilibrium constant remains the same at all temperatures

If temp. T_2 is higher than T_1

$$\frac{1}{T_2} - \frac{1}{T_1} < 0, \ \log K_2 - \log K_1 = \frac{+ve\Delta H}{2.303R}$$

(ii) When $\Delta H = +ve$ (endothermic reaction)

$\log K_2 - \log K_1 > 0$

or $\log K_2 > \log K_1$

$K_2 > K_1$

The value of equilibrium constant is higher at higher temperature in case of endothermic reactions.

$K_C \propto T$

(iii) When $\Delta H = -ve$ (exothermic reaction)

$\log K_2 - \log K_1 < 0$

$\log K_2 < \log K_1$

$K_2 < K_1$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.

$K_C \propto 1/T$

The value of equilibrium constant is independent of the following factors :-
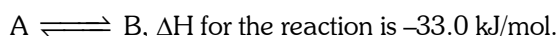
(a) Initial concentrations of reactants.

(b) The presence of a catalyst.

(c) The direction from which the equilibrium has been attained.

(d) Presence of inert materials.

Illustrations

Illustration 11*. For the reaction,

$A \rightleftharpoons B$, ΔH for the reaction is –33.0 kJ/mol.

Calculate :

(i) Equilibrium constant K_c for the reaction at 300 K

(ii) If $E_{a(f)}$ and $E_{a(r)}$ in the ratio of 20 : 31, calculate $E_a(f)$ and $E_a(r)$ at 300 K.

Assuming pre-exponential factor same for forward and reverse reaction.

Solution (i) $\Delta H = E_{a(f)} - E_{a(r)} = -33$ kJ

$k_f = Ae^{-E_{a(f)}/RT}$

$k_b = Ae^{-E_{a(r)}/RT}$

$\therefore \quad k_c = \frac{k_f}{k_b} = e^{\left[E_{a(f)} - E_{a(r)}\right]/RT}$

$\Rightarrow \quad e^{\frac{33\times10^3}{8.314\times300}} = 5.572 \times 10^5$ at 300 K

(ii) $\frac{E_{a(f)}}{E_{a(r)}} = \frac{20}{31} \quad E_{a(f)} - E_{a(r)} = -33$kJ

$\therefore \quad E_{a(r)} - \frac{31}{20} \times E_{a(f)} = -33$kJ

$\therefore \quad E_{a(f)} = \frac{33\times20}{11} = 60$kJ $\quad\quad E_{a(r)} = +93$ kJ
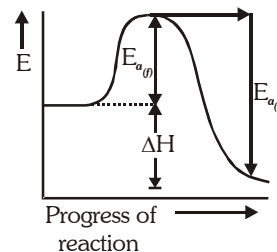
Illustration 12. The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

(A) -68000.05 J mol^{-1}
(B) -71080.57 J mol^{-1}
(C) -80071.75 J mol^{-1}
(D) 57080.75 J mol^{-1}

Solution **(B)**

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$
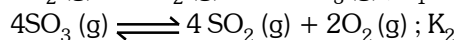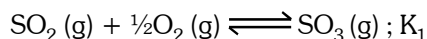
$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}.$$

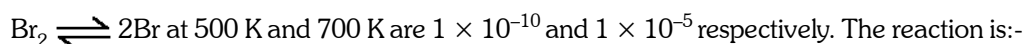## BEGINNER'S BOX–3

Factors Affecting Equilibrium Constant

1. Consider the two gaseous equilibrium involving SO$_2$ and the corresponding equilibrium constants at 299 K
$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$; K_1
$4SO_3(g) \rightleftharpoons 4SO_2(g) + 2O_2(g)$; K_2
The value of the equilibrium constant are related by :-

(A) $K_2 = \dfrac{1}{(K_1)^4}$ (B) $K_2 = K_1^4$ (C) $K_2 = \left(\dfrac{1}{K_1}\right)^{\frac{1}{4}}$ (D) $K_2 = \dfrac{1}{K_1}$

2. The equilibrium constant for the reaction
$Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is:-
(A) Endothermic   (B) Exothermic   (C) Fast   (D) Slow

3*. Which one of the following statements is correct about equilibrium constant:-
(A) Equilibrium constant of a reaction changes with temperature.
(B) Equilibrium constant of a reaction depends upon the concentration of reactants with which we start.
(C) Equilibrium constant of a reaction, $3Fe(s) + 4H_2O_{(g)} \rightleftharpoons Fe_3O_4(s) + 4H_{2(g)}$ is the same whether, the reaction is carried out in an open vessel or a closed vessel.
(D) Equilibrium constant of a reaction becomes double if the reaction is multiplied by 2 throughout.

4. The equilbrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at 2000 K is 4×10^4
In presence of catalyst the equilibrium is established ten times faster at the same temperature. What is the value of equilibrium constant in presence of catalyst :-
(A) 40×10^{-4} (B) 4×10^{-4} (C) 4×10^4 (D) None

5. $aA + bB \rightleftharpoons cC + dD$
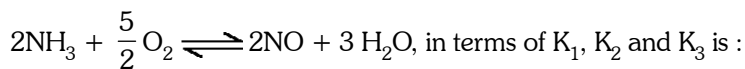in above reaction low pressure and high temperature conditions shift equilibrium in back direction so correct set:
(A) $(a + b) > (c + d), \Delta H > 0$ (B) $(a + b) < (c + d), \Delta H > 0$
(C) $(a + b) < (c + d), \Delta H < 0$ (D) $(a + b) > (c + d), \Delta H < 0$

6*. The following equilibrium are given

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ------------- K_1

$N_2 + O_2 \rightleftharpoons 2NO$ ------------- K_2

$H_2 + \dfrac{1}{2}O_2 \rightleftharpoons H_2O$ ------------- K_3

The equilibrium constant of the reaction

$2NH_3 + \dfrac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$, in terms of K_1, K_2 and K_3 is :
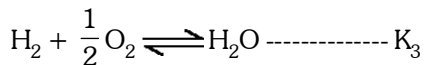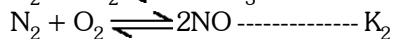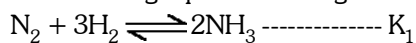
(A) $\dfrac{K_1K_2}{K_3}$
(B) $\dfrac{K_1K_3^2}{K_2}$
(C) $\dfrac{K_2K_3^3}{K_1}$
(D) $K_1K_2K_3$

7*. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_c = 66.9$ at 350°C and $K_c = 50.0$ at 448°C. The reaction has

(A) $\Delta H = +\,ve$
(B) $\Delta H = -\,ve$

(C) $\Delta H = $ Zero
(D) $\Delta H = $ Not found the signs

Illustrations

Illustration 13*. For the reaction.

$CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g) ; $K_p = 1.16$ atm. at 800°C. If 40 g of $CaCO_3$ was put into a 20 L container and heated to 800°C, what percent of $CaCO_3$ would remain unreacted at equilibrium.

Solution $K_p = P_{CO_2} = 1.16$ atm

$n(CO_2) = PV/RT = \dfrac{1.16 \times 20}{0.0821 \times 1073} = 0.26335$ mol

moles of $CaCO_3$ initially present
= 40/100 = 0.4 mol

So % decomposition of $CaCO_3 = \dfrac{0.26335}{0.4} \times 100 = 65.83$ % decomposed

Hence 34.17 % remain unreacted.

Illustration 14. For the reaction :

SnO_2 (s) + $2H_2$ (g) $\rightleftharpoons$ $2H_2O$ (g) + Sn (s)
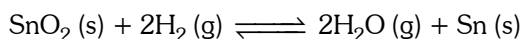
Calculate K_p at 900 K where the equilibrium steam hydrogen mixture was 35 % H_2 by volume.

Solution $K_p = \dfrac{(P_{H_2O})^2}{(P_{H_2})^2}$

given H_2 is 35% by volume at constant temperature in closed vessel (P $\propto$ V)

so $P_{H_2O} = 0.65$ atm and $P_{H_2} = 0.35$ atm

$K_p = \left(\dfrac{0.65}{0.35}\right)^2 = 3.448$

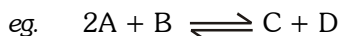## 6.0 REACTION QUOTIENT (Q)

SL **AL**

At each point in a reaction, we can write a ratio of concentration terms having the same form as the eqb^m constant expression. This ratio is called the reaction quotient denoted by symbol Q.

It helps in predicting the direction of a reaction.

The expression $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ at any time during reaction is called reaction quotient.

eg. $2A + B \rightleftharpoons C + D$

Q_C = Reaction quotient in terms of concentration

$$Q_C = \frac{[C][D]}{[A]^2[B]}$$

$$K_C = \frac{[C]_e[D]_e}{[A]_e^2[B]_e} \quad \text{[Here all the conc. are at equilibrium]}$$

Important :

(i) if $Q > K_c$ reaction will proceed in backward direction until equilibrium in reached.
(ii) if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
(iii) if $Q = K_c$ Reaction is at equilibrium.

Illustrations

Illustration 15. For the reaction $NOBr (g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2 (g)$

$K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively, will Br_2 be consumed or formed ?

Solution

$$Q_P = \frac{\left[P_{Br_2} \right]^{1/2} [P_{NO}]}{[P_{NOBr}]} = \frac{[0.20]^{1/2} \; [0.4]}{[0.50]} = 0.36$$

$$K_P = 0.15$$

$\therefore \quad Q_P > K_P$

Hence, reaction will shift in backward direction

$\therefore \quad Br_2$ will be consumed

7.0 DEGREE OF DISSOCIATION

SL AL

It is the fraction of one mole dissociated into the products.
(Defined for one mole of substance)
So, a = no. of moles dissociated / initial no. of moles taken
         = *fraction of moles dissociated out of 1 mole.*

Note : *% dissociation = $\alpha \times 100$*

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then a = $\frac{2}{5}$ = 0.4

Let a gas A_n dissociates to give n moles of A as follows-

$$A_n (g) \rightleftharpoons n A (g)$$

t = 0   a   0
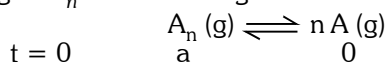
t = t_{eq} a – x   n.x $\alpha = \dfrac{x}{a} \implies x = a\alpha.$

       $a - a\alpha = a(A) - \alpha)$ $n \, a \, \alpha$

Total no. of moles $= a - a\alpha + n\,a\,\alpha$

                  $= [1 + (n-1)\alpha]\, a$

Significance of n

$$n = \frac{\text{sum of stoichiometric coeff of product}}{\text{sum of coeff of reactants}}$$

(i) for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (n = 2)

(ii) for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\left(n = \dfrac{3}{2} + \dfrac{1}{2} = 2 \right)$

(iii) for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ (n = 1)

Observed molecular weight and Observed Vapour Density of the mixture

$$\text{Observed molecular weight of } A_n(g) \quad = \quad \frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$$

$$= \quad \frac{a.M_{th}}{a(1+(n-1)\alpha)}$$

$$\therefore \qquad M_{obs} = \frac{M_{th}}{[1+(n-1)\alpha]}$$

where M_{th} = theoritical mol. wt., (n = atomicity)

$$M_{mixture} = \frac{M_{A_n}}{[1+(n-1)\alpha]} \ , \ M_{A_n} = \text{Molar mass of gas } A_n$$

V.D. : Density of the gas divided by density of hydrogen under same temp & pressure.

$$D = \text{vapour density without dissociation} = \frac{M_{A_n}}{2}$$

$$d = \text{vapour density of mixture} = \text{observed v.d.} = \frac{M_{mix}}{2}$$

$$\frac{D}{d} = 1 + (n-1)\ a$$

$$\therefore \qquad \alpha = \frac{D-d}{(n-1)\times d} = \frac{M_T - M_o}{(n-1)M_0}$$

where M_T = Theoritical molecular wt. M_0 = observed molecular wt. or molecular wt. of the mixture at eq.
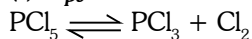
Note : *It is not applicable for n = 1 [eg. Dissociation of HI & NO].*

─────────────── Illustrations ───────────────

Illustration 16. At 250°C and 1 atm pressure, the v.d. of PCl_5 is 57.9. Calculate
(i) K_p for the reaction (ii) % dissociation when P is doubled

Solution. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
$(v.d.)_{obs.} = 57.9 \qquad \Rightarrow \qquad M_{mixture} = 2 \times 57.9 = 115.8$

$$\Rightarrow \quad \text{observed mol. wt.} = \frac{\text{Theoretical mol. wt.}}{\text{total no. of moles}}$$

$$M_{mixture} = \frac{M_{th}}{[1+(n-1)\alpha]} = \frac{208.5}{1+\alpha} \Rightarrow a = 0.8 \qquad \Rightarrow \qquad K_P = \frac{\alpha^2 \ P}{1-\alpha^2} = \frac{16}{9} \text{ (i) Ans.}$$

$$\frac{16}{9} = K_P = \frac{(\alpha')^2}{1-(\alpha')^2}P' \qquad [\because P' = 2 \text{ atm}] \qquad \therefore a = 0.69 \text{ (ii) } \textbf{Ans.}$$

8.0 HOMOGENEOUS LIQUID SYSTEM : FORMATION OF ETHYL ACETATE

SL AL

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$
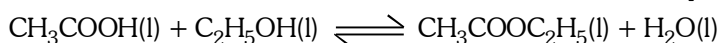
$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Equation involving ions : Equilibrium involving ions always take place in aquous medium . In case of expression of K_C concentration of ion is taken.

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)} \ K_c = \frac{1}{[Ag^+][Cl^-]}$$
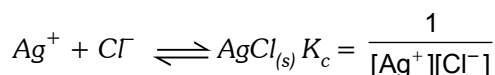
Illustrations

Illustration 17. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T^0C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

Solution

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial	1	1	0	1
At	1 – x	1 – x	x	1 + x
equilibrium	1 – 0.543	1 – 0.543	0.543	1 + 0.543
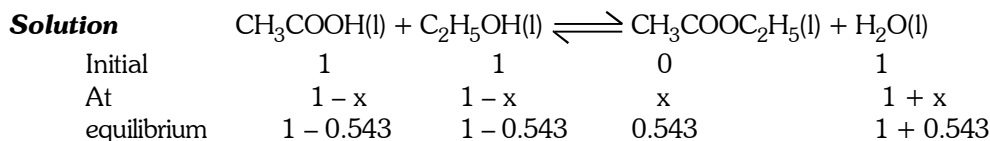
(54.3% of 1 mole $= \dfrac{1 \times 54.3}{100} = 0.543$ mole)

Hence given x = 0.543 mole

Applying law of mass action :

$$K_C = \frac{[ester][water]}{[acid][alcohol]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

9.0 HETEROGENOUS EQUILIBRIUM

AL

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as they remain constant throughout the reaction

(i) $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

$K_P = P_{CO_2}$, $K_C = [CO_2 (g)]$

$$[CaCO_3(s)] = \frac{moles}{volume} = \frac{\dfrac{W_{CaCO_3}}{M_{CaCO_3}}}{V} = \frac{density \ CaCO_3}{M_{CaCO_3}} = constant$$
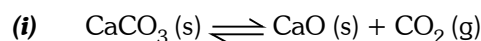
$$K = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

$$\frac{K.[CaCO_3(s)]}{[CaO(s)]} = [CO_2(g)]$$

$$K_C = [CO_2(g)]$$

(ii) $H_2O(l) \rightleftharpoons H_2O(g)$
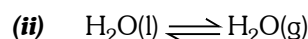
$K_P = P_{H_2O(g)}$, $K_C = [H_2O (g)]$

[For pure solid and pure liquid active mass is taken to unit i.e. = 1]

Illustrations

Illustration 18. In a reaction C(s) + CO_2 (g) $\rightleftharpoons$ 2CO(g), the equilibrium pressure is 12 atm. If 50% of CO_2 reacts. Calculate K_P.

Solution

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

t = 0	a	0	
t = t_{eq}	$a - \dfrac{a}{2}$	$2\dfrac{a}{2}$	
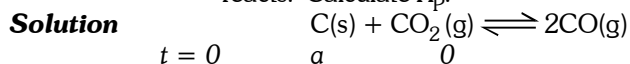
P_{eq} = 12 atm

$$X_{CO_2} = \frac{1}{3}, \ X_{CO} = \frac{2}{3}$$

$$P_{CO_2} = \frac{1}{3} \times 12 = 4$$

$$P_{CO} = \frac{2}{3} \times 12 = 8$$

$$\therefore \quad K_P = \frac{8 \times 8}{4} = 16$$

BEGINNER'S BOX–4

Degree of Dissociation & Observed Molecular weight & Observed vapour density of the mixture

1. For the reaction : $P \rightleftharpoons Q + R$. Initially 2 moles of P was taken. Up to equilibrium 0.5 moles of P was dissociated. What would be the degree of dissociation :
(A) 0.5 (B) 1 (C) 0.25 (D) 4.2

2. $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$
In above reaction, at equilibrium condition mole fraction of PCl_5 is 0.4 and mole fraction of Cl_2 is 0.3. Then find out mole fraction of PCl_3
(A) 0.3 (B) 0.7 (C) 0.4 (D) 0.6

3*. The dissociation of CO_2 can be expressed as $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$. If the 2 moles of CO_2 is taken initially and 40% of the CO_2 is dissociatated completely. What is the total number of moles at equilibrium:
(A) 2.4 (B) 2.0 (C) 1.2 (D) 5

4. One mole PCl_5 is heated in a closed container of one litre capacity. At equilibrium, 20% PCl_5 is not dissociated. What should be the value of K_c ?
(A) 32 (B) 3.2 (C) 2.4 (D) 42

5*. $A_3(g) \rightleftharpoons 3A (g)$
In the above reaction, the initial moles of A_3 is "a". If α is degree of dissociation of A_3. The total number of moles at equilibrium will be:-

(A) $a - \dfrac{a\alpha}{3}$ (B) $\dfrac{a}{3} - a$ (C) $\left(\dfrac{a-a\alpha}{2} \right)$ (D) None of these

6. The equation $\alpha = \dfrac{D-d}{(n-1)d}$ is correctly matched for :

Where D = Theoretical vapour density
d = Observed vapour density

(A) $A \rightleftharpoons \dfrac{nB}{2} + \dfrac{nC}{3}$ (B) $A \rightleftharpoons \dfrac{nB}{3} + \left(\dfrac{2n}{3} \right) C$

(C) $A \rightleftharpoons \left(\dfrac{n}{2} \right) B + \left(\dfrac{n}{4} \right) C$ (D) $A \rightleftharpoons \left(\dfrac{n}{2} \right) B + C$

7*. Before equilibrium is set-up for the chemical reaction $N_2O_2 \rightleftharpoons 2NO_2$, vapour density d of the gaseous mixture was measured. If D is the theoretical value of vapour density, variation of x with D/d is by the graph. What is value D/d at point A?
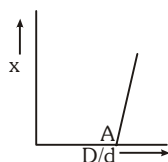
(A) 0 (B) 0.5 (C) 1 (D) 1.5

10.0 EXTERNAL FACTORS AFFECTING EQUILIBRIUM

SL AL

Le Chatelier's Principle:
If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change and the equilibrium is established again under new conditions.

10.1 Effect of concentration

SL AL

If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration.

- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction .
- If concentration of product is increased then reaction shifts in the backward direction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
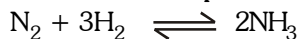
(reactant) $\uparrow$ Forward shift

(Product) $\uparrow$ Backward shift

Note : *The addition of any solid component does not affect the equilibrium.*

10.2 Effect of volume

SL AL

- If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- If volume is increased then,   for

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift. eg. $H_2 + I_2 \rightleftharpoons 2HI$ (No effect)

Explanation

(i) $\Delta n > 0$, eg. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (g)

$$Q_C = \frac{\dfrac{()}{V} \times \dfrac{()}{V}}{\dfrac{()}{V}} \qquad \Rightarrow \qquad Q_C \propto \frac{1}{V} \quad \text{for } \Delta n > 0 \qquad [() = \text{moles}]$$

On incerasing V, Q_C, decreases.

Now, for $Q_C < K_C$ reaction will shift in forward direction.

Thus, if, Volume $\uparrow$ Q_C $\downarrow$ Forward

           Volume $\downarrow$ Q_C $\uparrow$ Backward

(ii) $\Delta n < 0$, eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$Q_C = \frac{\left\{\dfrac{()}{V}\right\}^2}{\left\{\dfrac{()}{V}\right\}\left\{\dfrac{()}{V}\right\}^3} \qquad \Rightarrow \qquad Q_C \propto V^2 \quad \text{for} \quad \Delta n < 0$$

V $\uparrow$ Q_C $\uparrow$ – Backward

V $\downarrow$ Q_C $\downarrow$ – Forward

10.3 Effect of pressure

SL AL

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

         $\because$ P $\propto$ no. of moles

(i)   For $\Delta n = 0 \rightarrow$ No. effects

(ii)   For $\Delta n > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_p = \frac{()P.()P}{()P} \Rightarrow Q_P \propto P \qquad [() = \text{mole fraction}]$$

P $\downarrow$ $= Q_P \downarrow$ = Forward

P $\uparrow$ $= Q_P \uparrow$ = Backward

(iii) For $\Delta n < 0$, *eg.* $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$Q_P = \frac{[(\ )P)]^2}{[(\ ).P][(\ )P]^3} \Rightarrow Q_P \propto \frac{1}{P^2}$$

$P\uparrow = Q_P\downarrow$ = Forward

$P\downarrow = Q_P\uparrow$ = Backward

10.4 Effect of catalyst

SL AL

Due to catalyst, The state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus increasing the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less.

10.5 Effect of inert gas addition

SL AL

(i) At constant volume : Inert gas addition has no effect at constant volume

(ii) At constant pressure : If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

(a) $\Delta n > 0$, reaction will shift in the forward direction

(b) $\Delta n < 0$, reaction will shift in the backward direction

(c) $\Delta n = 0$, no effect

10.6 Effect of temperature

SL AL

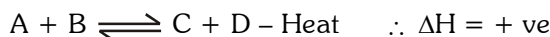*(i) Exothermic reaction :* The reaction in which heat is evolved

    $A + B \rightleftharpoons C + D + Heat \qquad \Delta H = -ve$

eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3 + Q$

    $T\uparrow \Rightarrow K'$ will decrease (from vant' hoff of equation)

$\Rightarrow$ Thus, $Q > K' \Rightarrow$ Backward shift

    $T\uparrow \Rightarrow$ Forward shift

(ii) Endothermic reaction : energy consumed.

    $A + B \rightleftharpoons C + D - Heat \qquad \therefore \ \Delta H = +ve$

    $T\uparrow \Rightarrow K\uparrow \Rightarrow$ Forward

    $T\downarrow \Rightarrow K\downarrow \Rightarrow$ Backward

11.0 APPLICATION OF LE CHATELIER'S PRINCIPLE: PRACTICAL EQUILIBRIUM SITUATIONS

11.1 Vapour Pressure of Liquid

SL AL

It is the pressure exerted by the vapour over it's liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called *aqueous tension*.

$$H_2O_{(\ell)} \rightleftharpoons H_2O\,(g) ; \qquad K_P = P_{H_2O} = \textbf{\textit{constant at fixed temperature}}$$
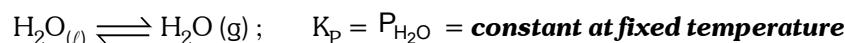
Hence V.P. of liquid is independent of pressure, volume and concentration change.

e.g. at 25°C, vapour pressure of water ≈ 24 mm of Hg

$$\textbf{\textit{Relative Humidity}} = \frac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$$

11.2 Formation of diamond
SL AL

$$C \text{ (graphite)} \rightleftharpoons C \text{ (diamond)} - Heat; \qquad \Delta H = + ve$$

↓	↓
Density Low	Density High
Volume High	Volume Low

Formation of diamond is favourable at high pressure and high temperature

11.3 Melting of ice
SL AL

$$H_2O \text{ (s)} \rightleftharpoons H_2O_{(\ell)}; \qquad \Delta H = + ve$$
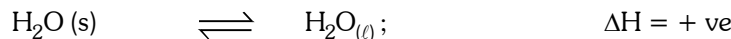
↓	↓
Density Low	Density High
Volume High	Volume Low

Melting of ice is favourable at high temperature and high pressure.
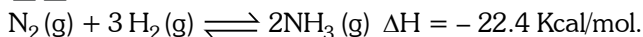
11.4 Boiling of water
SL AL

$$H_2O_{(\ell)} \rightleftharpoons H_2O(g)$$

↓	↓
Density High	Density Low
Volume Low	Volume High

On incerasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward.
Hence, on incerasing pressure, the boiling point increases.

11.5 Formation of ammonia by Haber's process
SL AL

$N_2 (g) + 3 H_2 (g) \rightleftharpoons 2NH_3 (g) \quad \Delta H = - 22.4 \text{ Kcal/mol.}$

(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.

(ii) At high pressure, reaction will shift in forward direction to form more product.
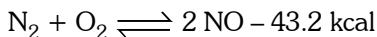
11.6 Manufacturing of SO$_3$ by contact process
SL AL

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45.2 \text{ kcal}$$
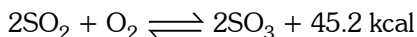
High pressure (A).5 to 1.7 atm),   Low temperature (500°C), Higher qunatity of SO$_2$ and O$_2$ are favourable conditions for the formation of SO$_3$.

11.7 Manufacturing of NO by Birkeland–Eyde process
SL AL

$$N_2 + O_2 \rightleftharpoons 2 NO - 43.2 \text{ kcal}$$

No effect on change of pressure
High temperature (A)200 °C to 2000 °C), High concentration of N$_2$ and O$_2$ are favourable condition for the formation of NO.

─────────────── Illustrations ───────────────

Illustration 19*. The equilibrium constant of the reaction at 25°C

$$CuSO_4.5H_2O \text{ (s)} \rightleftharpoons CuSO_4.3H_2O + 2H_2O(g)$$

is 1.084×10^{-4} atm^2. Find out under what conditions of relative humidity, CuSO$_4$.5H$_2$O will start loosing its water of crystalliziation according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

Solution $\qquad K_P = \left(P_{H_2O}\right)^2$

so $P_{H_2O} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2}$ atm ≈ 8 mm of Hg

* If in a room, pressure of water is greater than 8 mm of Hg then $CuSO_4.3H_2O$ will absorb water from air and will from $CuSO_4.5H_2O$ & will keep absorbing until partial pressure of H_2O becomes 8 mm of Hg.

* If P_{H_2O} < 8 mm of Hg then $CuSO_4.5H_2O$ will loose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity < P_{H_2O} < 33.33%

then $CuSO_4.5H_2O$ will loose water of crystallization.

12.0 THERMODYNAMICS OF EQUILIBRIUM

SL AL

For a general reaction, $mA + nB \rightleftharpoons pC + qD$, ΔG is given by-

$$\Delta G = \Delta G^0 + 2.303\ RT\ \log_{10}Q$$

where ΔG = Gibb's Free energy

ΔG^0 = Standard Gibb's Free energy

Q = reaction quotient

Since, at equlibrium, Q = K

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$$K = \frac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n}$$

Here a_X denotes the activity of X.

In fact, 'a_x' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

Note   (i) Themodynamics equilibrium constant is unitless since activity is unitless.

(ii) For pure solids & pure liquids, activity is unity.

(iii) For gases (ideal behaviour), the activity is its partial pressure in atm.

(iv) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$\Rightarrow$ $\Delta G^0 = -2.303\ RT\ \log_{10}K$

Now since, $\Delta G^0 = \Delta H^0 - T\Delta S^0$

where $\Delta H^0 = $ Standard enthalpy of the reaction

$\Delta S° = $ Standard entropy change

$\Rightarrow$ $-2.303\ RT\ \log_{10}K = \Delta H^0 - T\Delta S^0$

$\Rightarrow$ $\log_{10}K = -\dfrac{\Delta H^0}{2.303} \cdot \dfrac{1}{RT} + \dfrac{\Delta S^0}{2.303R}$

If plot of lnk vs $\dfrac{1}{T}$ is plotted then it is a straight line with slope $= -\dfrac{\Delta H°}{R}$, and intercept $= \dfrac{\Delta S°}{R}$
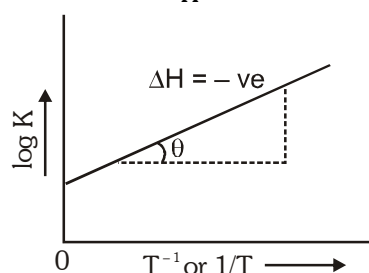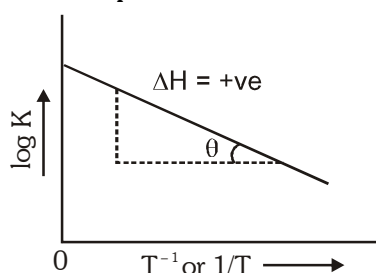
$$\text{Slope} = \frac{-\Delta H^0}{2.303R} = \tan\theta\ , \qquad \text{y intercept} = \frac{\Delta S^0}{2.303R}$$

If at temperature T_1, equilibrium constant is K_1 and at T_2, it is K_2 then ;

$$\log_{10} K_1 = \frac{-\Delta H^0}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^0}{2.303R} \qquad \text{.... (i)}$$

$$\log_{10} K_2 = \frac{-\Delta H^0}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^0}{2.303R} \qquad \text{.... (ii)}$$

[Assuming ΔH^0 and ΔS^0 remains constant in this temperature range.]

Subtract eq. (ii) from (i) we get   **Vant Hoff equation-**

$$\log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^0}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note : ΔH^0 should be substituted with sign.

Unit of ΔH^0 and gas constant R should be same.

* For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature

* For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for Spontaneity : $\Delta G^0 < 0$ **for spontaneous process or reaction.**

Since, $\Delta G = \Delta H - T\Delta S$

$\Rightarrow \qquad \Delta H - T\Delta S < 0 \qquad \Rightarrow \qquad T > \Delta H/\Delta S$

* $\qquad \Delta G > 0$ for non - spontaneous process or reaction
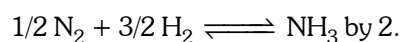
* $\qquad \Delta G = 0$ for equilibrium.

— Illustrations —

Illustration 20. $\Delta G°$ for $\frac{1}{2}$ $N_2 + 3/2\, H_2 \rightleftharpoons NH_3$ is -16.5 kJ mol^{-1}. Find out K_P for the reaction at 25°C. Also report K_P and $\Delta G°$ for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 25°C.

Solution $\qquad \log K_P = -\dfrac{\Delta G°}{2.303RT} = \dfrac{+16.5 \times 10^3}{2.303 \times 8.314 \times 298} = 2.8917$

$K_P = $ antilog $(2.8917) = 779.41$

Now given reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ can be obtained by multiplying eq.

$1/2\, N_2 + 3/2\, H_2 \rightleftharpoons NH_3$ by 2.

so $K_p' = (779.41)^2 = 6.07 \times 10^5$

and $\Delta G° = -2.303\, RT \log K_p' = -2.303 \times 8.314 \times 298 \log (6.07 \times 10^5)$ J

$\Delta G° = -32.998$ kJ mol^{-1}.

Illustration 21*. For the gaseous reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ the following thermodynamics data are given.

$\Delta H°_{300\,K} = -41.16$ kJ mol^{-1} ; $\Delta S°_{300\,K} = -0.0424$ kJ mol^{-1}.

$\Delta H°_{1200\,K} = -32.93$ kJ mol^{-1} ; $\Delta S°_{1200\,K} = -0.0296$ kJ mol^{-1}.

Assuming partial pressure of each component at 1 atm. determine the direction of spontaneous reaction at

(i) 300 K

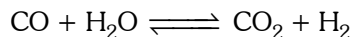(ii) 1200 K. Also calculate K_P for the reaction at each temperature.

Solution   Using $\Delta G° = \Delta H° - T\Delta S°$

$\Delta G°_{300\,K} = -41.16 - 300\,(-0.0424)$

$= -28.44\;kJ\;mol^{-1}$

so reaction is spontaneous in given direction since $\Delta G°$ is negative

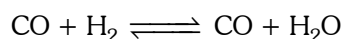$CO + H_2O \rightleftharpoons CO_2 + H_2$

at 1200 K

$\Delta G°_{1200\,K} = -32.93 - 1200\,(-0.0296)$

$= 2.56\;kJ\;mol^{-1}$

so reaction will not be spontaneous in given direction, but reverse reaction spontaneous i.e.

$CO + H_2 \rightleftharpoons CO + H_2O$

We know $\Delta G° = -2.303\;RT\;log\;K_P$

so K_P (300 K)

$= antilog\left(\dfrac{-28.44 \times 10^3}{-2.303 \times 8.314 \times 300}\right) = 8.8 \times 10^4$

$K_P = (A)200\;K)$

$= antilog\left(\dfrac{+2.59 \times 10^3}{-2.303 \times 8.314 \times 1200}\right) = 0.77$

13.0 SIMULTANEOUS EQUILIBRIUM

AL

If in any container there are two or more equilibria existing simultaneously involving one or more than one common species. Then in both/all the equilibrium the concentration of common species is the total concentration of that species due to all the equilibria under consideration.

e.g. $A(s) \rightleftharpoons X(g)\;\; + \;\;Y(g)$

t = 0   a   0   0

t = teq   a – t   t   t + u

$B(s) \rightleftharpoons Z(g)\;\; + \;\;Y(g)$
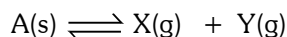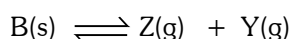
  b   0   0

b – u   u   u + t

$K_{C_1} = t\,(u + t)$

$K_{C_2} = (u + t)\,u$

— Illustrations —

Illustration 22*.   102 g of solid NH_4HS is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

$NH_4HS\;(s) \rightleftharpoons NH_3\;(g) + H_2S\;(g)$

$NH_3\;(g) \rightleftharpoons \dfrac{1}{2}\,N_2\;(g) + \dfrac{3}{2}\,H_2\;(g)$
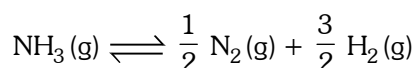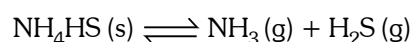
one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of H_2 was found at the equilibrium then find the equilibrium concentration of all the species and K_C for both the reaction.

Solution   Moles of $NH_4HS = \dfrac{102}{51} = 2$

$$NH_4HS \text{ (s)} \rightleftharpoons NH_3 \text{ (g)} + H_2S \text{ (g)} \qquad K_{C_1}$$

2	0	0
1	1 – x	1

$$NH_3 \text{ (g)} \rightleftharpoons \dfrac{1}{2} N_2 \text{ (g)} + \dfrac{3}{2} H_2 \text{ (g)} \qquad K_{C_2}$$

1 – x	$\dfrac{x}{2}$	$\dfrac{3x}{2}$
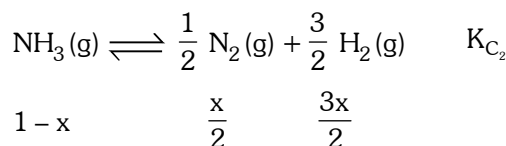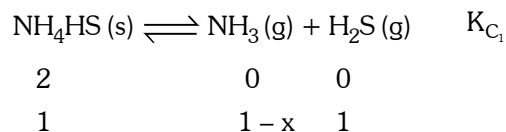
Given that moles of $\quad H_2 = \dfrac{3x}{2} = 0.75 \quad \Rightarrow \quad x = \dfrac{1}{2}$

$$K_{C_1} = \dfrac{1}{2}\dfrac{(1-x)}{2} = \dfrac{1}{8} \quad \text{[Since V = 2 L]}$$

$$K_{C_2} = \dfrac{\left(\dfrac{3x}{4}\right)^{3/2}\left(\dfrac{x}{4}\right)^{\frac{1}{2}}}{\left(\dfrac{1-x}{2}\right)} = \dfrac{\left(\dfrac{3}{8}\right)^{3/2}\left(\dfrac{1}{8}\right)^{\frac{1}{2}}}{\dfrac{1}{4}} = (3)^{3/2}\dfrac{1}{64}\times\dfrac{4}{1} = \dfrac{(3)^{3/2}}{16}$$

BEGINNER'S BOX–5

Le-Chatelier's Principle

1. Pure ammonia is placed in a vessel at a temperature At equilibrium:-
(A) K_p does not change significantly with pressure
(B) Degree of dissociation does not change with pressure
(C) concentration of NH_3 does not change with pressure
(D) K_C changes with pressure

2*. A reaction in equilibrium is represented by the following equation –
$2A_{(s)} + 3B_{(g)} \rightleftharpoons 3C_{(g)} + D(g) + Q$ if the pressure on the system is reduced to half of its original value:-
(A) The amounts of C and D decreases   (B) The amounts of C and D increases
(C) The amount of D decreases   (D) All the amounts remain constant

3*. When $NaNO_3$ (s) is heated in a closed vessel, O_2 is liberated and $NaNO_2$(s) is left behind.

$$NaNO_{3(s)} \rightleftharpoons NaNO_{2(s)} + \dfrac{1}{2} O_{2(g)}$$

At equilibrium –
(A) Addition of $NaNO_3$ favours forward reaction   (B) Addition of $NaNO_2$ favours reverse reaction
(C) Increasing pressure favours reverse reaction.   (D) Decreasing temperature favours forward reaction.

4. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts forward if :-
(A) A catalyst is used.
(B) An adsorbent is used to remove SO_3 as soon as it is formed.
(C) Small amounts of reactants are removed.
(D) None of these

5. In manufacture of NO, the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, DH +ve is favourable if :-
(A) Pressure is increased   (B) Pressure is decreased
(C) Temperature is increased   (D) Temperature is decreased

6. In which of the following equilibrium reactions, the equilibrium would shift to right side, if total pressure is decreased :-

(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(B) $H_2 + I_2 \rightleftharpoons 2HI$

(C) $N_2O_4 \rightleftharpoons 2NO_2$

(D) $N_2 + O_2 \rightleftharpoons 2NO$

7*. The oxidation of SO_2 by O_2 to SO_3 is exothermic reaction. The yield of SO_3 will be increased if :-

(A) Temperature is increased and pressure is kept constant

(B) Temperature is reduced and pressure is increased

(C) Both temperature and pressure are increased

(D) Both temperature and pressure are decreased

8. The reaction in which yield of product cannot be increased by the application of high pressure is :-

(A) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(B) $N_2(g) + O_2(g) \rightleftharpoons 2NO (g)$

(C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

9. In a vessel containing SO_3, SO_2 and O_2 at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le-Chatelier principle, the dissociation of SO_3 ,

(A) Increases   (B) Decreases   (C) Remains unaltered   (D) None of these

10. On decreasing temperature of following system at equilibrium $CO_{2(s)} \rightleftharpoons CO_{2(g)}$, $DH = +ve$:-

(A) There is no effect on the equilibrium state

(B) More CO_2 gas is formed

(C) More solid CO_2 is obtained

(D) None of above

11. For the equilibrium reaction, $H_2O (l) \rightleftharpoons H_2O_{(g)}$, What happens, if pressure is increased :-

(A) More water evaporates

(B) equilibrium shift in backword direction

(C) No effect on equilibrium

(D) None of the above

12. Densities of diamond and graphite are 3.5 and 2.3 g/ml respectively. Increase of pressure on equilibrium, $C_{(diamond)} \rightleftharpoons C_{(graphite)}$:

(A) Favours backward reaction

(B) Favours forward reaction

(C) Has no effect on reaction

(D) Increase the reaction rate

13. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of CO_2 (g) can be increased by

(A) adding a suitable catalyst

(B) adding an inert gas

(C) decreasing the volume of container

(D) increasing the amount of $CO(g)$

14*. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct.

(A) Concentrations of SO_2, Cl_2 and SO_2Cl_2 are changed

(B) No effect on equilibrium

(C) Concentration of SO_2 is reduced

(D) K_p of reaction is increasing

S. No.	Reaction	Δn		Relation between K_P & K_C	values of K_C	values of K_P	Unit of K_C	Unit of K_P	Relation between amount of dissociation (volume and pressure)	ΔH	Conditions for obtaining more product
1.	$H_2 + I_2 \rightleftharpoons 2HI$	0	$K_P = K_C(RT)^0$	$K_P = K_C$	$\dfrac{4x^2}{(a-x)(b-x)}$	$\dfrac{4x^2}{(a-x)(b-x)}$	None	None	None	$-ve$ (exothermic)	Low temperature No pressure High concentration
2.	$2HI \rightleftharpoons H_2 + I_2$	0	$K_P = K_C(RT)^0$	$K_P = K_C$	$\dfrac{x^2}{4(1-x)^2}$	$\dfrac{x^2}{4(1-x)^2}$	None	None	None	$+ve$ (endothermic)	High temperature No pressure High concentration
3.	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	$+1$	$K_P = K_C(RT)^1$	$K_P > K_C$	$\dfrac{x^2}{(1-x)v}$	$\dfrac{x^2 p}{(1-x^2)}$	gram mol^1 lit^{-1}	(Atm. press.)^1	$x \propto \sqrt{v}$ or $x \propto \dfrac{1}{\sqrt{p}}$	$+ve$ (endothermic)	High temperature Low pressure High concentration
4.	$N_2O_4 \rightleftharpoons 2NO_2$	$+1$	$K_P = K_C(RT)^1$	$K_P > K_C$	$\dfrac{4x^2}{(1-x)v}$	$\dfrac{4x^2 p}{(1-x^2)}$	gram mol^1 lit^{-1}	(Atm. press.)^1	$x \propto \sqrt{v}$ or $x \propto \dfrac{1}{\sqrt{p}}$	$+ve$ (endothermic)	High temperature Low pressure High concentration
5.	$2NH_3 \rightleftharpoons N_2 + 3H_2$	$+2$	$K_P = K_C(RT)^2$	$K_P > K_C$	$\dfrac{27x^4}{4(1-x)^2 v^2}$	$\dfrac{27x^4 p^2}{16(1+x)^2(1-x)^2}$	gram mol^2 lit^{-2}	(Atm. press.)^2	$x \propto \sqrt{v}$ or $x \propto \dfrac{1}{\sqrt{p}}$	$+ve$ (endothermic)	High temperature Low pressure High concentration
6.	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	-2	$K_P = K_C(RT)^{-2}$	$K_P < K_C$	$\dfrac{4x^2 v^2}{27(1-x)^4}$	$\dfrac{16x^2(2-x)^2}{27(1-x)^4} p^2$	gram mol^{-2} lit^2	(Atm. press.)$^{-2}$	$x \propto \dfrac{1}{v}$ or $x \propto p$	$-ve$ (exothermic)	Low temperature High pressure High concentration
7.	$PCl_3 + Cl_2 \rightleftharpoons PCl_5$	-1	$K_P = K_C(RT)^{-1}$	$K_P < K_C$	$\dfrac{xv}{(1-x)^2}$	$\dfrac{x(2-x)}{(1-x)^2} p$	gram mol^{-1} lit^{+1}	(Atm. press.)$^{-1}$	$x \propto \dfrac{1}{v}$ or $x \propto p$	$-ve$ (exothermic)	Low temperature High pressure High concentration
8.	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	-1	$K_P = K_C(RT)^{-1}$	$K_P < K_C$	$\dfrac{x^2 v}{(1-x)^3}$	$\dfrac{x^2(3-x)}{(1-x)^3 p}$	gram mol^{-1} lit^{+1}	(Atm. press.)$^{-1}$	$x \propto \dfrac{1}{\sqrt{v}}$ or $x \propto \sqrt{p}$	$-ve$ (exothermic)	Low temperature High pressure High concentration

GOLDEN KEY POINTS

- ***Law of mass action.*** It was put forward by Guldberg and Waage. It states that the rate at which a substance reacts is directly proportional to its active mass and hence the rate at which substances react together is directly proportional to the product of their active masses. Active mass means molar concentration.

- ***Law of chemical equilibrium.*** For the reaction $aA + bB \rightleftharpoons xX + yY$, $\dfrac{[X]^x[Y]^y}{[A]^a[B]^b} = K$, called equilibrium constant which is constant for a reaction at constant temperature.

- ***Equilibrium constant in terms of concentrations (K_c)*** is $K_c = \dfrac{[X]^x[Y]^y}{[A]^a[B]^b}$.

  It has units $= (mol\ L^{-1})^{(x + y) - (a + b)}$

  Equilibrium constant in terms of pressures is $K_p = \dfrac{P_X^x P_Y^y}{P_A^a P_B^b}$

  It has units $= (atm)^{(x + y) - (a + b)}$

  Expressed in terms of activities (in place of molar concentration), equilibrium constant is dimensionless.

- ***Relation between K_p and K_c.*** K_p and K_c are related to each other as $K_p = K_c (RT)^{\Delta n_g}$

  Where $\Delta n_g = (n_p - n_r)$ gaseous

- ***Concentration Quotient condition or Reaction Quotient (Q).***

  For the reaction $aA + bB \rightleftharpoons xX + yY$, at any other than the stage of equilibrium, the expression

  $\dfrac{[X]^x[Y]^y}{[A]^a[B]^b} = Q$ is called concentration quotient or reaction quotient.

  (i)   If $Q = K$, the reaction is in equilibrium.

  (ii) If $Q < K$, Q will tend to increase till it becomes equal to K. Hence, reaction proceeds in the forward direction.

  (iii) If $Q > K$, Q will tend to decrease. As a result, the reaction will proceed in the backward direction.

- ***Effect of temperature on K.*** For $aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$, $K = \dfrac{k_f}{k_b}$.

  For exothermic reaction, k_f decreases with increase of temperature, so K decreases.

  For endothermic reaction, k_f increases with increase of temperature, so K increases.

- ***Effect of adding inert gas at equilibrium.***

  (i)   For reactions in which $n_p = n_r$, there is no effect of adding an inert gas at constant volume or at constant pressure on the equilibrium.

  (ii) For reaction in which $n_p > n_r$ (e.g. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$), there is no effect of adding inert gas on the equilibrium at constant volume but at constant pressure, equilibrium shifts in the forward direction.

- ***Le Chatelier's principle*** states that "if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed."

- **Van't Hoff reaction isotherm.** It is an equation which gives the relationship between standard free energy change ($\Delta G°$) of a reaction and its equilibrium constant (K_p), i.e. $\Delta G° = -RT \ln K_p$

  This equation helps to calculate $\Delta G°$ of a reaction at temperature T if its equilibrium constant at this temperature is known or vice-versa.

- **Van't Hoff equation.** This equation gives the variation of equilibrium constant of a reaction with temperature. The equation is

$$\frac{d \ln K_p}{dT} = \frac{\Delta H°}{RT^2}$$

  The integrated form of this equation is

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

  where $\Delta H°$ = enthalpy change of the reaction (assumed to the constant in the temperature range T_1 to T_2).

- Units of equilibrium const. $= (mol\ L^{-1})^{(x + y) - (a + b)}$ or $(atm)^{(x + y) - (a + b)}$

- Degree of dissociation of PCl_5 or N_2O_4 is given by $\mu = \dfrac{D - d}{d} = \dfrac{M_t - M_o}{M_o}$

  where D = theoretical vapour density and d = vapour density after dissociation (observed V.D.), M_t = theoretical (calculated) molecular mass and M_o = observed molecular mass.

- From integrated form of van't Hoff equation,

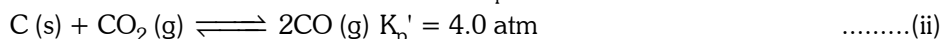$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

  We may conclude that

  (i)   If $\Delta H° = 0$, i.e. no heat is evolved or absorbed in the reaction.

        $\log (K_2/K_1) = 0$, i.e. $K_2/K_1 = 1$ or $K_2 = K_1$.

        So, equilibrium constant does not change with temperature.

  (ii) If $\Delta H° = +ve$, i.e. heat is absorbed in the reaction, then

        $\log (K_2/K_1) = +ve$ or $\log K_2 > \log K_1$ or $K_2 > K_1$.

        So, equilibrium constant increases with increase in temperature.

  (iii) If $\Delta H° = -ve$, i.e. heat is evolved in the reaction, then

        $\log (K_2/K_1) = -ve$, i.e. $\log K_2 < \log K_1$ or $K_2 < K_1$.

        So, equilibrium constant decreases with increase in temperature.

SOME WORKED OUT ILLUSTRATIONS

Illustration 1.

(i) Consider the heterogeneous equilibrium

$CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (s) $K_p = 4 \times 10^{-2}$ atm   ....(i)

C (s) + CO_2 (g) $\rightleftharpoons$ 2CO (g) $K_p' = 4.0$ atm   ....(ii)

Calculate the partial pressure of CO (g) when $CaCO_3$ and C are mixed and allowed to attain equilibrium at the temperature for which the above two equilibria have been studied.

(ii) Calculate the pressure of CO_2 gas at 700 K in the heterogeneous equilibrium reaction.

$CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)
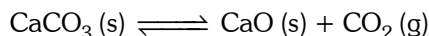
If $\Delta G°$ for this reaction is 120.2 kJ/mol.

Solution

(i) For Eq. (i), $K_p = P_{CO_2}$

From Eq. (ii), $K_p' = P_{CO}^2 / P_{Co_2}$

$\therefore$ $K_p \times K_p' = (P_{CO})^2 = 4 \times 10^{-2} \times 4 = 16 \times 10^{-2}$ atm^2

$\therefore$ $P_{CO} = \sqrt{16 \times 10^{-2} atm^2} = 0.4$ atm

(ii) $\Delta G° = -2.303$ RT log K_p

$\therefore$ $\log K_p = -\dfrac{\Delta G°}{2.303 \times R \times T} = -\dfrac{120.2 \times 10^3 \, Jmol^{-1}}{2.303 \times (8.314 JK^{-1}mol^{-1}) \times (700 K)}$

$\therefore$ $K_p = 1.00 \times 10^{-9}$ atm $= P_{CO_2}$
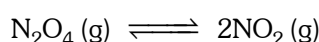
Illustration 2.

For the dissociation reaction N_2O_4 (g) $\rightleftharpoons$ 2NO_2 (g)

derive the expression for the degree of dissociation in terms of K_p and total pressure P.

Solution

$$N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)}$$

Let initial no. of moles   1   0

Moles at equilibrium   (1–α)   2α

$K_p = \dfrac{\left(n_{NO_2}\right)^2}{n_{N_2O_4}}\left[\dfrac{P}{\sum n}\right]^{\Delta n_g}$

$= \dfrac{(2\alpha)^2}{(1-\alpha)}\left[\dfrac{P}{(1-\alpha+2\alpha)}\right]^{(2-1)}$

$= \dfrac{4\alpha^2}{(1-\alpha)}\left[\dfrac{P}{(1+\alpha)}\right]^1 = \dfrac{4\alpha^2}{(1-\alpha^2)}\times P$

$\Rightarrow \dfrac{4P}{K_P} = \dfrac{(1-\alpha^2)}{\alpha^2} = \dfrac{1}{\alpha^2} - 1$

$\dfrac{1}{\alpha^2} = \left(1+\dfrac{4P}{K_p}\right) = \dfrac{4P+K_p}{K_p} \Rightarrow \alpha^2 = \dfrac{K_p}{4P+K_p} \Rightarrow \alpha = \sqrt{\dfrac{K_p}{4P+K_p}}$

Illustration 3*.

When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria.

$$B \rightleftharpoons A \qquad \Delta G_1^\circ = ?$$
$$B \rightleftharpoons C \qquad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° and ΔG_1° indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

Solution

$$\text{Pentyne} \xrightleftharpoons{\text{KOH}} \text{2-Pentyne} + \text{1,2-Pentadiene}$$

$$\qquad (A) \qquad\qquad (B) \qquad\quad (C)$$

At eqm.% 1.3   95.5   3.5

$$K_c = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31 \qquad\qquad .....(i)$$

From eqm. $B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]}$$

From Eqs. (i) and (ii), $K_1 = \dfrac{[C]}{K_c} = \dfrac{3.5}{256.31} = 0.013 \qquad .....(ii)$

$$\begin{aligned}
\Delta G^\circ \quad &= -2.303 \, RT \log_{10} K_1 \\
&= -2.303 \times 8.314 \times 448 \log_{10} 0.013 \\
&= 16178.4 \\
&= 16.1784 \, kJ
\end{aligned}$$

Stability order for A and B is B > A

Similarly, $B \rightleftharpoons C$

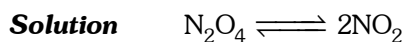$$K_2 = \frac{[C]}{[B]} = \frac{K_c \times [A]}{[B]^2} = \frac{256.31 \times 3.1}{95.2 \times 95.2} = 0.0876$$

$$\therefore \Delta G^\circ_2 = -2.303 \, RT \log_{10} K_2$$
$$= -2.303 \times 8.314 \times 448 \log_{10} 0.0876$$
$$= 9068.06 \, J = 9.068 \, kJ$$

Thus, stability order for B and C is B > C

Total order of stability is B > C > A.

Illustration 4*.

The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/L at 288 K and 1.84 g/L at 348 K. Calculate the entropy change during the reaction at 348 K.

Solution $N_2O_4 \rightleftharpoons 2NO_2$

Case (i)

$$PV = nRT = \frac{w}{m_{mix}} RT$$

$$\Rightarrow \qquad\qquad m_{mix} = \frac{w}{V} \times \frac{RT}{P} = \frac{dRT}{P} = 3.62 \times 0.082 \times 288 = 85.6$$

Let, a mole of N_2O_4 and $(1-a)$ mole of NO_2 exist at equilibrium

$\therefore$ $a \times 92 + (1-a) \times 46 = 85.6$

$\therefore$ $\qquad\qquad a = 0.86$

$\therefore$ $\qquad\qquad n_{N_2O_4} = 0.86$ mol, $n_{NO_2} = 0.14$ mol

$$K_p = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1}\right]^1 = 0.0228 \text{ atm at } 288 \text{ K.}$$

Case (ii)

$$m_{mix} = \frac{dRT}{P} = 1.84 \times 0.0821 \times 348 = 52.57$$

Let, a' mol of N_2O_4 and $(1-a')$ mol of NO_2 exist at equilibrium

$\therefore$ $a' \times 92 + (1-a') \times 46 = 52.57$

$\therefore$ $\qquad\qquad\qquad a' = 0.14$

$\therefore$ $n_{N_2O_4} = 0.14$ mol, $n_{NO_2} = 0.86$ mol

$$\therefore K_p = \frac{0.86 \times 0.86}{0.14}\left[\frac{1}{1}\right]^1 = 5.283 \text{ atm at } 348 \text{ K}$$

$$\log_{10}\left(\frac{K_{p_2}}{K_{p_1}}\right) = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \qquad \log_{10}\frac{5.283}{0.0228} = \frac{\Delta H}{2 \times 2.303}\left[\frac{348 - 288}{348 \times 288}\right]$$

$\therefore \quad \Delta H = 18195.6$ cal $= 18.196$ Kcal

$\qquad\qquad \Delta G = -2.303 \text{ RT} \log K_p$

$\qquad\qquad\qquad = -2.303 \times 2 \times 348 \times \log 5.283$

$\qquad\qquad\qquad = -1158.7$ cal.

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{18195.6 + 1158.7}{348} = 55.62 \text{ cal}$$
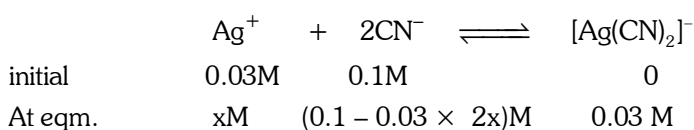
Illustration 5.

For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant, K_c at 27°C is 4.0×10^{-19}. To find the silver ion concentration in a solution which is originally 0.10 M in KCN and 0.03 M in $AgNO_3$.

Solution $\qquad Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$

$$K_c' = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = \frac{1}{K_c} = 2.5 \times 10^{20} \qquad\qquad ....(i)$$

Very high value of K_c' show that complex forming equilibrium is spontaneous and almost all the Ag^+ ion would have reacted leaving xM in solution :

$\qquad\qquad\qquad\qquad Ag^+ \quad + \quad 2CN^- \rightleftharpoons \quad [Ag(CN)_2]^-$

initial $\qquad\qquad$ 0.03M $\qquad$ 0.1M $\qquad\qquad\qquad$ 0

At eqm. $\qquad\qquad$ xM $\qquad$ $(0.1 - 0.03 \times 2x)$M $\qquad$ 0.03 M

$$K_c' = 2.5 \times 10^{20} = \frac{0.03}{x(0.1 - 0.03 \times 2x)^2}$$

$\therefore$ $x = [Ag^+] = 7.5 \times 10^{-18}$ M

Illustration 6*.

In an experiment, 5 moles of HI were enclosed in a 10 litre container. At 817 K equilibrium constant for the gaseous reaction, $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$, is 0.025. Calculate the equilibrium concentrations of HI, H_2 and I_2. What is the fraction of HI that decomposes?

Solution

Let, 2n be the number of moles of HI which is decomposed, the number of moles of H_2 and I_2 produced will be n mole each. Then molar concentrations of various species at equilibrium are

$$[HI] = \frac{(5-2n)}{10}\ \text{mol/L}, \qquad [H_2] = \frac{n}{10}\ \text{mol/L, and}\ \ [I_2] = \frac{n}{10}\ \text{mol/L}$$

Also, $\ K_c = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{\dfrac{n}{10} \times \dfrac{n}{10}}{\left(\dfrac{5-2n}{10}\right)^2}$

$$0.025 = \frac{n^2}{(5-2n)^2}$$

Solving for n, we get $\quad$ n = 0.6

$\therefore \qquad\qquad [HI] = \dfrac{5 - 2 \times 0.6}{10} = \dfrac{3.8}{10} = 0.38\ \text{mol/L}$

$\qquad\qquad [H_2] = \dfrac{0.6}{10} = 0.06\ \text{mol/L}$

$\qquad\qquad [I_2] = \dfrac{0.6}{10} = 0.06\ \text{mol/L}$

Fraction of HI decomposed $= \dfrac{2 \times 0.6}{5} = 0.24$ or 24%

Illustration 7.

For the reaction, $CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2\,(g)$; K = 0.059 atm at 1000 K. 1 g of $CaCO_3$ is placed in a 10 litre container at 1000 K to reach the equilibrium. Calculate the mass of $CaCO_3$ left at equilibrium.

Solution
$\qquad\qquad CaCO_3\,(s) \rightleftharpoons \qquad CaO(s) + CO_2\,(g)$

At equilibrium $\qquad$ a – x $\qquad\qquad\qquad$ x $\qquad$ x

Here, a = initial moles of $CaCO_3$

$K_p = P_{CO_2} = 0.059$
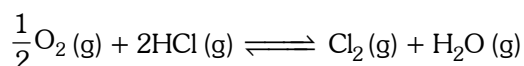
$n_{CO_2} = \dfrac{P_{CO_2}V}{RT} = \dfrac{0.059 \times 10}{0.082 \times 1000} = 7.2 \times 10^{-3}$ moles

Moles of $CaCO_3$ left = 0.01 – 0.0072 = 0.0028

Mass of $CaCO_3$ left = 0.28 g

Illustration 8.

The value of K_p for the reaction, $2H_2O\,(g) + 2Cl_2\,(g) \rightleftharpoons 4HCl\,(g) + O_2\,(g)$ is 0.035 atm at 500°C, when the partial pressures are expressed in atmosphere. Calculate K_c for the reaction,

$\dfrac{1}{2}O_2\,(g) + 2HCl\,(g) \rightleftharpoons Cl_2\,(g) + H_2O\,(g)$

Solution

$$K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = \text{moles of products – moles of reactants} = 5 - 4 = 1$$

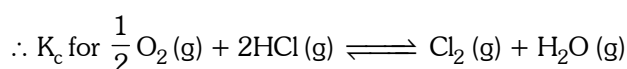$$R = 0.0821 \text{ L atm/mol/K, T} = 500 + 273 = 773 \text{ K}$$

$$\therefore \quad 0.035 = K_c (0.0821 \times 773)$$

$$K_c = 5.515 \times 10^{-4} \text{ mol L}^{-1}$$

$\therefore K_c'$ for the reverse reaction would be $\dfrac{1}{K_c}$

$$\therefore \quad K_c' = \frac{1}{5.515 \times 10^{-4}} = 1813.24 \, (\text{mol L}^{-1})^{-1}$$

When a reaction is multiplied by any number n (integer or a fraction) then K_c' or K_p' becomes $(K_c)^n$ or $(K_p)^n$ of the original reaction.

$\therefore K_c$ for $\dfrac{1}{2} O_2 (g) + 2HCl (g) \rightleftharpoons Cl_2 (g) + H_2O (g)$

is $\sqrt{1813.24} = 42.58 \, (\text{mol.L}^{-1})^{-\frac{1}{2}}$

Illustration 9.

K_p for the reaction $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ is 0.66 at 46°C. Calculate the percent dissociation of N_2O_4 at 46°C and a total pressure of 0.5 atm. Also calculate the partial pressure of N_2O_4 and NO_2 at equilibrium.

Solution

This problem can be solved by two methods.

Method 1 : Let, the number of moles of N_2O_4 initially be 1 and α is the degree of dissociation of N_2O_4.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial moles   1   0

Moles at equilibrium $1-\alpha$ 2α

Total moles at equilibrium $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P_T$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha} \times P_T$$

$$\therefore K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{4\alpha^2 P_T}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 \times 0.5}{1-\alpha^2}$$

$\alpha = 0.5$, i.e. 50% dissociation

Hence, partial pressure of $N_2O_4 = 0.167$ atm.

and partial pressure of $NO_2 = 0.333$ atm.

Method 2 : Let, the partial pressure of NO_2 at equilibrium be p atm, then the partial pressure of N_2O_4 at equilibrium will be $(0.5 - p)$ atm.

$$\therefore K_p = \frac{p^2}{(0.5 - p)} = 0.66$$

$$p^2 + 0.66 \, p - 0.33 = 0$$

On solving, p = 0.333 atm.

$$\therefore p_{NO_2} = 0.333 \text{ atm and } p_{N_2O_4} = 0.167 \text{ atm.}$$

Illustration 10.

In a mixture of N_2 and H_2, initially they are in a mole ratio of 1 : 3 at 30 atm and 300°C, the percentage of ammonia by volume under the equilibrium is 17.8%. Calculate the equilibrium constant (K_p) of the mixture, for the reaction, N_2 (g) + $3H_2$(g) $\rightleftharpoons$ $2NH_3$ (g).

Solution

Let, the initial moles N_2 and H_2 be 1 and 3 respectively (this assumption is valid as K_p will not depend on the exact number of moles of N_2 and H_2. One can even start with x and 3x)

$$N_2(g) \ + 3H_2(g) \ \rightleftharpoons \ 2NH_3 \text{ (g)}$$

Initially   1   3   0

At equilibrium   1–x   3–3x   2x
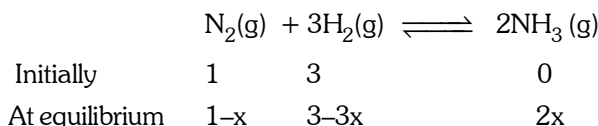
Since % by volume of a gas is same as % by mole,

$$\therefore \qquad\qquad\qquad \frac{2x}{4-2x} = 0.178$$

$$\therefore \qquad\qquad x = \frac{4 \times 0.178}{(2 + 2 \times 0.178)} = 0.302$$

$\therefore$ Mole fraction of H_2 at equilibrium = $\dfrac{3-3x}{4-2x}$ = 0.6165

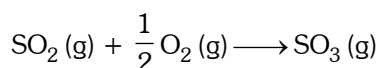Mole fraction of N_2 at equilibrium = $1 - 0.6165 - 0.178 = 0.2055$

$$\therefore \qquad K_p = \frac{(X_{NH_3} \times P_T)^2}{(X_{N_2} \times P_T)(X_{H_2} \times P_T)^3} \ = \ \frac{(0.178 \times 30)^2}{(0.2055 \times 30)(0.6165 \times 30)^3}$$

$$K_p = 7.31 \times \ 10^{-4} \, \text{atm}^{-2}.$$

Illustration 11.

Given below are the values of $\Delta H°$ and $\Delta S°$ for the reaction at 27°C,

$$SO_2 \text{ (g)} + \frac{1}{2}O_2 \text{ (g)} \longrightarrow SO_3 \text{ (g)}$$

$\Delta H° = 98.32$ kJ/mol $\Delta S° = -95$ J/mol. Calculate the value of K_p for the reaction.

Solution

$$\log_{10}K_p = \frac{\Delta H°}{2.303\,RT} + \frac{\Delta S°}{2.303 \times R}$$

$$\therefore \ \log_{10}K_p = \frac{98320}{2.303 \times 8.314 \times 300} - \frac{95}{2.303 \times 8.314} \Rightarrow K_p = 1.44 \times 10^{12} \ \text{atm}^{-1/2}$$

Illustration 12.

The volume of a closed reaction vessel in which the equilibrium :

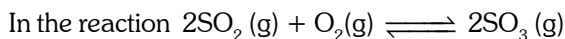$2SO_2$ (g) + O_2(g) $\rightleftharpoons$ $2SO_3$ (g) sets is halved, Now -

(A) the rates of forward and backward reactions will remain the same.

(B) the equilibrium will not shift.

(C) the equilibrium will shift to the left.

(D) the rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Solution. (D)

In the reaction $2SO_2 (g) + O_2(g) \rightleftharpoons 2SO_3 (g)$

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

Illustration 13*.

$H_2(g) + I_2(g) \rightleftharpoons 2HI (g)$
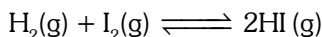
When 92 g of I_2 and 1g of H_2 are heated at equilibrium at 450°C, the equilibrium mixture contained 1.9 g of I_2. How many moles of I_2 and HI are present at equilibrium.

(A) 0.0075 & 0.147 moles   (B) 0.0050 & 0.147 moles

(C) 0.0075 & 0.7094 moles   (D) 0.0052 & 0.347 moles

Solution (C)

$$\text{moles of } I_2 \text{ taken} = \frac{92}{254} = 0.3622$$

$$\text{moles of } H_2 \text{ taken} = \frac{1}{2} = 0.5$$

$$\text{moles of } I_2 \text{ remaining} = \frac{1.9}{254} = 0.0075$$

moles of I_2 used $= 0.3622 - 0.0075 = 0.3547$

moles of H_2 used $= 0.3547$

moles of H_2 remaining $= 0.5 - 0.3547 = 0.1453$

moles of HI formed $= 0.3547 \times 2 = 0.7094$

At equilibrium

moles of $I_2 = 0.0075$ moles

moles of HI $= 0.7094$ moles

Illustration 14.

When 1.0 mole of N_2 and 3.0 moles of H_2 was heated in a vessel at 873 K and a pressure of 3.55 atm. 30% of N_2 is converted into NH_3 at equilibrium. Find the value of K_P for the reaction.

(A) 3.1×10^{-2} atm^{-2} (B) 4.1×10^{-2} atm^{-2} (C) 5.1×10^{-2} atm^{-2} (D) 6.1×10^{-2} atm^{-2}

Solution. (C)
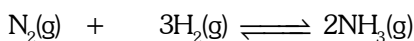
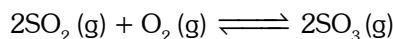| $N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	
1 mole		3 moles		0	Initial moles
1–0.3		3.0 –0.9		0.6 moles	at equilibrium
= 0.7 moles		=2.1 moles			

Total no. of moles at equilibrium = 3.4

$$K_P = \frac{\left(\dfrac{0.6}{3.4} \times 3.55\right)^2}{\left(\dfrac{0.7}{3.4} \times 3.55\right)\left(\dfrac{2.1}{3.4} \times 3.55\right)^3} = 5.1 \times 10^{-2} \text{ atm}^{-2}$$

Illustration 15.

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

If the partial pressure of SO_2, O_2 and SO_3 are 0.559, 0.101 and 0.331 atm respectively. What would be the partial pressure of O_2 gas, to get equal moles of SO_2 and SO_3.

(A) 0.188 atm   (B) 0.288 atm   (C) 0.388 atm   (D) 0.488 atm

Solution (B)

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$
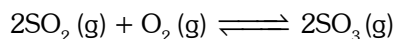
$$K_P = \frac{[P_{SO_3}]^2}{[P_{SO_2}]^2[P_{O_2}]} = \frac{(0.331)^2}{(0.559)^2(0.101)} = 3.47$$

If SO_2 and SO_3 have same number of moles, their partial pressure will be equal and

$$P_{SO_3} = P_{SO_2} \therefore P_{O_2} = \frac{1}{3.47} = 0.288\,\text{atm}$$

Illustration 16*.

$A_2(g)$ and $B_2(g)$ at initial partial pressure of 98.4 and 41.3 torr, respectively were allowed to react at 400 K. At equilibrium the total pressure was 110.5 torr. Calculate the value of K_P for the following reaction at 400 K.
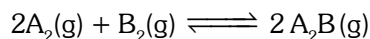
$2A_2(g) + B_2(g) \rightleftharpoons 2\,A_2B\,(g)$

(A) 124   (B) 134   (C) 154   (D) 174

Solution (B)

The given reaction is,

	$2A_2(g)$ +	$B_2(g)$	$\rightleftharpoons$	$2A_2B\,(g)$
Initial pressure (torr)	98.4	41.3		0
At equilibrium	98.4–x	$41.3 - \dfrac{x}{2}$		x

Total pressure at equilibrium = 110.5 torr.

$$(98.4 - x) + (41.3 - \frac{x}{2}) + x = 110.5$$

$\therefore \qquad\qquad x = 58.4$ torr (760 torr = 1 atm)

$P_{(A_2B)} = 58.4$ torr $= 7.68 \times 10^{-2}$ atm

$P_{(A_2)} = 98.4 - 58.4 = 40$ torr $= 5.26 \times 10^{-2}$ atm

$P_{(B_2)} = 41.3 - \dfrac{58.4}{2} = 12.1$ torr $= 1.59 \times 10^{-2}$ atm

$$K_P = \frac{P_{A_2B}^2}{P_{A_2}^2 \times P_{B_2}} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})(1.59 \times 10^{-2})} = 134$$

Illustration 17.

K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 3.28×10^{-4}. Calculate K_c.

(A) 0.3 mole^{-2} litre^2 (B) 0.4 mole^{-2} litre^2 (C) 1.0 mole^{-2} litre^2 (D) 0.6 mole^{-2} litre^2

Solution (C)

$N_2 + 3H_2 \rightleftharpoons 2NH_3$
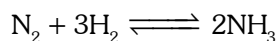
$\Delta n = -2$ and $K_P = K_C (RT)^{\Delta n}$

$3.28 \times 10^{-4} = K_c (0.0821 \times 673)^{-2}$

and $K_c = 1.0 \text{ mole}^{-2} \text{ litre}^2$.

Illustration 18.

A mixture of H_2 and I_2 in molecular proportion of 2 : 3 was heated at 444°C till the reaction $H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI.

(K_C at 444°C is 0.02)
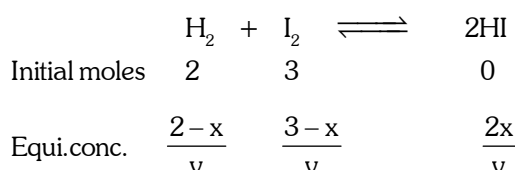
(A) 3.38 %   (B) 4.38%   (C) 5.38%   (D) 6.38%

Solution   (C)

$$\begin{array}{cccc} & H_2 & + \quad I_2 & \rightleftharpoons & 2HI \end{array}$$

Initial moles   2   3   0

Equi.conc. $\dfrac{2-x}{v}$ $\dfrac{3-x}{v}$ $\dfrac{2x}{v}$

$K_C = \dfrac{4x^2}{(2-x)(3-x)} = 0.02$

$199 x^2 + 5x - 6 = 0$

$x = 0.1615$

Out of 3 moles, 0.1615 moles I_2 is converted into HI.

∴   Percentage of I_2 converted to HI $= \dfrac{0.1615 \times 100}{3} = 5.38\%$

Illustration 19.

The equilibrium composition for the reaction is :

$$\begin{array}{cccc} PCl_3 & + \quad Cl_2 & \rightleftharpoons & PCl_5 \\ 0.20 & 0.05 & & 0.40 \text{ moles/litre} \end{array}$$
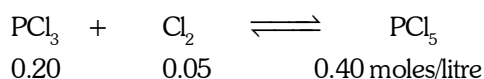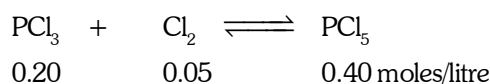
If 0.25 moles of Cl_2 is added at same temperature. Find equilibrium concentration of PCl_5 ($K_C = 20$)
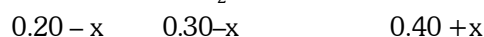
(A) 0.48 moles/litre   (B) 0.38 moles/litre   (C) 0.56 moles/litre   (D) 1.20 moles/litre

Solution. (A)

$$\begin{array}{cccc} PCl_3 & + \quad Cl_2 & \rightleftharpoons & PCl_5 \\ 0.20 & 0.05 & & 0.40 \text{ moles/litre} \end{array}$$

If 0.25 moles of Cl_2 is added then at equilibrium [Let V = 1L]

0.20 – x   0.30–x   0.40 +x

$20 = \dfrac{0.40 + x}{(0.20 - x)(0.30 - x)}$ or   x = 0.08

$[PCl_5] = 0.4 + 0.08 = 0.48$ moles/litre

Illustration 20.

The equilibrium constant K, for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm^{-2} at 300°C. What will be the equilibrium constant at 400°C, if heat of reaction in this temperature range is – 105185.8 Joules.

(A) 0.64×10^{-5} atm^{-2} (B) 6.4×10^{-3} atm^{-2} (C) 0.64×10^{-3} atm^{-2} (D) 0.64×10^{-1} atm^{-2}

Solution   (A)

$K_{p_1} = 1.64 \times 10^{-4}$ atm^{-2}, $K_{p_2} = ?$

$T_1 = 300 + 273 = 573$ K

$T_2 = 400 + 273 = 673$ K

$\Delta H = -105185.8$ Joules

$R = 8.314$ J/K/mole

Applying equation

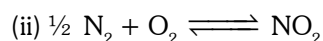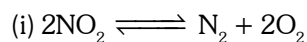$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log K_{p_2} - \log 1.64 \times 10^{-4} = -\frac{105185.8}{2.303 \times 8.314}\left(\frac{673 - 573}{673 \times 573}\right)$$

or $K_{p_2} = 0.64 \times 10^{-5}$ atm^{-2}

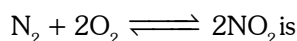### Illustration 21*.

The value of K_C for the reaction,

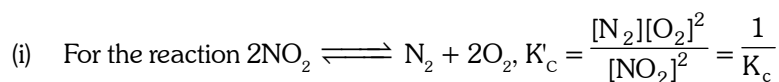$N_2 + 2O_2 \rightleftharpoons 2NO_2$ at a certain temperature is 900. Calculate the value of equilibrium constant for

(i) $2NO_2 \rightleftharpoons N_2 + 2O_2$

(ii) $\frac{1}{2}\,N_2 + O_2 \rightleftharpoons NO_2$

Solution

Equilibrium constant (K_C) for the reaction

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ is

$$K_C = \frac{[NO_2]^2}{[N_2][O_2]^2} = 900$$

(i)   For the reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$, $K'_C = \dfrac{[N_2][O_2]^2}{[NO_2]^2} = \dfrac{1}{K_c}$

$$K'_C = \frac{1}{900} = 0.0011 \text{ mole litre}^{-1}$$

(ii)   For the reaction $\frac{1}{2}\,N_2 + O_2 \rightleftharpoons NO_2$
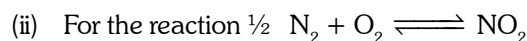
$$K''_C = \frac{[NO_2]}{[N_2]^{\frac{1}{2}}[O_2]} = \sqrt{K_C}$$

$$K''_C = \sqrt{900} = 30 \text{ lit}^{\frac{1}{2}}\ \text{mol}^{-\frac{1}{2}}$$

Illustration 22.

Ice melts slowly at higher altitude, why ?

Solution

According to Le Chatelier principle, the melting of ice is favoured at high pressure because the forward reaction ice $\longrightarrow$ water shows a decrease in volume. At higher altitude atmospheric pressure being low and thus ice melts slowly.

Illustration 23.

Both metals Mg and Fe can reduce copper from a solution having Cu^{+2} ion according to equilibria.

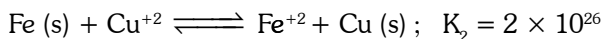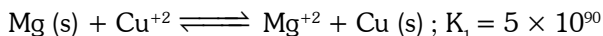$Mg \ (s) + Cu^{+2} \rightleftharpoons Mg^{+2} + Cu \ (s) ; K_1 = 5 \times 10^{90}$

$Fe \ (s) + Cu^{+2} \rightleftharpoons Fe^{+2} + Cu \ (s) ; \ K_2 = 2 \times 10^{26}$

Which metal will remove cupric ion from the solution to a greater extent.

Solution

Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one. Mg thus removes more Cu^{+2} from solution than Fe does.

Illustration 24.

The equilibrium constant K_C for $Y \ (g) \rightleftharpoons Z \ (g)$ is 1.1. Which gas has molar concentration greater than 1.

Solution For $Y \ (g) \rightleftharpoons Z \ (g)$

$K_C = \dfrac{[Z]}{[Y]} = 1.1$

if $Z = 1$; $[Y] = 0.91$
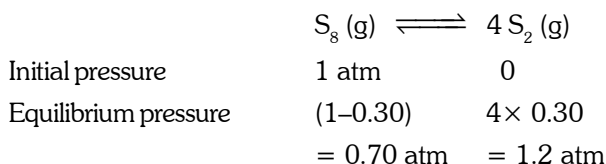
Case I $\quad 0.9 < [Y] < 1$ only $Z = 1$

Case II $\quad [Y] > 1$ both $[Y]$ and $[Z] > 1$

Illustration 25.

When S in the form of S_8 is heated 800 K, the initial pressure of 1 atmosphere falls by 30 % at equilibrium. This is because of conversion of some S_8 to S_2. Calculate the K_P for reaction.

Solution

$$S_8 \ (g) \rightleftharpoons 4 \ S_2 \ (g)$$

Initial pressure	1 atm	0
Equilibrium pressure	(1–0.30)	4× 0.30
	= 0.70 atm	= 1.2 atm

Now, $K_P = \dfrac{P_{S_2}^4}{P_{S_8}} = \dfrac{(1.2)^4}{0.70} = 2.9622 \ atm^3$

Illustration 26.

A vessel at 1000 K contains CO_2 with a pressure of 0.6 atm. some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.9 atm.

Solution

$$CO_2 \ (g) \ + \ C \ (s) \rightleftharpoons 2 \ CO \ (g)$$

Initial pressure	0.6 atm	–	0
Equilibrium pressure	(0.6–x)atm		2x atm

From question, $(0.6 – x) + 2x = 0.9$ hence, $x = 0.3$ atm.
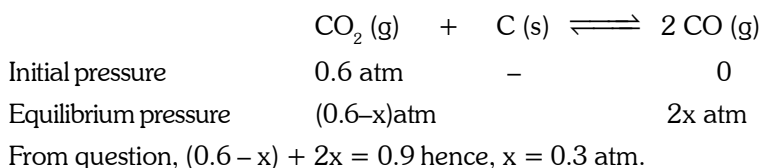
Now, $K_P = \dfrac{P_{CO}^2}{P_{CO_2}} = \dfrac{(2x)^2}{(0.6 - x)} = 1.2 \ atm.$

ANSWERS

BEGINNER'S BOX-1

1.	(D)	**2.**	(D)	**3.**	(D)	**4.**	(C)	**5.**	(B)
6.	(D)	**7.**	(B)						

BEGINNER'S BOX-2

1.	(C)	**2.**	(C)	**3.**	(C)	**4.**	(D)	**5.**	(B)
6.	(B)	**7.**	(A)	**8.**	(A)	**9.**	(D)	**10.**	(B)
11.	(C)	**12.**	(D)	**13.**	(A)				

BEGINNER'S BOX-3

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(C)	**5.**	(D)
6.	(C)	**7.**	(B)						

BEGINNER'S BOX-4

1.	(C)	**2.**	(A)	**3.**	(A)	**4.**	(B)	**5.**	(D)
6.	(B)	**7.**	(C)						

BEGINNER'S BOX-5

1.	(A)	**2.**	(B)	**3.**	(C)	**4.**	(B)	**5.**	(C)
6.	(C)	**7.**	(B)	**8.**	(B)	**9.**	(C)	**10.**	(C)
11.	(B)	**12.**	(A)	**13.**	(D)	**14.**	(B)		

EXERCISE – 1   **MCQ (SINGLE CHOICE CORRECT)**

1. In a reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ degree of dissociation is 30%. If initial moles of PCl_5 is one then total moles at equilibrium is
(A) 1.3   (B) 0.7   (C) 1.6   (D) 1.0

2. For reaction $HI \rightleftharpoons \frac{1}{2} H_2 + \frac{1}{2} I_2$ value of K_c is 1/8 then value of K_c for $H_2 + I_2 \rightleftharpoons 2HI$.

(A) $\dfrac{1}{64}$ (B) 64   (C) $\dfrac{1}{8}$ (D) 8

3. In a equilibrium reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
$\Delta H = -3000$ calories,
which factor favours dissociation of HI :-
(A) Low temp.   (B) High Pressure   (C) High temp.   (D) Low pressure.

4. $N_2 + 3H_2 \rightleftharpoons 2NH_3$
If temp. of following equilibrium reaction increase then -
(A) Shift Right side   (B) Shift left side   (C) Unchanged   (D) Nothing say.

5. $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$
by increasing pressure following equilibrium
(A) Unaffected   (B) Proceed in backward direction
(C) Proceed in forward direction   (D) Unfixed

6*. Unit of equilibrium constant K_c for following homogenous reaction :
$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ is
(A) $(Conc^n)^{-1}$ (B) $(Conc^n)^{+1}$ (C) $(Conc^n)^{+10}$ (D) Have no unit

7. Which of the following factor shifted the reaction $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ at left side.
(A) Adding PCl_5 (B) Increase pressure   (C) Constant temp.   (D) Catalyst

8. In which of the following process reaction is fastest complete.
(A) $K = 10$ (B) $K = 1$ (C) $K = 10^3$ (D) $K = 10^{-2}$

9. In the following reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at constant temp. rate of backward reaction is increase by :
(A) Inert gas mixed at constant volume   (B) Cl_2 gas mixed at constant volume
(C) Inert gas mixed at constant pressure   (D) PCl_5 mixed in constant volume

10*. Some gaseous equilibrium are following :

$CO + H_2O \xrightleftharpoons{K} CO_2 + H_2$

$2CO + O_2 \xrightleftharpoons{K_1} 2CO_2$

$2H_2 + O_2 \xrightleftharpoons{K_2} 2H_2O$

then find out the relation between equilibrium constants :
(A) $K = K_1 K_2$ (B) $K = (K_1 K_2)^2$ (C) $K = (K_1 K_2)^{-1/2}$ (D) $K = (K_1/K_2)^{1/2}$

11. For the equilibrium process $x + y \rightleftharpoons xy$. If the $conc^n$. of x and y is doubled, then equilibrium constant.
(A) Become twice   (B) Become half   (C) Unchanged   (D) Become thrice

12*. The reaction $A(g) + B(g) \rightleftharpoons 2C(g)$ is occur by mixing of 3 moles of A and 1 mole of B in one litre Container.

if α of B is $\dfrac{1}{3}$, then K_C for this reaction is :-

(A) 0.12   (B) 0.25   (C) 0.50   (D) 0.75

13. Reaction $2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$; $\Delta H = +ve$. At equilibrium condition, Pressure of O_2 is depends on :-
(A) Increase mass of BaO_2 (B) Increase mass of BaO
(C) Increase temp. at Eq^m.   (D) Increase mass of BaO_2 and BaO both

14*. Consider the following equilibrium in a closed container $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements held true regarding the equilibrium constant (K_p) and degree of dissociation (α) :-
(A) Neither K_p nor α changes   (B) Both K_p and α- changes
(C) K_p changes, but α does not change   (D) K_p does not change, but α - changes

15. $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$
According to above reaction, partial Pressure of CO_2 & CO are 4 & 8 respectively then find out K_p of the above reaction :-
(A) 6   (B) 2   (C) 16   (D) 32

16. For the reaction, $A+B \rightleftharpoons C + D$, $K_c = 9$. If A and B are taken in equal amounts, then amount of C at equilibrium is :-
(A) 1   (B) 0.25   (C) 0.75   (D) None of these

17. The equilibrium constant of the reaction $SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is 4×10^{-3} atm$^{-1/2}$. The equilibrium constant of the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ would be :
(A) 250 atm   (B) 4×10^3 atm   (C) 0.25×10^4 atm   (D) 6.25×10^4 atm

18. An equilibrium mixture in a vessel of capacity 100 litre contain 1 mol N_2, 2 mol O_2 and 3 mol NO. No. of moles of O_2 to be added so that at new equilibrium the conc. of NO is found to be 0.04 mol/lit :
(A) (101/18)   (B) (101/9)   (C) (202/9)   (D) None of these

19*. Ammonia gas at 15 atm is introduced in a rigid vessel at 300 K. At equilibrium the total pressure of the vessel is found to be 40.11 atm at 300 C. The degree of dissociation of NH_3 will be :
(A) 0.6   (B) 0.4   (C) unpredictable   (D) none of these

20. Given the following reaction at equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected :
(A) more $NH_3(g)$ is produced   (B) less $NH_3(g)$ is produced
(C) no affect on the equilibrium   (D) K_p of the reaction is decreased

21. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct :
(A) concentrations of SO_2, Cl_2 and SO_2Cl_2 are changed
(B) no effect on equilibrium
(C) concentration of SO_2 is reduced
(D) K_p of reaction is increasing

22. Variation of $\log_{10} K$ with $\dfrac{1}{T}$ is shown by the following graph in which straight line is at $45°$, hence $\Delta H°$ is :
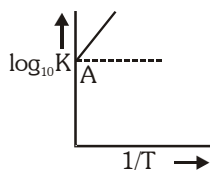
(A) $+4.606$ cal   (B) -4.606 cal   (C) 2 cal   (D) -2cal

23. An exothermic reaction is represented by the graph :

(A) lnK_p $1/T$ (B) lnK_p $1/T$ (C) lnK_p $1/T$ (D) lnK_p $1/T$
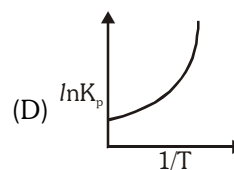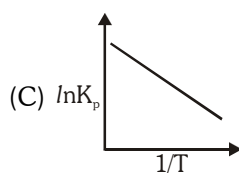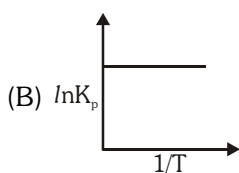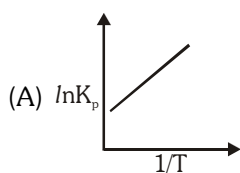
24. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :

(A) $-\Delta G° = RT \, ln \, K$ (B) $\Delta G = RT \, ln \, K$ (C) $-\Delta G = RT \, ln \, K$ (D) $\Delta G° = RT \, ln \, K$

25. For the reaction $H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)}$ which of the following options is incorrect regarding possilbe value of vapour pressure at given temperature.

(A) 1 atm at 373 K   (B) 0.8 atm at 400 K   (C) 1 bar at 372.6 K   (D) $\dfrac{1}{2}$ atm at 353 K

26. For the dissociation of $MgCO_3$ as $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$ identify the correct option regarding extent of dissociation of $MgCO_3$.
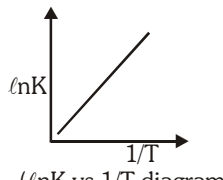
(A) As temperature is increased, extent of dissocation decreases.

(B) Extent of dissociation at equilibrium will increase if equilibrium is attained at the same temperature in a container of lesser volume

(C) Extent of dissociation of $MgCO_3$ will increase if taken in a larger container.

(D) Extent of dissociation will remain unchanged on changing volume of the container.

27. Which of the following statements are correct with respect to solubility of gas in water ?

(A) On adding more water into the solution, solubility in terms of moles dissolved per litre will increase.

(B) As pressure of the gas increase solubility will decreases.

(C) As temperature of the gas increases solubility also increase

(D) None of the above.

EXERCISE – 2   **MCQ (ONE OR MORE CHOICE CORRECT)**

1. For the gas phase reaction, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal), carried out in a closed vessel, the equilibrium moles of C_2H_4 can be increased by :
(A) increasing the temperature   (B) decreasing the pressure
(C) removing some H_2 (D) adding some C_2H_6

2*. $N_2 + O_2 \rightleftharpoons 2NO$, K_1 ; $\left(\dfrac{1}{2}\right)N_2 + \left(\dfrac{1}{2}\right)O_2 \rightleftharpoons NO$, K_2

$2NO \rightleftharpoons N_2 + O_2$, K_3 ; $NO \rightleftharpoons \left(\dfrac{1}{2}\right)N_2 + \left(\dfrac{1}{2}\right)O_2$, K_4

Correct relation between K_1, K_2, K_3 and K_4 is :
(A) $K_1 \times K_3 = 1$ (B) $\sqrt{K_1} \times K_4 = 1$ (C) $\sqrt{K_3} \times K_2 = 1$ (D) None

3. Variation of equilibrium constant K for the reaction ;
$2A(s) + B(g) \rightleftharpoons C(g) + 2D(g)$ is plotted against

absolute temperature T in figure as - ℓnK Vs (1/T) :

(ℓnK vs 1/T diagram)

(A) the forward reaction is exothermic   (B) the forward reaction is endothermic

(C) the slope of line is proportional to ΔH (D) removing C favours forward reaction

4. The equilibrium of which of the following reactions will not be disturbed by the addition of an inert gas at constant volume?

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (B) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(C) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ (D) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

5. The dissociation of ammonium carbamate may be represented by the equation :

$$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

ΔH^0 for the forward reaction is negative. The equilibrium will shift from right to left if there is
(A) a decrease in pressure   (B) an increase in temperature
(C) an increase in the concentration of ammonia   (D) an increase in the concentration of carbon dioxide

6*. The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures 400°C and 500°C. Which of the following *not correctly* represents the two graphs ?
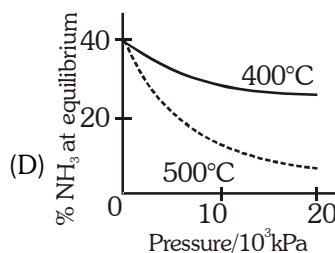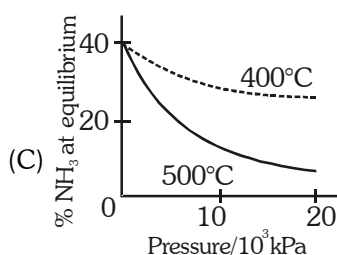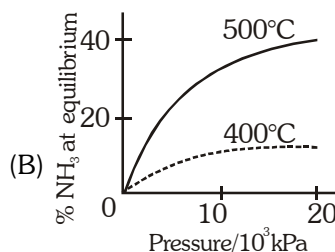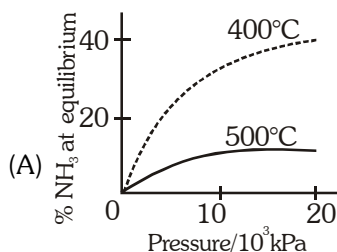
7. The dissociation of phosgene, which occurs according to the reaction

    $$COCl_2 \text{ (g)} \rightleftharpoons CO(g) + Cl_2(g)$$
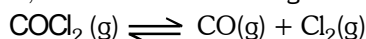
    Is an endothermic process. Which of the following will increase the degree of dissociation of $COCl_2$?
    (A) Adding Cl_2 to the system
    (B) Adding helium to the system at constant pressure
    (C) Decreasing the temperature of the system
    (D) Reducing the total pressure

8. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ, the equilibrium concentration of SO_3 will be affected by
    (A) doubling the volume of the reaction vessel
    (B) increasing the temperature at constant volume
    (C) adding more oxygen to the reaction vessel
   (D) adding helium to the reaction vessel at constant volume

9. For the reaction

    $$2ClF_3(g) \rightleftharpoons Cl_2(g) + 3F_2(g)$$
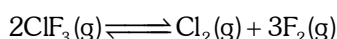
    $\log k_{eq} \, v/s \dfrac{1}{T}$ (where temperature is in K) curve is obtained as following.

    Which of the following change will increase the concentration of Cl_2 in an equilibrium mixture of Cl_2, F_2 & ClF_3:
    (A) Addition of inert gas at constant pressure
    (B) Increase in temperature at constant volume
    (C) Addition of catalyst at equilibrium
    (D) Removal of $F_2(g)$ at equilibrium
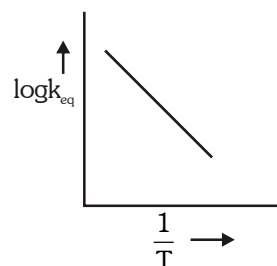
10. Following two equilibrium is simultaneously established in a container

    $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

    $$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$
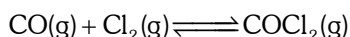
    If some Ni(s) is introduced in the container forming $Ni(CO)_4(g)$ then at new equilibrium
   (A) PCl_5 concentraion will increase
    (B) PCl_3 concentration will decrease
    (C) Cl_2 concentration will remain same
    (D) CO concentration will remain same

11. The equilibrium of which of the following reactions will not be disturbed by the addition of an inert gas at constant volume ?
    (A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
    (B) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
    (C) $CO_2(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
    (D) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

12*. For the reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
    The forward reaction at constant temperature is favoured by
    (A) introducing chlorine gas at constant volume
    (B) introducing an inert gas at constant pressure
    (C) increasing the volume of the container
    (D) introducing PCl_5 at constant volume

13*. For the gas phase reaction carried out in a vessel

    $$C_2H_4 + H_2 \rightleftharpoons C_2H_6; \ \Delta H = -32.7 \, Kcal$$
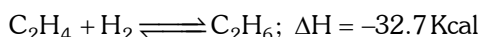
    The equilibrium concentration of C_2H_4 can be increase by
    (A) Addition of C_2H_6
    (B) Removing H_2
    (C) Increasing temperature
    (D) Decreasing pressure

14. Which of the following is/are **incorrect** with respect to dissociation of $CaCO_{3(s)}$.

    $$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$
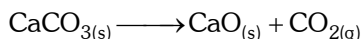
    (A) It is a phase transition
    (B) K_{eq} will be dependent on pressure of CO_2
    (C) K_{eq} will increases as temperature increases
    (D) Equilibrium can be established in an open container

Match the Column

15*.

	Column-I (Reactions)		Column-II (Favourable conditions)
(A)	Oxidation of nitrogen $N_2(g) + O_2(g) + 180.5\,kJ \rightleftharpoons 2NO(g)$	(p)	Addition of inert gas at constant pressure
(B)	Dissociation of $N_2O_4(g)$ $N_2O_4(g) + 57.2\,kJ \rightleftharpoons 2NO_2(g)$	(q)	Decrease in pressure
(C)	Oxidation of $NH_3(g)$ $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $+ 905.6\,kJ$	(r)	Decrease in temperature
(D)	Formation of $NO_2(g)$ $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$ $+ 200\,kJ$	(s)	Increase in temperature

16*.

	Column-I (Reaction)		Column-II (If α is negligiable w.r.t. 1)
(A)	$2X(g) \rightleftharpoons Y(g) + Z(g)$	(p)	$\alpha = 2 \times \sqrt{K_c}$
(B)	$X(g) \rightleftharpoons Y(g) + Z(g)$	(q)	$\alpha = 3 \times \sqrt{K_c}$
(C)	$3X(g) \rightleftharpoons Y(g) + Z(g)$	(r)	$\alpha = (2K_c)^{1/3}$
(D)	$2X(g) \rightleftharpoons Y(g) + 2Z(g)$	(s)	$\alpha = \sqrt{K_c}$

Comprehension Based Questions

Comprehension-1

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to (Nulify) the effect of that change.

Change of pressure : If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more and the equilibirum will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there is decrease in volume.

Effect of pressure on melting point : There are two types of solids :

(a) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increase on melting, e.g., Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

(c) **Solubility of substances :** When solid substance are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$$KCl + aq \rightleftharpoons KCl(aq) - heat$$

In such cases, solubility increase with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

$$KOH + aq \rightleftharpoons KOH(aq) + heat$$

In such cases, solubility decrease with increase in temperature.

(d) **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

17*. A gas 'X' when dissolved in water heat is evolved. Then solublity of 'X' will increase

(A) Low pressure, high temperature   (B) Low pressure, low temperature

(C) high pressure, high temperature   (D) high pressure, low temperature

18*. $Au(s) \rightleftharpoons Au(\ell)$

Above equilibrium is favoured at

(A) High pressure low temperature   (B) High pressure high temperature

(C) Low pressure, high temperature   (D) Low pressure, low temperature

Comprehension-2

Questions are based on the manufacture of Na_2CO_3 by Solvay process :

In the manufacture of $Na_2CO_3(s)$ by Solvay process, $NaHCO_3(s)$ is decomposed by heating :

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_p = 0.23 \text{ at } 100°C \quad \Delta H° = 136 \text{ kJ}$$

19. If a sample of $NaHCO_3$ (s) is brought to a temperature of 100°C in a closed container total gas pressure at equilibrium is :

(A) 0.96 atm   (B) 0.23 atm   (C) 0.48 atm   (D) 0.46 atm

20. A mixture of 1.00 mol each of $NaHCO_3(s)$ and $Na_2CO_3(s)$ is introduced into a 2.5 L flask in which $P_{CO_2} = 2.10$ atm and $P_{H_2O} = 0.94$ atm.When equilibrium is established at 100°C, then partial pressure of:

(A) $CO_2(g)$ and $H_2O(g)$ will be greater than their initial pressure

(B) $CO_2(g)$ and $H_2O(g)$ will be less than their initial pressure

(C) $CO_2(g)$ will be larger and that of $H_2O(g)$ will be less than their initial pressure

(D) $H_2O(g)$ will be larger and that of $CO_2(g)$ will be less than their initial pressure

EXERCISE – 3   **SUBJECTIVE**

1*. The initial concentration or pressure of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the directions in which each system will shift to reach equilibrium.

(a) $2NH_3 (g) \rightleftharpoons N_2 (g) + 3H_2 (g)$ K = 17
     $[NH_3] = 0.20$ M ; $[N_2] = 1.00$ M ; $[H_2] = 1.00$ M

(b) $2NH_3 (g) \rightleftharpoons N_2 (g) + 3H_2 (g)$ $K_p = 6.8 \times 10^4$ atm^2
     Initial pressure : $NH_3 = 3.0$ atm ; $N_2 = 2.0$ atm ; $H_2 = 1.0$ atm
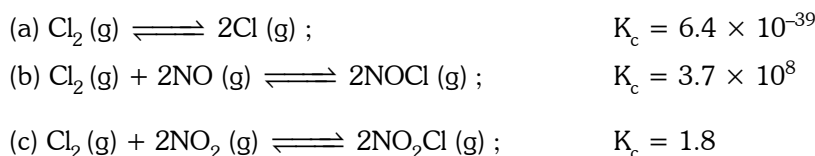
(c) $2SO_3(g) \rightleftharpoons 2SO_2 (g) + O_2 (g)$ K = 0.230 atm
     $[SO_3] = 0.00$ M ; $[SO_2] = 1.00$ M ; $[O_2] = 1.00$ M

(d) $2SO_3 (g) \rightleftharpoons 2SO_2 (g) + O_2 (g)$ $K_p = 16.5$ atm
     Initial pressure : $SO_3 = 1.0$ atm ; $SO_2 = 1.0$ atm ; $O_2 = 1.0$ atm

(e) $2NO (g) + Cl_2 (g) \rightleftharpoons 2NOCl (g)$ K = 4.6×10^4
     $[NO] = 1.00$ M ; $[Cl_2] = 1.00$ M ; $[NOCl] = 0$ M
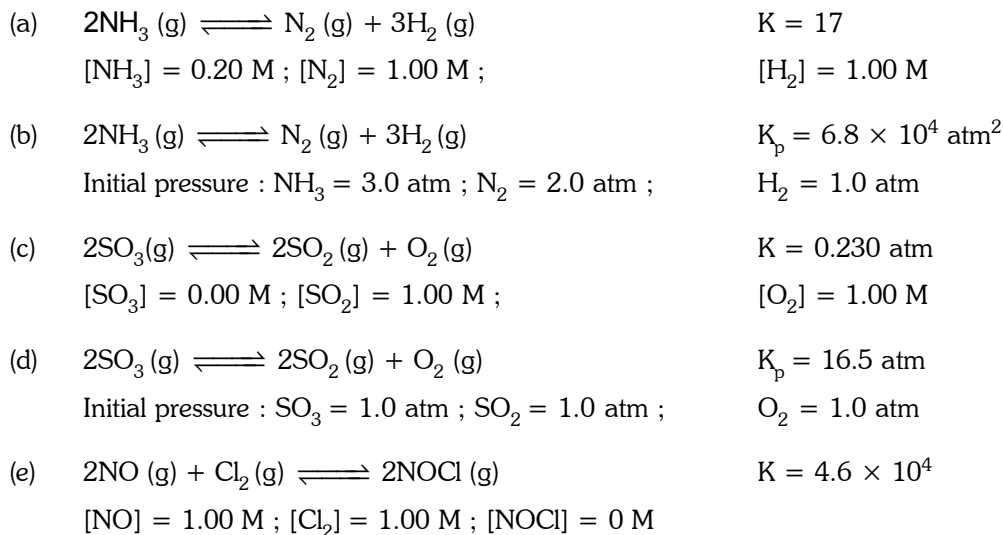
2. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene.
$$3C_2H_2 \longrightarrow C_6H_6$$
Would this reaction be most useful commercially if K were about 0.01, about 1, or about 10? Explain your answer.
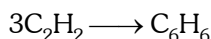
3*. For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products?

(a) $Cl_2 (g) \rightleftharpoons 2Cl (g)$; $K_c = 6.4 \times 10^{-39}$

(b) $Cl_2 (g) + 2NO (g) \rightleftharpoons 2NOCl (g)$; $K_c = 3.7 \times 10^8$

(c) $Cl_2 (g) + 2NO_2 (g) \rightleftharpoons 2NO_2Cl (g)$; $K_c = 1.8$

4. An equilibrium mixture of N_2, H_2 and NH_3 at 700 K contains 0.036 M N_2 and 0.15 M H_2. At this temperature, K_c for the reaction $N_2(g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ is 0.29. What is the concentration of NH_3?

5*. The air pollutant NO is produced in automobile engines from the high temperature reaction $N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$; $K_c = 1.7 \times 10^{-3}$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.40 M, what are the concentration of NO, N_2 and O_2 when the reaction mixture reaches equilibrium?

6*. At 700 K, $K_p = 0.140$ for the reaction $ClF_3 (g) \rightleftharpoons ClF (g) + F_2 (g)$. Calculate the equilibrium partial pressure of ClF_3, ClF and F_2 if only ClF_3 is present initially ; at a partial pressure of 1.47 atm.

**7.** The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmosphere and 40°C is 0.25. Calculate its K_p at 40°C. Also report degree of dissociation at 10 atmospheric pressure at same temperature.

8. At 46°C, K_p for the reaction $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46°C at a total pressure of 380 Torr.

9*. When 36.8 g N_2O_4 (g) is introduced into a 1.0 - litre flask at 27°C. The following equilibrium reaction occurs:

$$N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)} ; K_p = 0.1642 \text{ atm.}$$
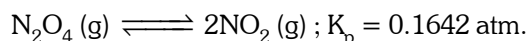
(a) Calculate K_c of the equilibrium reaction.

(b) What are the number of moles of N_2O_4 and NO_2 at equilibrium?

(c) What is the total gas pressure in the flask at equilibrium?

(d) What is the percent dissociation of N_2O_4?

10. In a mixture of N_2 and H_2 in the ratio of 1 : 3 at 64 atmospheric pressure and 300°C, the percentage of ammonia under equilibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation.

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g)}$$
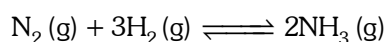
11*. 20.0 grams of $CaCO_3$ (s) were placed in a closed vessel, heated & maintained at 727°C under equilibrium

$CaCO_3 \text{(s)} \rightleftharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$ and it is found that 75% of $CaCO_3$ was decomposed. What is the value of K_p? The volume of the container was 15 litres.

12. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the equation

$$N_2 \text{ (g)} + 2H_2 \text{ (g)} \rightleftharpoons N_2H_4 \text{ (g)} \qquad\qquad \Delta H = 95 \text{ kJ}$$
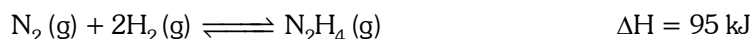
13. How will an increase in temperature and increase in pressure affect each of the following equilibria?

(a) $2NH_3 \text{ (g)} \rightleftharpoons N_2 \text{ (g)} + 3H_2 \text{ (g)}$ \qquad\qquad $\Delta H = 92 \text{ kJ}$

(b) $N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)}$ \qquad\qquad $\Delta H = 181 \text{ kJ}$

(c) $2O_3 \text{ (g)} \rightleftharpoons 3 O_2 \text{ (g)}$ \qquad\qquad $\Delta H = -285 \text{ kJ}$

(d) $CaO \text{ (s)} + CO_2 \text{ (g)} \rightleftharpoons CaCO_3 \text{ (s)}$ \qquad\qquad $\Delta H = -176 \text{ kJ}$

14. Ammonia is weak base that reacts with water according to the equation

$$NH_3 \text{ (aq)} + H_2O \text{ (}l\text{)} \rightleftharpoons NH_4^+ \text{ (aq)} + OH^- \text{ (aq)}$$
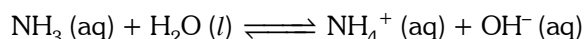
Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH. \qquad (b) Addition of HCl. \qquad (c) Addition of NH_4Cl.

15*. Suggest two ways in which equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+ and NO_3^-, in contact with solid AgCl.

$Na^+ \text{ (aq)} + Cl^- \text{ (aq)} + Ag^+ \text{ (aq)} + NO_3^- \text{ (aq)} \rightleftharpoons AgCl \text{ (s)} + Na^+ \text{ (aq)} + NO_3^- \text{ (aq)} \ \Delta H = -65.9 \text{ kJ}$

16. Consider a general single-step reaction of the type $A + B \rightleftharpoons C$. Show that the equilibrium constant is equal to the ratio of the rate constant for the forward and reverse reaction, $K_c = K_f/K_r$.

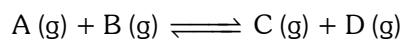**17.** Listed in the table are forward and reverse rate constants for the reaction $2NO \text{ (g)} \rightleftharpoons N_2 \text{ (g)} + O_2 \text{ (g)}$

Temperature (K)	k_f (M^{-1}s^{-1})	k_r (M^{-1}s^{-1})
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic?

18*. For the reaction at 298 K

$$A \, (g) + B \, (g) \rightleftharpoons C \, (g) + D \, (g)$$

$\Delta H° = -29.8$ kcal ; $\Delta S° = -0.1$ kcal/K

Calculate $\Delta G°$ and K.

19. PCl_5 dissociates according to the reaction $PCl_5 \, (g) \rightleftharpoons PCl_3 \, (g) + Cl_2 \, (g)$. At 523 K, $K_p = 1.78$ atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

18*. For the reaction at 298 K

1. Reaction $CO_{(g)} + \dfrac{1}{2} O_{2(g)} \rightleftharpoons CO_{2(g)}$. The value of $\dfrac{K_P}{K_c}$ is-   *[AIEEE-2002]*

(A) $\dfrac{1}{RT}$ (B) $\sqrt{RT}$ (C) $\dfrac{1}{\sqrt{RT}}$ (D) RT

2. One of the following equilibrium is not affected by change in volume of the flask -   *[AIEEE-2002]*
(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(C) $N_2(g) + O_2 \rightleftharpoons 2NO(g)$ (D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

3*. For the reaction equilibrium,
$N_2O_4 (g) \rightleftharpoons 2NO_2(g)$ the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_C for the reaction is-   *[AIEEE-2003]*
(A) 3×10^{-3} mol L^{-1} (B) 3×10^3 mol L^{-1} (C) 3.3×10^2 mol L^{-1} (D) 3×10^{-1} mol L^{-1}

4. Consider the reaction equilibrium   *[AIEEE-2003]*
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2 SO_{3(g)}$; $\Delta H° = - 198$ kJ
On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is -
(A) Lowering the temperature and increasing the pressure
(B) Any value of temperature as well as pressure
(C) Lowering of temperature as well as pressure
(D) Increasing temperature as well as pressure

5. What is the equilibrium expression for the reaction $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$?   *[AIEEE-2004]*
(A) $K_C = [P_4O_{10}] / [P_4] [O_2]^5$ (B) $K_C = [P_4O_{10}] / 5 [P_4] [O_2]$
(C) $K_C = [O_2]^5$ (D) $K_C = 1 / [O_2]^5$

6. For the reaction $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ the $\dfrac{K_P}{K_C}$ is equal to -   *[AIEEE-2004]*

(A) $\dfrac{1}{RT}$ (B) RT   (C) $\sqrt{RT}$ (D) 1.0

7. For the reaction $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$, $(K_c = 1.8 \times 10^{-6}$ at 184° C) (R = 0.831 kJ(mol.K)) When K_p and k_c are compared at 184°C it is found that   *[AIEEE-2005]*
(A) K_p is less than K_c
(B) K_p is greater than K_c
(C) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
(D) $K_p = K_c$

8*. The exothermic formation of ClF_3 is represented by the equation   *[AIEEE-2005]*
$Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)}$; $\Delta H_r = - 329$ kJ
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?
(A) Removing Cl_2 (B) Increasing the temperature
(C) Adding F_2 (D) Increasing the volume of the container

9. A schematic plot of $\ln K_{eq}$ verus inverse of temperature for a reaction is shown below. The reaction must be

[AIEEE-2005]

(A) endothermic

(B) exothermic

(C) highly spontaneous at ordinary temperature

(D) one with negligible enthalpy change
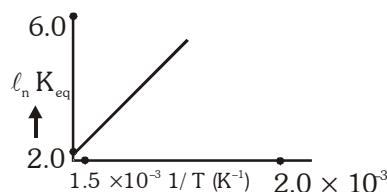
10*. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel,   *[AIEEE-2006]*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be-

(A) $\left(\dfrac{2x}{1-x}\right)P$ (B) $\left(\dfrac{x}{x-1}\right)P$ (C) $\left(\dfrac{x}{1-x}\right)P$ (D) $\left(\dfrac{x}{x+1}\right)P$

11. The equilibrium constant for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \dfrac{1}{2}O_2(g)$ is $K_C = 4.9 \times 10^{-2}$. The value of K_C

for the reaction   *[AIEEE-2006]*

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be

(A) 2.40×10^{-3} (B) 9.8×10^{-2} (C) 4.9×10^{-2} (D) 416

12*. The equlibrium constants K_{p_1} and K_{p_2} for the reaction $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in

the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is   *[AIEEE-2008]*

(A) 1 : 36   (B) 1 : 1   (C) 1 : 3   (D) 1 : 9

13. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :   *[AIEEE-2011]*

(A) 0.3 atm   (B) 0.18 atm   (C) 1.8 atm   (D) 3 atm

14. The equilibrium constant (K_C) for the reaction $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The

value of K_C for the reaction. $NO(g) \longrightarrow \dfrac{1}{2}N_2(g) + \dfrac{1}{2}O_2(g)$ at the same temperature is :

[AIEEE-2012]

(A) 50.0   (B) 0.02   (C) 2.5×10^2 (D) 4×10^{-4}

15. For the reaction $SO_{2(g)} + \dfrac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_P = K_C(RT)^x$ where the symbols have usual meaning then the

value of x is : (assuming ideality)   *[JEE MAINS-2014]*

(A) –1   (B) $-\dfrac{1}{2}$ (C) $\dfrac{1}{2}$ (D) 1

16*. The following reaction is performed at 298 K.
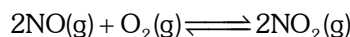
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of $NO(g)$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K ? ($K_p = 1.6 \times 10^{12}$) **[JEE MAINS-2015]**

(A) R(298) ℓn (1.6 × 10¹²) – 86600

(B) 86600 + R(298) ℓn (1.6 × 10¹²)

(C) $86600 - \dfrac{\ell n(1.6 \times 10^{12})}{R(298)}$

(D) 0.5[2 × 86,600 – R(298) ℓn (1.6 × 10¹²)]

17*. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \dfrac{1}{2}, [B] = 2$ and $[C] = \dfrac{1}{2}$. The reaction proceeds in the :

[R = 8.314 J/K/mol, e = 2.718]   **[JEE MAINS-2015]**

(A) forward direction because Q > K_C

(B) reverse direction because Q > K_C

(C) forward direction because Q < K_C

(D) reverse direction because Q < K_C

18*. The equilibrium constant at 298 K for a reaction A + B $\rightleftharpoons$ C + D is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L⁻¹) will be: **[JEE MAINS-2016]**

(A) 0.182   (B) 0.818   (C) 1.818   (D) 1.182

19. Consider the following reversible chemical reactions :

$$A_2(g) + B_2(g) \xrightleftharpoons{K_1} 2AB(g) \qquad\qquad ...... (1)$$

$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g) \qquad ...... (2)$$
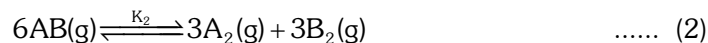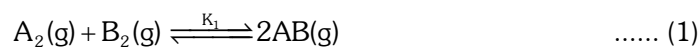
The relation between K_1 and K_2 is :   **[JEE-MAIN-2019]**

(A) $K_2 = K_1^3$ (B) $K_2 = K_1^{-3}$ (C) $K_1K_2 = 3$ (D) $K_1K_2 = \dfrac{1}{3}$
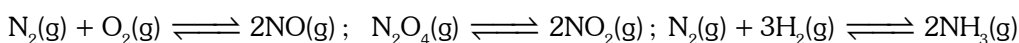
20. 5.1g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The Kp of the reaction at 327°C is (R = 0.082 L atm moHKr¹, Molar mass of S = 32 g mol⁰¹, molar mass of N = 14g mol⁻¹)   **[JEE-MAIN-2019]**

(A) 1 × 10⁻⁴ atm²   (B) 4.9 × 10⁻³ atm²   (C) 0.242 atm²   (D) 0.242 × 10⁻⁴ atm²

21. In a chemical reaction, $A + 2B \xrightleftharpoons{K} 2C + D$ m, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant(K) for the aforesaid chemical reaction is :   **[JEE-MAIN-2019]**

(A) 16   (B) 4   (C) 1   (D) $\dfrac{1}{4}$

22. The value of Kp/K_c for the following reactions at 300K are, respectively :

(At 300K, RT = 24.62 dm³atm mol⁻¹)   **[JEE-MAIN-2019]**

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) ; \quad N_2O_4(g) \rightleftharpoons 2NO_2(g) ; \quad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(A) 1, 24.62 dm³atm moh¹, 606.0 dm⁶atm²mol⁻²

(B) 1, 4.1 × 10⁻² dm⁶atm¹ moh¹, 606.0 dm⁶ atm² moh²

(C) 606.0 dm⁶atm²mol–², 1.65 × 10⁻³ dm³atm⁻² moh¹

(D) 1, 24.62 dm³atmmoh¹, 1.65 × 10⁻³ dm⁻⁶atm⁻² mol²

23. Consider the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ **[JEE-MAIN-2019]**

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $P_{NH_3} << P_{total}$ at equilibrium)

(A) $\dfrac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{4}$
(B) $\dfrac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{16}$
(C) $\dfrac{K_P^{\frac{1}{2}} P^2}{16}$
(D) $\dfrac{K_P^{\frac{1}{2}} P^2}{4}$

24. Two solids dissociate as follows

$A(s) \rightleftharpoons B(g) + C(g)$; $K_{p_1} = x$ atm^2 $D(s) \rightleftharpoons C(g) + E(g)$; $K_{p_2} = y$ atm^2

The total pressure when both the solids dissociate simultaneously is : **[JEE-MAIN-2019]**

(A) $x^2 + y^2$ atm
(B) $x^2 + y^2$ atm
(C) $2(\sqrt{x + y})$ atm
(D) $\sqrt{x + y}$ atm

25. For the following reactions, equilibrium constants are given :

$S(s) + O_2(g) \rightleftharpoons SO_2(g)$; $K_1 = 10^{52}$; $2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g)$; $K_2 = 10^{129}$

The equilibrium constant for the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is :

(A) 10^{181}
(B) 10^{154}
(C) 10^{25}
(D) 10^{77}

26. For the reaction,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$,
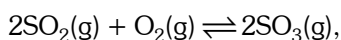
$\Delta H = -57.2$ kJ mol^{-1} and

$K_c = 1.7 \times 10^{16}$.

Which of the following statement is INCORRECT? **[JEE-MAIN-2019]**

(A) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

(B) The equilibrium will shift in forward direction as the pressure increase.

(C) The equilibrium constant decreases as the temperature increases.

(D) The addition of inert gas at constant volume will not affect the equilibrium constant.

27. The INCORRECT match in the following is : **[JEE-MAIN-2019]**

(A) $\Delta G^\circ < 0$, $K < 1$
(B) $\Delta G^\circ = 0$, $K = 1$
(C) $\Delta G^\circ > 0$, $K < 1$
(D) $\Delta G^\circ < 0$, $K > 1$

28. In which one of the following equilibria, $K_p \neq K_c$? **[JEE-MAIN-2019]**

(A) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(B) $2 HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(C) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(D) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

EXERCISE – 5 — RECAP OF IIT-JEE/JEE (ADVANCED)

1. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ *[JEE 2006]*

Which is correct statement if N_2 is added at equilibrium condition?

(A) The equilibrium will shift to forward direction because according to II law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} \rightleftharpoons 2\,G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

(C) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

(D) Catalyst will not alter the rate of either of the reaction.

2*. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is : *[JEE 2007]*

(Given : $\Delta_r H°_{298K} = -54.07$ kJ mol^{-1}, $\Delta_r S°_{298K} = 10$ JK^{-1} mol^{-1} and
$R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

3. The thermal dissociation equilibrium of $CaCO_3$(s) is studied under different conditions :

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ *[JEE 2013]*

For this equilibrium, the correct statement(s) is(are)

(A) ΔH is dependent on T   (B) K is independent of the initial amount of $CaCO_3$

(C) K is dependent on the pressure of CO_2 at a given T (D) ΔH is independent of the catalyst, if any

4*. The %yield of ammonia as a function of time in the reaction *[JEE 2015]*

$N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g), \Delta H < 0$ at (P, T) is given below.

If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the %yield of ammonia as a function of time is represented by
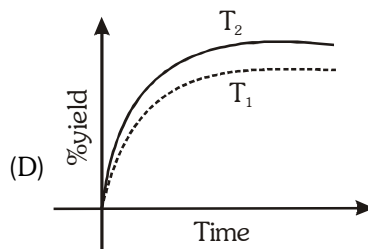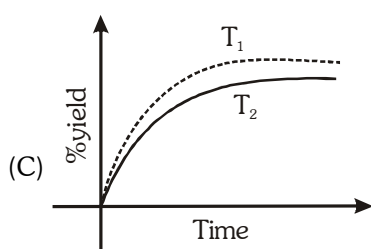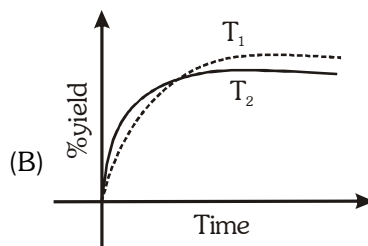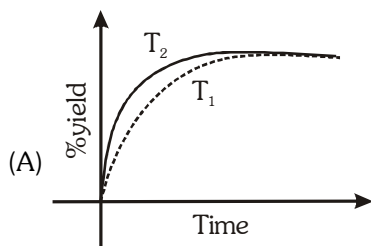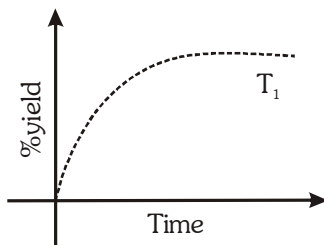
Paragraph for Q.5 to Q.6

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2(g) \rightleftharpoons 2X(g)$$
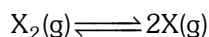
The standard reaction Gibbs energy, $\Delta_r G^o$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

[**Given :** R = 0.083 L bar K^{-1} mol^{-1}]

5*. The equilibrium constant K_P for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is *[JEE 2016]*

(A) $\dfrac{8\beta_{equilibrium}^2}{2 - \beta_{equilibrium}}$ 　　　　(B) $\dfrac{8\beta_{equilibrium}^2}{4 - \beta_{equilibrium}^2}$ 　　　　(C) $\dfrac{4\beta_{equilibrium}^2}{2 - \beta_{equilibrium}}$ (D) $\dfrac{4\beta_{equilibrium}^2}{4 - \beta_{equilibrium}^2}$

6*. The **INCORRECT** statement among the following, for this reaction, is *[JEE 2016]*

(A) Decrease in the total pressure will result in formation of more moles of gaseous X.

(B) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously.

(C) $\beta_{equilibrium} = 0.7$

(D) $K_C < 1$

7. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}.
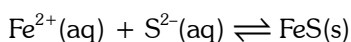
$$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s) \qquad \text{[JEE 2019]}$$

When equal volumes of 0.06 M Fe^{2+}(aq) and 0.2 M S^{2-}(aq) solutions are mixed, the equilibrium concentration of Fe^{2+}(aq) is found to be $Y \times 10^{-17}$ **M**. The value of Y is ————

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	B	C	B	B	B	A	C	B	D	C	B	C	D	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27			
Ans.	C	D	A	B	B	B	B	A	A	B	C	D			

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	ABCD	ABC	ACD	ABCD	BCD	BCD	BD	ABC	ABD	AB
Que.	11	12	13	14						
Ans.	ABCD	BCD	ABCD	ABD						

- ***Match the Column***

   15*. A - (s), B - (p,q,s), C - (p,q,r), D - (r)

   16*. A - (p), B - (s), C - (q), D - (r)

- ***Comprehension Based Questions***

   Comprehension 1 :   **17*.** (D)   **18*.** (C)

   Comprehension 2 :   **19.** (A)   **20.** (B)

EXERCISE-3

1*.   (a) $Q = \dfrac{[H_2]^3[N_2]}{[NH_3]^2} = \dfrac{[1]^3[1]}{[0.20]^2} = 25 \ (\text{shift left of } Q.k)$ (b) $Q = \dfrac{(2)(1)^3}{(3)^2} = 0.22 \, (Q < k, \text{shift left})$

       (c) $Q = \dfrac{(1)^2(1)}{0} = \infty \, (Q > k, \text{shift left})$ (d) $Q = \dfrac{(1)^2(1)}{(1)^2} = 1 \, (Q < k, \text{shift Right})$

       (e) $Q = \dfrac{0}{(1)^2(1)} = 0 \, (Q < k, \text{shift Right})$

2.   Reaction is usefull when value of K is high (K about 10).
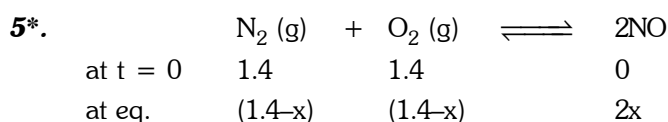
3*.   As it has value of K_{eq} around 1.

4. $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 0.29$

     $= \dfrac{[NH_3]^2}{[0.036][0.15]^3} = 0.29$
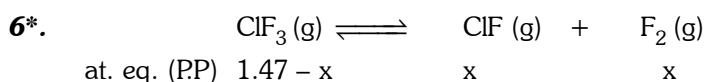
     $= [NH_3] = 5.9 \times 10^{-3}.$

5*. N_2 (g)   + O_2 (g) $\rightleftharpoons$ 2NO

       at t = 0   1.4   1.4   0

       at eq.   (1.4–x)   (1.4–x)   2x

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(1.4-x)^2} = 1.7 \times 10^{-3}$$

$$\Rightarrow \frac{2x}{1.4-x} = 7.6 \times 10^{-2}$$

$\Rightarrow x = 0.028$

so, at *eq.* amount of

$NO = 2x = 0.056$ M

$O_2 = (1.4 - x) = 1.37$ M

$N_2 = (1.4 - x) = 1.37$ M

6*.

$$ClF_3\,(g) \rightleftharpoons ClF\,(g) + F_2\,(g)$$

at. *eq.* (P.P) $1.47 - x$ x x

$$K_P = \frac{x^2}{1.47-x} = 0.14$$

$x = 0.389$ atm

so $P_{ClF} = P_F = 0.389$

$P_{ClF_3} = 1.47 - 0.389 = 1.08\,\text{atm}$

7.

$$N_2O_4 \rightleftharpoons 2NO_2$$

at t = 0 P_O O

at *eq.* $P_O(1-0.25)$ $P_O \times 0.25 \times 2$
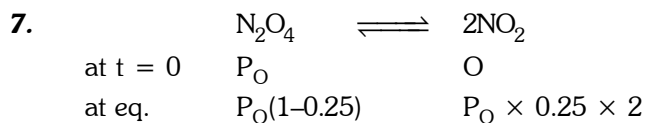
given in question

$P_O(1-0.25) + P_O \times 0.5 = 1.5$

$\Rightarrow$ $P_O(0.75 + 0.5) = 1.5$

$\Rightarrow$ $P_O = 1.5/1.25$ atm

$$K_P = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{[0.5P_O]^2}{0.75P_O} = \frac{0.5 \times 0.5}{0.75} \times P_O$$

$$= \frac{0.5 \times 0.5}{0.75} \times \frac{1.5}{1.25} = 0.4$$

at t = 0 $N_2O_4 \rightleftharpoons 2NO_2$

at equation P_O O
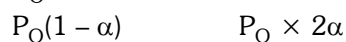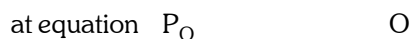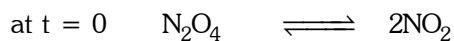
    $P_O(1-\alpha)$ $P_O \times 2\alpha$

so total pressure $= P_O(1-\alpha) + P_O 2\alpha = 10$

     $P_O + P_O\alpha = 10$

     $P_O(1+\alpha) = 10$

$$P_O = \frac{10}{1} + \alpha$$

$$K_P = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2P_O\alpha)^2}{P_O(1-\alpha)} = \frac{4P_O^2\alpha^2}{P_O(1-\alpha)} = 0.4$$

$$= 4P_O \frac{\alpha^2}{(1-\alpha)} = 0.4$$

$$= 4 \times \frac{10}{(1+\alpha)} \times \frac{\alpha^2}{(1-\alpha)} = 0.4$$

$$= \frac{40 \times \alpha^2}{(1-\alpha^2)} = 0.4$$

Cas $[(a + b)(a - b) = a^2 - b^2]$

$\Rightarrow \quad \alpha^2 = 0.01(1 - \alpha)$

$$\alpha = \sqrt{\frac{0.01}{1.01}} = 0.099 \approx 0.1$$

8. Total pressure at equation $= \dfrac{380}{760} = 0.5 \, atm$

$$N_2O_4 \rightleftharpoons 2NO_2$$

at t = Partial presure $\qquad P_O \qquad\qquad O$

at equation $\qquad\qquad\qquad P_O(1-\alpha) \quad P_O \times 2\alpha$

total pressure at equation at equation $= P_O(1-\alpha) + 2P_O\alpha = 0.05$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = P_O(1+\alpha) = 0.5$

$$K_P = \frac{[NO_2]^2}{[N_2O_4]} = \frac{4P_O^2\alpha^2}{P_O(1-\alpha)} = 0.667$$

$$= 4 \times P_O \frac{\alpha^2}{(1-\alpha)} = 0.667$$

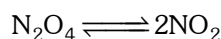$$= 4 \times \frac{0.5}{(1+\alpha)} \cdot \frac{\alpha^2}{(1-\alpha)} = 0.667$$

$$= \frac{2 \times \alpha^2}{1-\alpha^2} = 0.667$$

$\Rightarrow \qquad\qquad\qquad \alpha = 0.5$

9*. (a) $K_P = K_C(RT)^{\Delta ng} = K_C \times RT$

$$K_C = \frac{K_P}{RT} = 6.66 \times 10^{-3}$$

(b) $\qquad\qquad N_2O_4 \quad \rightleftharpoons \quad 2NO_2$
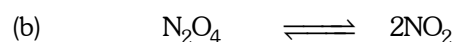
at t = 0 $\quad \dfrac{36.8}{92} = 0.4 \qquad\qquad O$

at equation $\quad 0.4 - \alpha \qquad\qquad 2\alpha \qquad\qquad\qquad (v = 1 \, litre)$

$$K_C = \frac{4\alpha^2}{0.4 - \alpha} = 6.66 \times 10^{-3}$$

$\alpha = 0.025$

So conc. of $NO_2 = 2 \times 0.025 = 0.05$

$\qquad\qquad N_2O_4 = 0.4 - 0.025 = 0.375$

(C) total moles at equation $= 0.375 + 0.55 = 0.425$

$$P = \frac{nRT}{V} = \frac{0.425 \times 0.0821 \times 300}{1} = 10.47 \, atm$$

(D) precent decomposition $= \dfrac{0.025}{0.4} \times 100 = 6.25\%$

10. P.P. of $N_2 = \dfrac{64}{1+3} \times 1 = 16$

$H_2 = \dfrac{64}{1+3} \times 3 = 48$

$$N_2 \quad + \quad 3H_2 \quad \rightleftharpoons \quad 2NH_3$$

at t = 0   16   48   0
at equation   16 – x   48 – 3x   2x
Total moles at equation = (16 – x) + (48 – 3x) + 2x = 64 – 2x

Given in eq. that NH_3 is 33.33% or $\dfrac{1}{3}$ by volume (so by pressure as well as by mol) of total

so $\qquad \dfrac{2x}{64 - 2x} = \dfrac{1}{3}$
$\qquad\qquad x = 8$

so $\qquad K_P = \dfrac{[2x]^2}{(16-x)(48-3x)3} = \dfrac{(2 \times 8)^2}{(16-8)(48-24)^3} = 1.3 \times 10^{-3}\,atm^{-2}$

11*. total moles of $CaCO_3 = \dfrac{20}{100} = 0.2$

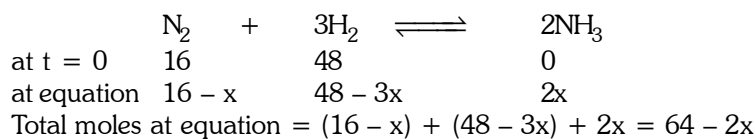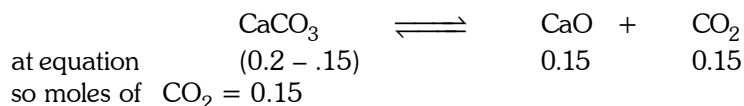decomposed amount of $CaCO_3$ = 75% of 0.2 = $0.2 \times \dfrac{75}{100} = 0.15$

$$CaCO_3 \quad \rightleftharpoons \quad CaO \quad + \quad CO_2$$

at equation   (0.2 – .15)   0.15   0.15
so moles of $CO_2 = 0.15$

pressure of $CO_2 = \dfrac{nRT}{V} = \dfrac{0.15 \times 0.0821 \times 1000}{15} = 0.821$

$\qquad K_P = P_{(CO_2)} = 0.821$

12. (i) Increasing pressure   (ii) Increasing temperature
     (iii) addition of N_2 (iv) Addition of H_2

13. (a) shift right, shift left,   (b) shift right, no effect,
     (c) shift left, shift left,   (d) shift left, shift right

14. (b) Addition of HCl (H^+ ion) will remove $\overset{\ominus}{O}H$ ion, so equation will shift in forward direction.

15*. Add NaCl or some other salt that produces Cl^- in the solution. Cool the solution

16. $k_f\,[A][B] = k_r\,[C]$; $\dfrac{k_f}{k_r} = \dfrac{[C]}{[A][B]} = k_c$

17. at 1400K $\qquad K_{eq} = \dfrac{0.29}{1.1 \times 10^{-6}} = 2.6 \times 10^5$

at 1500 $\qquad K_{eq} = \dfrac{1.3}{1.4 \times 10^{-5}} = 9.2 \times 10^4$

so $\qquad\qquad K_{eq}$ decreases at high temperature, so Rx^4 is exothernic

18*. $\Delta G° = \Delta H° - T\Delta S°$
$\qquad\quad = -29.8 - 298(-0.1)$
$\qquad\quad = -29.8 + 29.8 = 0$
$\Delta G° = -2.303\ RT \log K = 0$
$\qquad$ so $\log K = 0$
$\qquad\qquad K = 1$

19.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

at t = 0 P_O O   O

at equation $P_O(1 - \alpha)$ $P_O\alpha$ $P_O\alpha$

so $K_P = \dfrac{P_O\alpha \times P_O\alpha}{P_O(1 - \alpha)}$

total pressure $= P_O(1 - \alpha) + P_O\alpha + P_O\alpha = P_O(1 + \alpha)$

so average moleculer mass $= \dfrac{P_O(1 - \alpha) \times 208.5 + (P_O\alpha \times 137.5) + (P_O\alpha \times 71)}{P_O(1 + \alpha)}$

$$= \dfrac{208.5 - 208.5\alpha + 208.5\alpha}{(1 + \alpha)}$$

$$= \dfrac{208.5}{1 + \alpha}$$

we know that   PM = dRT

$$d = \dfrac{PM}{RT} = \dfrac{1 \times \dfrac{208.5}{1 + \alpha}}{0.0821 \times 523} = 27\,g/L$$
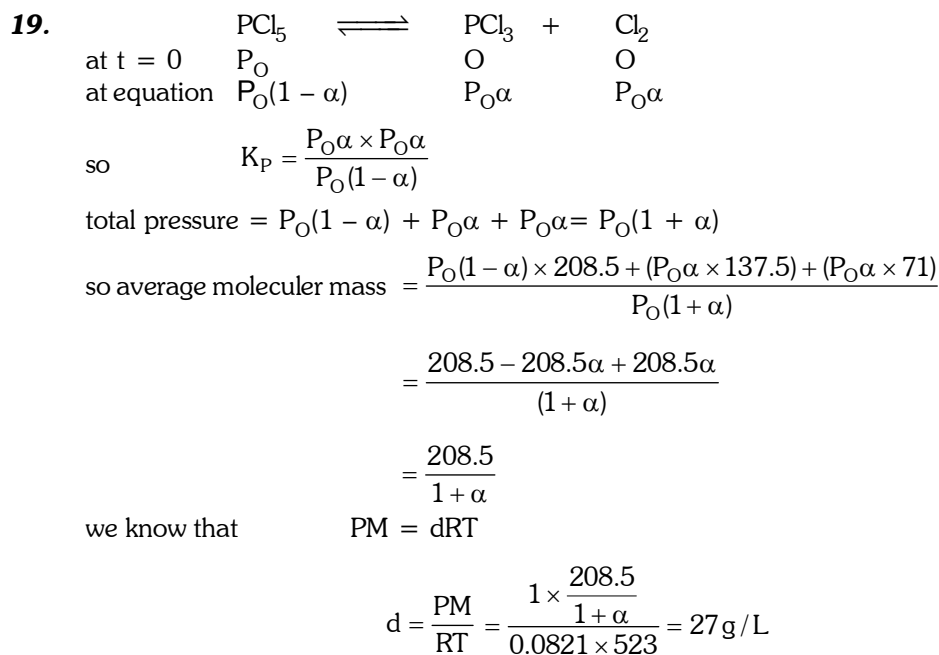
EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	C	A	A	D	A	B	C	B	D	D	A	C	A	B
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	D	B	C	B	C	B	D	B	C	C	A	A	D		

EXERCISE-5

1.   (B)

2*. $\Delta G° = \Delta H° - T\Delta S°$

         $= -54.07 \times 1000 - 298 \times 10$

         $= -54070 - 2980 = -57050$

     $\Delta G° = -2.303\,RT\,\log_{10}K$

         $-57050 = -2.303 \times 298 \times 8.314\,\log_{10}K = -5705\,\log_{10}K$

         $\log10\,K = 10$

3.   (ABD)   **4*.**   (B)   **5*.**   (B)   **6*.**   (C)   **7.**   (8.70 or 9.10)

IONIC EQUILIBRIUM

Recap of Early Classes

In Chemical equilibrium, we developed concepts regarding a reversible reaction. We continue to use those concepts in ionic equilibrium. Ionic equilibrium is an equilibrium which involves ions. In this chapter we discuss about pH calculations, buffers, hydrolysis of salts and solubility of salts.

IONIC EQUILIBRIUM

## 1.0 INTRODUCTION

All the substances can be classified into

Non electrolytic substances
- Will not dissociate into ions on dissolving in solvent like water. Eg. C_6H_6, diethyl ether

Electrolytic substances
- Will dissociate on dissolving in water into ions.
- Solution will be conductor of electricity. Eg. Salt like NaCl, $BaCl_2$
- Hg_2Cl_2 dissolve but dissociate negligible.

When an electrolyte is dissolved in a solvent(water), it spontaneously dissociates into oppositely charged ions, partially or sometimes fully

$$NaCl_{(aq)} \rightleftharpoons Na^+ (aq) + Cl^- (aq)$$
$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^- (aq) + H^+ (aq)$$
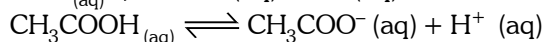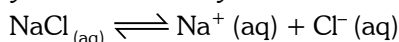
The degree of dissociation of an electrolyte (α) is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of α depends on

(A) nature of the electrolyte 　　　　　　　　(B) nature of the solvent

(C) the dilution 　　　　　　　　　　　　　　(D) temperature

Electrolytes 100% dissociated at all reasonable concentrations under normal temperatures - **strong electrolytes**. Strong acids(generally ***HClO₄, HI, HBr, HCl, H₂SO₄, HNO₃***), strong bases (generally (***NaOH, KOH, RbOH, CsOH*** and ***Ba(OH)₂***) and all type of salts (SASB, SAWB, WASB, or WAWB)are all examples of strong electrolytes.

electrolytes not 100% dissociated - **weak electrolytes**. weak acids (CH_3COOH, HCN), weak bases(NH_3, $Zn(OH)_2$) are examples.

2.0 ACIDS BASES AND SALTS

2.1 Arrhenius concept

SL AL

Arrhenius Acid : Substance which generate H^+ ion on dissolving in water (H^+ generator)

eg. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

If acid release only one H^+ ion is known as mono basic/monoprotic, symbol - H.A.

If two H^+ ion releases then known as dibasic/diprotic symbol $\rightarrow H_2A$

If triprotic / tribasic eg. H_3PO_4 (symbol H_3A)

- H_3BO_3 is not Arrhenius acid.
- Due to high charge density, H^+ ion in water is extremely hydrated (in form of H_3O^+, $H_5O_2^+$, $H_7O_3^+$)
- The structure of solid $HClO_4$ is studied by X-ray, It is found to be consisting of H_3O^+ and ClO_4^-.
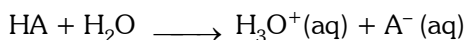 $$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^- \text{ (better representation)}$$

Arrhenius base :

Any substance which releases OH^- ion in water (OH^- ion generator)

- mono acidic base : CsOH, RbOH, NH_4OH symbol BOH
- diacidic base : $Ba(OH)_2$, $Ca(OH)_2$ symbol $B(OH)_2$
- Tri-acidic base : $Fe(OH)_3$
- OH^- ion also exit in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$

2.2 Bronsted - Lowery concept : (Conjugate acid - base concept) (Protonic concept)
$\boxed{\text{SL}}\ \boxed{\text{AL}}$

Acid : H^+ donor

Base : H^+ acceptor

$$HA + H_2O \longrightarrow H_3O^+(aq) + A^-(aq)$$
$$\text{Hydronium ion}$$

$$\underset{\text{Base-1}}{NH_3} + \underset{\text{Acid -2}}{H_2O} \rightleftharpoons \underset{\text{Acid-1}}{NH_4^+} + \underset{\text{Base-2}}{OH^-}$$

$$\underset{\text{Acid-1}}{HCl} + \underset{\text{Base-2}}{H_2O} \rightleftharpoons \underset{\text{Acid-2}}{H_3O^+} + \underset{\text{Base-1}}{Cl^-}$$

Conjugate acid - base pair

Acid - base which differ only in one proton.

	Acid	**Conjugate base**
(i)	HCl	Cl^-
(ii)	H_2SO_4	HSO_4^-
(iii)	HSO_4^-	SO_4^{2-}
(iv)	H_2O	OH^-

	Base	**Conjugate acid**
(i)	NH_3	NH_4^+
(ii)	H_2O	H_3O^+
(iii)	RNH_2	RNH_3^+

(a) Strong acid will have weak conjuagate base.

(b) Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\underset{\text{S.A}}{H_2SO_4} + \underset{\text{S.C.B.}}{HCO_3^-} \rightleftharpoons \underset{\text{W.A}}{H_2CO_3} + \underset{\text{W.C.B}}{HSO_4^-}$$
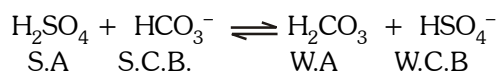
Amphoteric (amphiprotic) : Can act as acid as well as base.

$$HCl + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

$$NH_3 + \underset{\text{Acid}}{H_2O} \rightleftharpoons NH_4^+ + OH^-$$
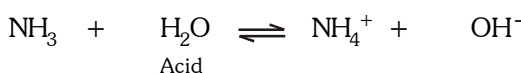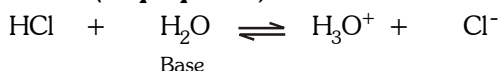
BEGINNER'S BOX–1

Acid base theory

1. If equal concentrations are mixed (of products & reactants) then which of the reaction will proceed to the right and which will proceed to the left.

(A) H_2SO_4 (aq) + NH_3 (aq) $\rightleftharpoons$ NH_4^+ (aq) + HSO_4^- (aq)

(B) HCO_3^- (aq) + SO_4^{2-} (aq) $\rightleftharpoons$ HSO_4^- (aq) + CO_3^{2-} (aq)

2. (a) Write conjugate acids of
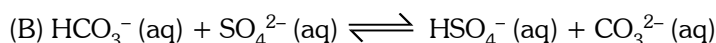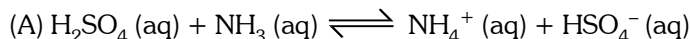
SO_4^{2-} , RNH_2 , NH_2^- , C_2H_5O C_2H_5 , F^-
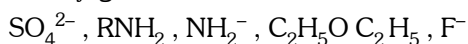
(b) Write conjugate base of

HNO_2 , OH^-, H_2CO_3, $HClO_4$.
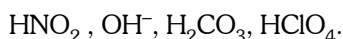
(c) Write conjugate acids and conjugate base of amphoteric species.

HS^- , NH_3, C_2H_5OH, H_2O
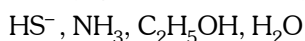
2.3 Lewis concept (electronic concept)

SL AL

An acid is any molecule/ion which can accept an electron pair with the formation of a coordinate bond.

A base is any molecule/ion which has a lone pair of electrons which can be donated.

Acid → e⁻ pair acceptor

- BF_3, $AlCl_3$
- H^+, Fe^{2+}, Na^+
- SF_4, PF_3

Base → (One electron pair donor)

- NH_3, PH_3, H_2O, CH_3OH

3.0 OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTE)

SL AL

When a weak electrolyte A^+B^- is dissolved is water and if α is the degree of dissociation then

$$AB \rightleftharpoons A^+ + B^-$$

initial conc $\qquad$ C $\qquad$ 0 $\quad$ 0

conc-at eq. $\qquad$ C(1 – α) $\quad$ Cα $\quad$ Cα

Then according to law of mass action,

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte}$$

$[C = \dfrac{1}{V}$, then V = 1/C(volume of solution is which 1 mole is present) is called ***dilution***, so $k_{eq} = \dfrac{\alpha^2}{(1-\alpha)V}$]

If α is negligible in comparision to unity $1 - \alpha \simeq 1$. $\qquad$ so $k_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\dfrac{k_{eq}}{C}} = \sqrt{k_{eq}.\ V}$
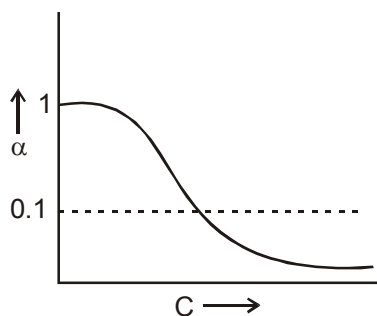
as ***concentration increases*** ⇒ α ***decreases*** ⇒ ***dilution decreases*** and ***at infinite dilution α reaches its maximum value, unity***.

4.0 ACIDITY AND pH SCALE

SL AL

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water and basic strength means the tendency of a base to give OH^- ions in water. So more the tendency of the substance to give H^+ or OH^- ions, more will be the acidic or basic strength of the substance.

The concentration of H^+ ions is written in a simplified scale introduced by Sorenson known as pH scale. pH is negative logarithm of activity of H^+ ions.

∴ $\quad$ pH = – log a_{H^+} $\qquad$ (where a_{H^+} is the activity of H^+ ions)

Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution.

For dilute solutions $[H^+] \leq 1M$ concentration can be taken as activity of H^+ ions while for higher concentrations the activity would be much less than the concentration itself, so is calculated experimentally.

The pH scale was marked from 0 to 14 with central point at 7 at 25°C taking water as solvent. If the temperature and the solvent are changed, the pH range of the scale will also change. For example

   0 – 14   at 25°C

   0 –13   at 80°C ($K_w = 10^{-13}$)

Note : *pH can also be negative or > 14*

pH = – log $[H^+]$; $[H^+] = 10^{-pH}$

pOH = – log $[OH^-]$; $[OH^-] = 10^{-pOH}$

pK_a = – log K_a ; $K_a = 10^{-pKa}$

pK_b = – log K_b ; $K_b = 10^{-pKb}$

4.1 Properties of Water

SL AL

1.   ***Acid/base nature:***

   Water - an acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can only be taken as base only.

   In pure water $[H^+] = [OH^-]$ so it is Neutral.

2.   ***Mole concentration / Molarity of water :***

   No. of moles/liter of water = $\dfrac{\text{mass of } 1 - \text{litre water in garms}}{\text{molecular mass of water}}$

   Molarity = No. of moles/litre = $\dfrac{1000gm}{18gm}$ = 55.55 mole /litre = ***55.55 M*** (density = 1 gm/cc)

3.   ***Ionic product of water :***

   According to Arrhenius concept

   $H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water, $\boldsymbol{k_w = [H^+][OH^-] = 10^{-14}}$ ***at 25° (exp.)***

   increasing temp $\Rightarrow k_w$ increases (dissociation of water is endothermic, so on increasing temperature $K_{eq.}$ increases)

   Now ***pH = –log$[H^+]$ = 7*** and   ***pOH = –log$[OH^-]$ = 7*** for water at 25° (exp.)

   pH = 7 = pOH $\Rightarrow$ neutral

   pH < 7 or pOH > 7 $\Rightarrow$ acidic

   pH > 7 or pOH < 7 $\Rightarrow$ Basic

Note. *Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.*

4.   ***Degree of dissociation of water :***
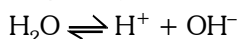
   $H_2O \rightleftharpoons H^+ + OH^-$

   $\Rightarrow \alpha = \dfrac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \dfrac{10^{-7}}{55.55} = 18 \times 10^{-10}$ or $1.8 \times 10^{-7}\%$

5.   ***Absolute dissociation constant of water :***

   $H_2O \rightleftharpoons H^+ + OH^- \quad K_a = K_b = \dfrac{[H^+][OH^-]}{[H_2O]} = \dfrac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$

   So, $pK_a = pK_b$ = – log (1.8×10^{-16}) = 16 – log 1.8 = 15.74

   For a conujugate acid base pair

   $\boxed{pK_a + pK_b = pK_w}$ $(pK_w = -\log K_w) = 14$ or $\boxed{K_a \times K_b = K_w}$

Note : pK_a of H_3O^+ ions = –1.74

Note : pK_b of OH^- ions = –1.74

4.2 pH Calculations of Different Types of Solutions
SL AL

- pH of strong acid and strong base
- $pH = -\log_{10}[H^+]$, $pOH = -\log_{10}[OH^-]$

─────────── Illustrations ───────────

Illustration 1*. Which one is not an acid salt?
(A) NaH_2PO_4 (B) NaH_2PO_2 (C) NaH_2PO_3 (D) Na_3PO_4.
Solution   ***(BD)***

Illustration 2*. Out of the following, amphiprotic species are
I. HPO_3^{2-} II. OH^- III. $H_2PO_4^-$ IV. HCO_3^-
(A) I, III, IV   (B) I and III   (C) III and IV   (D) All
Solution   ***(C)***

Illustration 3. Which of the following pair is Lewis acid & Lewis base & Product of these is also Lewis base
(A) BF_3, NH_3 (B) $SiCl_4$, $2Cl^-$ (C) $CH_3^{\oplus}$, $^{\ominus}OC_2H_5$ (D) None of these
Solution   ***(C)***

Illustration 4. Calculate the α of water and pH of 10^{-7} M HCl solution.
Solution.
$[H^+]_{HCl} = 10^{-7}$ M
$H_2O \rightleftharpoons H^+ + OH^-$
       $(10^{-7}+x)$ x
$K_w = [H^+][OH^-]$
$10^{-14} = x(10^{-7}+x)$
$x^2 + 10^{-7}x - 10^{-14} = 0$
$x = 0.618 \times 10^{-7}$
Net $[H^+] = 10^{-7} + x$
$= 10^{-7} + 0.618 \times 10^{-7}$
$= 1.618 \times 10^{-7}$
$\therefore$ pH $= 7 - \log 1.618$
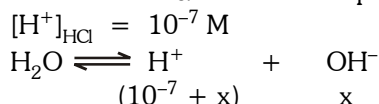
$= 7 - 0.2 = 6.8$ $\alpha = \dfrac{x}{\frac{1000}{18}} \times 100\%$

$= 0.618 \times 1.8 \times 10^{-9}/0.618 \times 1.8 \times 10^{-7}\%$

% change in α of water $= \dfrac{(1-0.618)\times 1.8 \times 10^{-9}}{1.8 \times 10^{-9}} \times 100\% = 38.2\%$

Illustration 5. At a temperature under high pressure $K_w(H_2O) = 10^{-10}$, A solution of pH 5.4 under these conditions is said to be:
(A) acidic   (B) basic   (C) neutral   (D) amphitoric
Ans.   ***(B)***

- **pH of a weak acid(monoprotic) solution**
AL
We have to use Ostwald's Dilution law(as have been derived earlier)
$HA \rightleftharpoons H^+ + A^-$
t = o   C   0   0

teq. $C(1-\alpha)$ $C\alpha$ $C\alpha$ $K_a = \dfrac{[H^+][OH^-]}{[HA]} = \dfrac{C\alpha^2}{1-\alpha}$

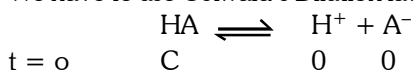if $\alpha << 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\dfrac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

$[H^+] = C\alpha = C\sqrt{\dfrac{K_a}{C}} = \sqrt{K_a \times C}$ So $pH = \dfrac{1}{2}(pK_a - \log C)$

on increasing the dilution $\Rightarrow C\downarrow \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$
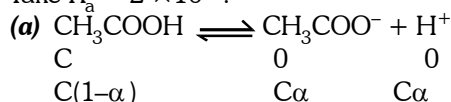
Illustrations

Illustration 6*.   Calculate pH of

(a) 10^{-1} M CH_3COOH (b) 10^{-3} M CH_3COOH (c) 10^{-6} M CH_3COOH

Take $K_a = 2\times 10^{-5}$.

Solution   **(a)** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\quad\quad$ C $\quad\quad\quad\quad\quad$ 0 $\quad\quad$ 0

$\quad\quad$ C(1–α) $\quad\quad\quad$ Cα $\quad\quad$ Cα

$K_a = \dfrac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{2\times 10^{-5}}{10^{-1}}} = \sqrt{2\times 10^{-4}}$ ($\alpha << 0.1$)

So, $[H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow pH = 3 - \dfrac{1}{2}\log 2 = 2.85$

(b) $\alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{2\times 10^{-5}}{10^{-3}}} = \sqrt{2\times 10^{-2}}$ ($\alpha > 0.1$)

So we have to do the *exact* calculations

$K_a = \dfrac{C\alpha^2}{1-\alpha} \Rightarrow 2\times 10^{-5} = \dfrac{10^{-3}\times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$

$[H^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow pH = 4 - \log(1.314) \approx 3.8$

(c) If approximation is used then, $\alpha = \sqrt{\dfrac{2\times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1$,

so we have to do the exact calculation, $2\times 10^{-5} = 10^{-6}\dfrac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$ or 95%

$[H^+] = 0.95 \times 10^{-6} = 9.5\times 10^{-7} \Rightarrow pH = 7 - \log(9.5) = 6.022$

At very low concentration (∞ dilution) weak electrolyte will show almost 100% dissociation, so behave as strong electrolyte

[pH of 10^{-6} M HCl $\simeq$ pH of 10^{-6} M $CH_3COOH \simeq 6$; pH of 10^{-8} M HCl = pH of 10^{-8} M CH_3COOH]

- **pH of a solution of a polyprotic weak acid**

AL

Let us take a weak diprotic acid (H_2A) in water whose concentration is c M. Diprotic acid is the one, which is capable of giving 2 protons in water.

In an aqueous solution of a diprotic acid, following equilbria exist.

$\quad\quad\quad\quad\quad\quad\quad\quad H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$

Conc. at equilbrium $\quad\quad\quad c(1-\alpha_1) \quad\quad ca_1(1-\alpha_2) \quad (c\alpha_1 + c\alpha_1\alpha_2)$

$\quad\quad\quad\quad\quad\quad\quad\quad HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$

Conc. at equilbrium $\quad\quad\quad c\alpha_1(1-\alpha_2) \quad\quad c\alpha_1\alpha_2 \quad (c\alpha_1 + c\alpha_1\alpha_2)$
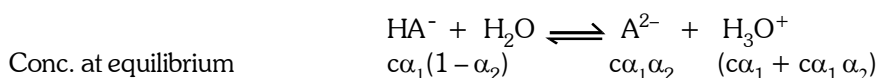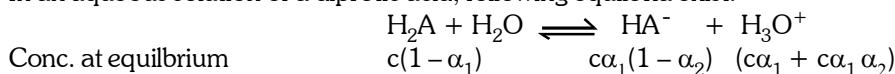
where α_1 is the degree of ionization (dissociation) of H_2A in presence of HA^- and α_2 is the degree of ionisation of HA^- in presence of H_2A.

Knowing the values of K_{a_1}, K_{a_2} and c, the values of α_1 and α_2 can be calculated using equations (i) and (ii).

After getting the values of α_1 and α_2 $[H_3O^+]$ can be calculated as.

$\quad\quad [H_3O^+]_T = c\alpha_1 + c\alpha_1\alpha_2$

- **Approximation**

  For diprotic acids, $K_{a_2} << K_{a_1}$ and α_2 would be even smaller than α_1.

  $\therefore \quad 1 - \alpha_2 \approx 1$ and $1 + \alpha_2 \approx 1$

  Thus, equation (i) can be reduced to $K_{a_1} = \dfrac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$ So $[H^+] = C\alpha_1$

  This is an expression similar to the expression for a weak monoprotic acid. Hence, even for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression along provided $K_{a_2} << K_{a_1}$.
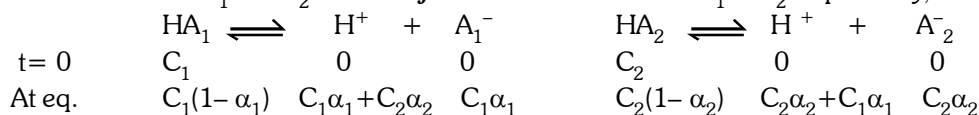
  Finally, if the total $[H_3O^+]$ from the acid is less than 10^{-6} M, the contribution of H_3O^+ from water should be taken into account for calculating pH while if it is $> 10^{-6}$ M, then $[H_3O^+]$ contribution from water can be ignored.

  Using this $[H_3O^+]$, pH of the solution can be calculated.

- **pH of a mixture of two weak acid(both monoprotic) solutions**

  AL

  let the acid are HA_1 & HA_2 and their **final** concentrations are C_1 & C_2 respectively, then

  $$HA_1 \rightleftharpoons H^+ + A_1^- \qquad HA_2 \rightleftharpoons H^+ + A_2^-$$

  t= 0 $\quad C_1 \qquad 0 \qquad 0 \qquad\qquad C_2 \qquad 0 \qquad 0$

  At eq. $\quad C_1(1-\alpha_1) \quad C_1\alpha_1+C_2\alpha_2 \quad C_1\alpha_1 \qquad C_2(1-\alpha_2) \quad C_2\alpha_2+C_1\alpha_1 \quad C_2\alpha_2$

  $$K_{a1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \qquad ; \qquad K_{a2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

  $$K_{a1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \ (\alpha_1 <<< 1) ; \quad K_{a2} = (c_1\alpha_1 + c_2\alpha_2)\alpha_2 \qquad (\alpha_2 <<< 1)$$

  $$\frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

  $$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \qquad \Rightarrow \quad [H^+] = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

  If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.
  So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$

  - **If water is considered third weak acid in solution of two weak acid then**

    $$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2 + K_w}$$

    $$C_w = \frac{1000}{18} = 55.5$$

    $$K_{aw} = 1.8 \times 10^{-16}$$
    $$C_wK_{aw} = 10^{-14} = K_w$$

    $$[H^+] = \sqrt{C_1K_{a1} + C_2K_{a2} + 10^{-14}}$$

Illustrations

Illustration 7. Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH$_3$COOH solution given that K_{a1} (HOCl) $= 2 \times 10^{-4}$ (log2 = 0.3) K_{a2} (CH$_3$COOH) $= 2 \times 10^{-5}$ also calculate OH$^-$, OCl$^-$, CH$_3$COO$^-$

Solution. Final solution volume become double
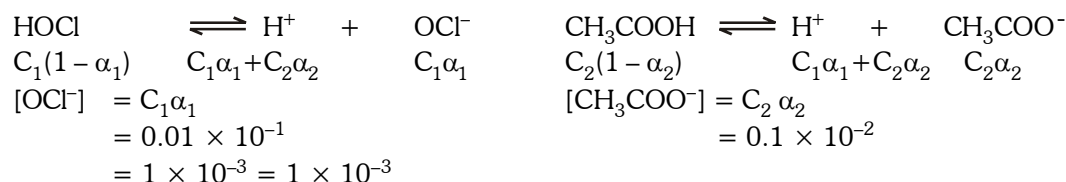$\quad C_1 = 0.01, C_2 = 0.1$

$\quad [H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$

$$= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3 = 2.7$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \; ; \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$C_1(1-\alpha_1) \quad C_1\alpha_1 + C_2\alpha_2 \quad C_1\alpha_1 \qquad C_2(1-\alpha_2) \quad C_1\alpha_1 + C_2\alpha_2 \quad C_2\alpha_2$$

$$[OCl^-] = C_1\alpha_1 \qquad\qquad\qquad [CH_3COO^-] = C_2\alpha_2$$
$$= 0.01 \times 10^{-1} \qquad\qquad\qquad\qquad = 0.1 \times 10^{-2}$$
$$= 1 \times 10^{-3} = 1 \times 10^{-3}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

$$[HOCl] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$
$$[CH_3COOH] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

- **pH of a mixture of weak acid(monoprotic) and a strong acid solution**

  AL

  For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

  To be precise we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

  If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from $SA = C_1$ and $[H^+]$ from $WA = C_2$

  Let HA is a weak acid

  $$HA \rightleftharpoons H^+ + A^-$$
  $$t = 0 \qquad C_2 \qquad 0 \qquad 0$$
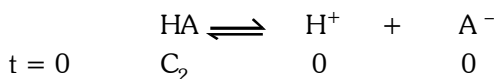
  $$t = t_{(eq)} \qquad C_2(1-\alpha) \quad C_2\alpha + C_1 \quad C_2\alpha \qquad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha <<< 1)$$

  (The weak acids dissociation will be further suppressed because of presence of strong acid)
  $$K_a = (C_2\alpha + C_1)\alpha$$

Finally, if the total $[H^+]$ from the acid is greater than 10^{-6} M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

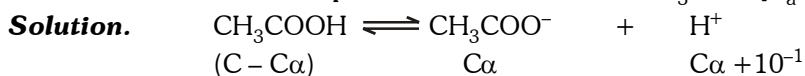- ***If a strong acid of low conc is added in water then $[H^+]$ of solution can be calculated as***

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}$$

$K_a C = K_w$ for water and this solution can be treated as SA + WA solution.

Illustrations

Illustration 8. Calculate pH 10^{-1} M HCl in 10^{-3} M CH_3OOH [$K_a = 2 \times 10^{-5}$]

Solution.
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$(C - C\alpha) \qquad C\alpha \qquad C\alpha + 10^{-1}$$

H^+ ion can be treated completely from HCl due to less dissociation of CH_3COOH and its low conc.

$$2 \times 10^{-5} = \frac{C\alpha \times 10^{-1}}{C} \qquad \Rightarrow \qquad \alpha = 2 \times 10^{-4}$$

$$[H^+] CH_3COOH = C\alpha = 2 \times 10^{-7}$$

BEGINNER'S BOX–2

pH Calculation & Acid base concept

1. The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :

(A) 3.3   (B) 3.5   (C) 4.5   (D) 4.0

2*. How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3:

(A) 1   (B) 0.02   (C) 0.009   (D) 0.01

3. A metal hydroxide of molecular formula $M(OH)_4$ is 50% ionised. Its 0.0025M solution will have the pH:

(A) 12   (B) 2   (C) 4   (D) 11.7

4*. Consider an aqueous solution, 0.1 M each in HOCN, HCOOH, $(COOH)_2$ and H_3PO_4, for HOCN, we can write

$$K_a(HOCN) = \frac{[H^+]\ [OCN^-]}{[HOCN]} .[H^+]$$ in this expression refers to

(A) H^+ ions released by HOCN

(B) Sum of H^+ ions released by all monoprotic acids

(C) Sum of H^+ ions released only the first dissociation of all the acids.

(D) Overall H^+ ion concentration in the solution.

5. Calculate the number of H^+ present in one ml of solution whose pH is 13.

6. Boric acid is a weak monobasic acid. It ionizes in water as

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ : K_a = 5.9 \times 10^{-10}$$

Calculate pH of 0.3 M boric acid.

7. Classify the following into acid, base and amphiprotic in terms of protonic concept.

(i) $H_2PO_2^-$ *(ii)* $H_2PO_3^-$ *(iii)* $H_2PO_4^-$ *(iv)* HPO_3^{2-}

(v) HPO_4^{2-} *(vi)* NH_4^+ *(vii)* $CH_3COOH_2^+$

8*. Calculate $[H^+]$, $[HCOO^-]$ and $[OCN^-]$ in a solution that contains 0.1M HCOOH ($K_a = 2.4 \times 10^{-4}$) and 0.1 M HOCN ($K_a = 4 \times 10^{-4}$).

5.0 pH OF A MIXTURE OF AN ACID AND A BASE WHERE AT LEAST ONE OF THEM IS WEAK

SL AL

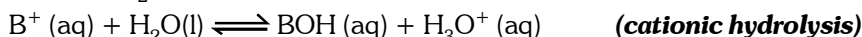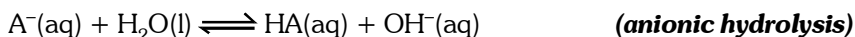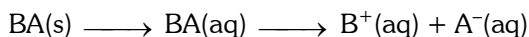For this type of mixtures there can be two cases in general,

(i) if the acids and bases are mixed in equal amounts(equivalents)

(ii) if the acids and bases are mixed in different amounts(equivalents)

First case will lead to phenomenon of **SALT HYDROLYSIS** and second case will lead to formation of **BUFFER SOLUTIONS**.

- **Salt Hydrolysis (Reverse of neutralisation)**   Salt +Water $\rightleftharpoons$ acid +base

  When acids and bases are mixed in equal amounts(equivalents), then we will be having salt solutions only in the water and we have to calculate pH of salt solutions.

  When a salt is added to water, the solid salt first dissolves and breaks into ions completely(unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will always produce H_3O^+ ions and the anions on reaction with water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions the solution can be acidic, basic or neutral. If salt is BA, then

$BA(s) \longrightarrow BA(aq) \longrightarrow B^+(aq) + A^-(aq)$

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ *(anionic hydrolysis)*

$B^+(aq) + H_2O(l) \rightleftharpoons BOH(aq) + H_3O^+(aq)$ *(cationic hydrolysis)*

- **Anionic Hydrolysis**

  Anions can function as a base on reaction with water and hydrolyze as follows :

  $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$
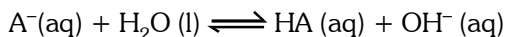
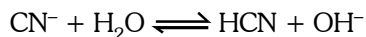 The extent of hydrolysis of a given anion depends on its basic strength

  (a) **Complete hydrolysis**

  The anions, which are stronger bases than OH^- and the conjugate acids of the anions which are weaker acid than H_2O, they will show complete hydrolysis in aqueous medium.

  (b) **Hydrolysis to a limited extent**

  The anions, which are weaker base than OH^- and the conjugate acids are stronger acid than H_2O but weaker acid than H_3O^+ will hydrolyse to a limited extent in aqueous medium
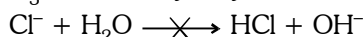
  For Example

  $CN^- + H_2O \rightleftharpoons HCN + OH^-$

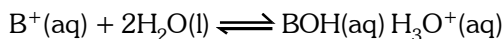 Other examples are CH_3COO^-, NO_2^-, S^{2-} etc.

  (c) **No hydrolysis**

  The anions that are weaker base than OH^- and the conjugate acids are stronger than both H_2O and H_3O^+ do not hydrolyse at all.

  $Cl^- + H_2O \xrightarrow{\quad\times\quad} HCl + OH^-$

  Other examples include SO_4^{2-}, NO_3^-, ClO_4^- etc.

- **Cationic Hydrolysis**

  Cations can function as acid on reaction with water and hydrolyze as follows.

  $B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq) H_3O^+(aq)$

 The extent of hydrolysis of a given cation depends on its acidic strength.

  (a) **Complete hydrolysis**

  The cations, which are stronger acid than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis. Example is PH_4^+ ion.

  $PH_4^+ + H_2O \longrightarrow H_3O^+ + PH_3$

  (b) **Hydrolysis to a limited extent**

  The cations, which weaker acid than H_3O^+ ion and their conjugate bases are stonger than H_2O but weaker than OH^-, show hydrolysis to a limited extent. For example

  $NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$
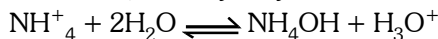
  Other ions showing hydrolysis to limited extent are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

  (c) **No hydrolysis**

  The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and OH^- do not hydrolyze at all. Example is alkali and alkaline earth metal ions.

  $Na^+ + 2H_2O \xrightarrow{\quad\times\quad} NaOH + H_3O^+$
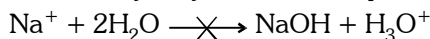
  There are four types of salt.

  (i) Salt of strong acid and strong base

  (ii) Salt of strong acid and weak base

  (iii) Salt of weak acid and strong base
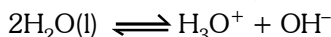
  (iv) Salt of weak acid and weak base

  Salts of first type does not undergo hydrolysis and rest three types undergo hydrolysis.

5.1 Salt of strong acid and strong base

SL AL

Neither of the ions will undergo hydrolysis so the solution contain only the equilibrium of ionization of water.

$$2H_2O(l) \rightleftharpoons H_3O^+ + OH^-$$

Thus, the pH of solution will be 7(neutral solution). at 25°C

5.2 Salt of strong acid and weak base

SL AL

The examples can be $NH_4Cl, (NH_4)_2 SO_4, C_6H_5NH_4^+Cl^-, CuSO_4, ZnCl_2, FeCl_3, AlCl_3,$

Only the cation will undergo hydrolysis and the solution will be acidic in nature. for example in the solution of NH_4Cl of concentration c, we will have

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

t = 0	c	0	0
at eq.	c(1– h)	ch	ch

(h - degree of hydrolysis)
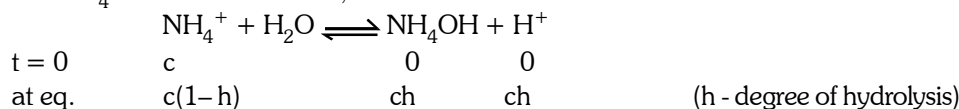
$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \text{called hydrolysis constant of the salt}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$H_2O \rightleftharpoons H^+ + OH^-, \qquad K_w = [H^+][OH^-]$$
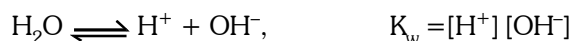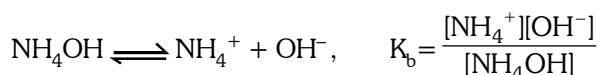
From above equations we can get

$$\mathbf{K_h \times K_b = K_w}$$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \qquad \text{(genarally 1-h} \simeq 1) \text{ so we get,} \qquad \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$\mathbf{[H^+]} = ch = \sqrt{K_h \times c} = \sqrt{\frac{\mathbf{K_w}}{\mathbf{K_b}} \times \mathbf{c}}$$

$$\boldsymbol{pH} = -\log[H^+] = -\frac{1}{2}[\log K_w - \log K_b + \log c] = \frac{1}{2}\boldsymbol{[pK_w - pK_b - \log c]}$$

Illustrations

Illustration 9. Equal vol. of 0.2 M NH_4OH (or ammonia) of 0.1 M H_2SO_4 are mixed calculate pH of final solution. Given : K_b of $NH_3 = 1.8 \times 10^{-5}$

Solution.
$$2NH_4 OH + H_2SO_4 \rightleftharpoons (NH_4)_2 SO_4 + H_2O$$

0.2V	0.1V	0.1V

$$(NH_4)_2SO_4 \Rightarrow 2NH_4^+$$

0.1	Cation undergoing hydrolysis

$$pH = \frac{1}{2}[14 - 4.7 + 1] \qquad = \frac{9.96}{2} = 4.98$$

5.3 Salt of weak acid and strong base

SL AL

The examples can be $CH_3COONa, KCN, Na_2C_2O_4, K_3PO_4$

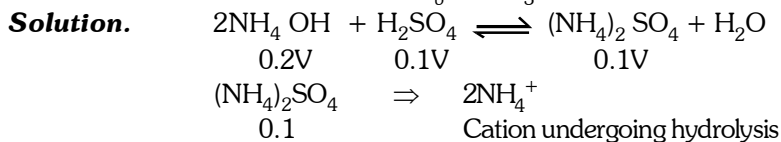Similar to above analysis we will get

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \qquad \text{(genarally 1-h} \simeq 1) \text{ so we get,} \qquad \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$\mathbf{K_h \times K_a = K_w}$$

$$[OH^-] = ch = \sqrt{K_h \times c} = \sqrt{\frac{K_w}{K_a} \times c}$$

$$pH = -\log[H^+] = -\frac{1}{2}[\log K_w + \log K_a - \log C] = \frac{1}{2}[pK_w + pK_a + \log C]$$

―――――――――――――― Illustrations ――――――――――――――

Illustration 10*. Caluclate degree of hydrolysis(h) and pH of solution obtanied by dissolving 0.1 mole of CH_3COONa in water to get 100ml of solution(take K_a of acetic acid = 2×10^{-5}), (log2 = 0.3)

Solution. $C = \frac{0.1}{100} = 1 \times 10^{-3}$
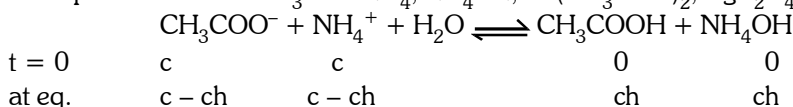
$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$, $\Rightarrow h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{5 \times 10^{-10}}{2 \times 10^{-5}}} = 5 \times 10^{-3} = 0.5\%$

$pH = \frac{1}{2}[pK_w + pK_a + \log C] = \frac{1}{2}[14 + 5 - \log 2 + \log(10^{-3})] = \frac{1}{2}(15.7) = 7.85$

5.4 Salt of weak acid and weak base
SL AL

Examples can include CH_3COONH_4, NH_4CN, $Ca(CH_3COO)_2$, MgC_2O_4

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

| t = 0 | c | c | | 0 | 0 |
| at eq. | c – ch | c – ch | | ch | ch |

$K_h = \dfrac{[CH_3COOH]\ [NH_4OH]}{[CH_3COO^-]\ [NH_4^+]}$ **...(i)**

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ **...(ii)**

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$, $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$ **...(iii)**

$H_2O \rightleftharpoons H^+ + OH^-$, $K_w = [H^+][OH^-]$ **...(iv)**

So, $K_h \times K_a \times K_b = K_w$,

$K_h = \dfrac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \left(\dfrac{h}{1-h}\right)^2$ $\Rightarrow$ $\left(\dfrac{h}{1-h}\right) = \sqrt{K_h}$

from (ii) equation

$[H^+] = K_a \dfrac{[CH_3COOH]}{[CH_3COO^-]} = K_a \dfrac{ch}{c(1-h)} = K_a \times \dfrac{h}{1-h} = K_a \times \sqrt{K_h} = K_a \times \sqrt{\dfrac{K_w}{K_a \times K_b}} = \sqrt{\dfrac{K_w \times K_a}{K_b}}$

$$\boxed{pH = -\log[H^+] = \frac{1}{2}[pK_w + pK_a - pK_b]}$$

―――――――――――――― Illustrations ――――――――――――――

Illustration 11*. Calcuate pH of 10^{-2} M NH_4CN Solution given K_a of HCN = 5×10^{-10} and K_b of NH_3(aq.) = 2×10^{-5}.

Solution. $pH = \frac{1}{2}[14 + pK_a - pK_b] = \frac{1}{2}[14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2}[18.6] = 9.3$

$\dfrac{h}{1-h} = \sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a \times K_b}} = \sqrt{\dfrac{10^{-14}}{5 \times 10^{-10} \times 2 \times 10^{-5}}} = 1 \Rightarrow 2h = 1 \Rightarrow h = \dfrac{1}{2} = 0.5$

5.5 Hydrolysis of ployvalent anions or cations

AL

The hydrolysis of these species will take place in steps(just like dissociation of weak acids). Out of different steps generally first step hydrolysis dominants mainly because of two reasons

(a) The hydrolysis constant of second and further steps is generally negligible in comparison to first step hydrolysis constant.

(b) The second and further step hydrolysis will be suppressed in presence of ions produced due to first step hydrolysis.

For a polyprotic acid (H_2S, H_3PO_4 ,H_2CO_3 ,$H_2 C_2O_4$) we already know that the disscociation always takes place in steps, so for example for H_3PO_4
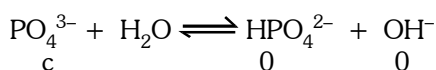
$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \qquad \text{... (1)}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad \text{... (2)}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \qquad \text{... (3)}$$

For all acids we always have $K_{a1} >> K_{a2} >> K_{a3}$

pH of the solution can be caculated from I^{st} step only because $[H^+]$ from IInd & IIIrd step can be neglected as
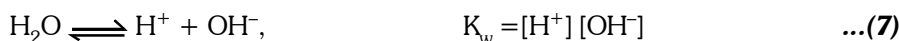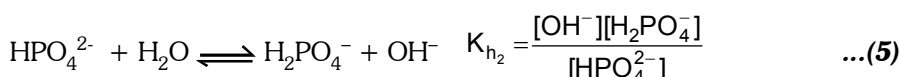
(a) $K_{a1} >> K_{a2} >> K_{a3}$

(b) $[H^+]$ from I^{st} dissociation will suppress the dissociation of IInd & IIIrd step.

Now for the hydrolysis of polyvalent ions(of salts like K_3PO_4 , $Na_2C_2O_4$, $ZnSO_4$, $FeCl_3$, $(NH_4)_2 C_2O_4$ or ions like PO_4^{3-}, $C_2O_4^{2-}$, Zn^{2+}, Fe^{3+} etc.)

Consider

$$\begin{array}{ccc} PO_4^{3-} + H_2O & \rightleftharpoons HPO_4^{2-} + & OH^- \\ c & 0 & 0 \end{array}$$

$$\begin{array}{ccc} c(1-h) & ch & ch \end{array} \qquad K_{h_1} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]} \qquad \text{...(4)}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad K_{h_2} = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} \qquad \text{...(5)}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \qquad K_{h_3} = \frac{[OH^-][H_3PO_4]}{[H_2PO_4^-]} \qquad \text{...(6)}$$

$$H_2O \rightleftharpoons H^+ + OH^-, \qquad K_w = [H^+][OH^-] \qquad \text{...(7)}$$

From above equations we get,

$K_{a1} \times K_{h3} = K_w$
$K_{a2} \times K_{h2} = K_w$
$K_{a3} \times K_{h1} = K_w$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch.Ch}{C(1-h)} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{c}} \qquad \Rightarrow [OH^-] = ch = \sqrt{K_{h1} \times c} \qquad \Rightarrow [H^+] = \frac{K_w}{[OH^-]} = K_w\sqrt{\frac{K_{a3}}{K_w c}} = \sqrt{\frac{K_W \times K_{a3}}{C}}$$

So $\quad pH = \dfrac{1}{2}[pK_w + pK_{a3} + \log C]$

——————————— Illustrations ———————————

Illustration 12. Calculate the pH of a 0.1 M K_3PO_4 solution. The third dissociation constant of orthophosphoric acid is 1.5×10^{-12}. (log3 = 0.48, log 2 = 0.3)

Solution. PO_4^{3-} + H_2O $\rightleftharpoons$ HPO_4^{2-} + OH^-

$$pH = 7 + \frac{1}{2} pK_{a3} + \frac{1}{2} \log C = 7 + \left(\frac{12 - \log 1.5}{2}\right) + \frac{1}{2} (\log 0.1)$$

$$= 7 + 5.91 - 0.5 = \textbf{12.41}$$

AL

Cation is not Hydrolysed : $NaHCO_3$, NaHS, etc., can undergo ionisation to from H^+ ion and can undergo hydrolysis to form OH^- (Na^+ ion is not hydrolysed)

(a) (i) HCO_3^- + H_2O $\xrightleftharpoons{\text{ionisation}}$ CO_3^{2-} + H_3O^+
                                                                  acid

  (ii) HCO_3^- + H_2O $\xrightleftharpoons{\text{hydrolysis}}$ H_2CO_3 + OH^-
                                                                  base

$$pH\left(HCO_3^-\right) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$$

(b) Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH_{(H_2PO_4^-)} = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right) \quad \text{and} \quad pH_{(HPO_4^{2-})} = \left(\frac{pK_{a_2} + pK_{a_3}}{2}\right)$$

Now H_3PO_4 $\xrightarrow{K_{a1}}$ $H_2PO_4^-$ $\xrightarrow{K_{a2}}$ HPO_4^{2-} $\xrightarrow{K_{a3}}$ PO_4^{3-} ionisation

$\xleftarrow{K_{h1}=\frac{K_w}{K_{a_1}}}$ $\xleftarrow{K_{h2}=\frac{K_w}{k_{a2}}}$ $\xleftarrow{K_{h3}=\frac{K_w}{K_{a3}}}$ Hydrolysis (reverse of ionisation)

The   pH of $H_3PO_4 = \frac{1}{2} (pK_{a1} - \log C)$ $\therefore K_{a1} >> K_{a2} >> K_{a3}$

pH of NaH_2PO_4 $= \frac{1}{2} (pK_{a1} + pK_{a2})$

pH of Na_2HPO_4 $= \frac{1}{2} (pK_{a2} + pK_{a3})$ $\therefore$ sec ionisation can be neglected

pH of Na_3PO_4 $= \frac{1}{2} (pKw + pKa_3 + \log C)$ $\therefore$ Sec hydrolysis can be neglected

$$= 7 + \frac{1}{2} pKa_3 + \frac{1}{2} \log C$$

——————————— Illustrations ———————————

Illustration 13*. Calculate the pH of a mixture of equal volumes of 0.1 M NaOH and 0.1 M H_2CO_3.
(H_2CO_3 $pKa_1 = 7$, $pKa_2 = 11$)

Solution. As $NaHCO_3$ contains amphoprotic species, pH $= \frac{7+11}{2} = 9$

BEGINNER'S BOX–3

Salt hydrolysis & hydrolysis of polyvalent anion & amphiprotic species

1*. The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be
(A) 100%   (B) 50%   (C) 25%   (D) none of these

2. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be :
(A) 8.58   (B) 4.79   (C) 7.01   (D) 9.22

3*. Which of the following salts undergoes anionic hydrolysis?
(A) $CuSO_4$ (B) NH_4Cl (C) $AlCl_3$ (D) K_2CO_3.

4. What is the OH^- concentration of a 0.08 M solution of CH_3COONa. [$K_a(CH_3COOH)=1.8 \times 10^{-5}$]

5. 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N?

6. What is the pH of 0.1M $NaHCO_3$? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

7*. Calculate the percentage hydrolysis & the pH of 0.02 M CH_3COONH_4 : $K_b(NH_3) = 1.6 \times 10^{-5}$, $K_a(CH_3COOH) = 1.6 \times 10^{-5}$.

6.0 BUFFER SOLUTION
SL AL

Buffer solutions are those, which resist a change in pH upon addition of small amount of acid or base. This does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred in absence of buffer.

6.1. Acidic buffer
SL AL

(i) Mixing of WASB salt and weak acid. $CH_3COOH + CH_3COONa$

(ii) Mixing of WA and strong base [Condition [WA] > [SB]]

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$
$$\begin{array}{llll} 1 & 0.5 & & \\ 0.5 & 0 & 0.5 & 0.5 \end{array}$$
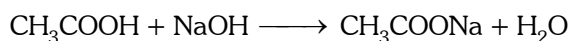
           └──────────┘
                buffer

(iii) Mixture of SBWA salt and SA [condition [Salt] > [SA]]

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$
$$\begin{array}{llll} 1 & 0.5 & 0.5 & 0.5 \\ 0.5 & 0 & 0.5 & 0.5 \end{array}$$
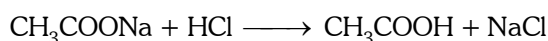
           └──────────┘
                buffer

To calculate the pH of a buffer solution made up of a weak acid and its salt with a strong base. We have
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
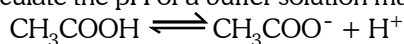
$$K_a = \frac{[CH_3COO^-]\ [H^+]}{[CH_3CO_2H]} = \frac{[Salt][H^+]}{[Acid]} \Rightarrow [H^+] = K_a \times \frac{[Acid]}{[Salt]}$$

Taking log of both sides. $\log [H^+] = \log K_a + \log \frac{[Acid]}{[Salt]}$
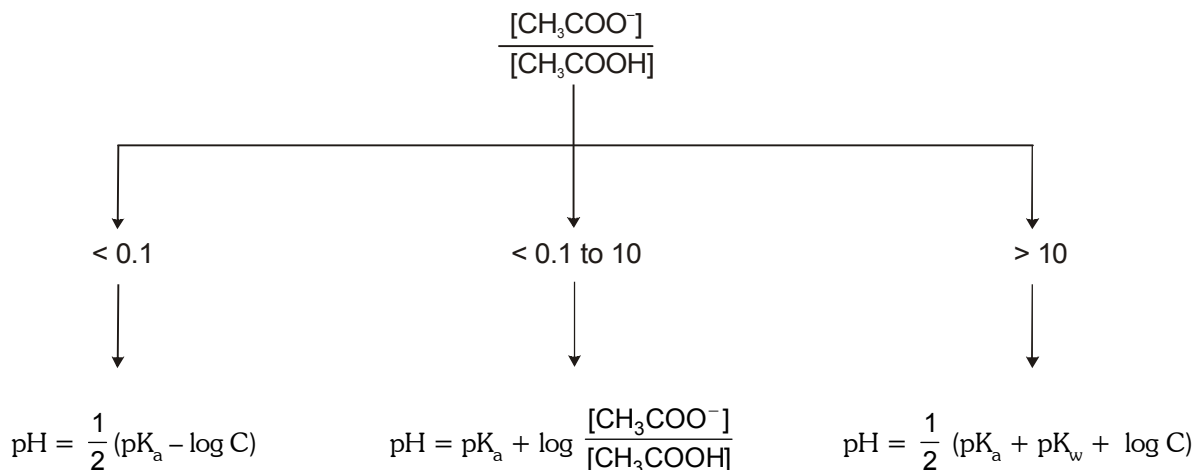
$\therefore$ $$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

This is known as the ***Henderson's equation of a buffer.***

- **Use of various relations**

Let us consider three situations, (i) a solution of CH_3COOH (ii) a solution of CH_3COONa and (iii) a solution of CH_3COOH and CH_3COONa (buffer). In all the three solutions, there will be some CH_3COO^- and CH_3COOH. But the relations used for calculating the pH differs. For (i), the relation used is : $pH = \frac{1}{2}(pK_a - \log c)$; for (ii)

the relation used is : $\frac{1}{2}(pK_w + pK_a + \log c)$ and for (iii), the relation used is $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$.

To understand as to when a particular relation is to be used, the following chart should be kept in mind.

$$\dfrac{[CH_3COO^-]}{[CH_3COOH]}$$

< 0.1	< 0.1 to 10	> 10
$pH = \dfrac{1}{2}(pK_a - \log C)$	$pH = pK_a + \log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$	$pH = \dfrac{1}{2}(pK_a + pK_w + \log C)$

Although it is difficult to give an exact limit up to which a buffer can be used, it is generally accepted that a buffer solution can be used for practical purposes when its [Salt]/[Acid] lies within the range of 0.1 to 10 (as shown above).

Therefore, it can be concluded that a particular weak acid (or base) can be employed for making useful buffer solution of pH (or pOH) lying within the range of $(pK_a \pm 1)$ or $(pK_b \pm 1)$. For example, acetic acid ($pK_a = 4.75$ at 25^0C) and sodium acetate mixture can be used for preparing buffer solutions whose pH values are roughly in the range of 3.75 to 5.75. Outside this range, the buffer capacity of acetic acid–sodium acetate solution is too small to be used for any practical purpose.

—————————— Illustrations ——————————

Illustration 14*. 4 gm of NaOH were dissolved in 1 litre of a solution containing 1 mole of CH_3COOH and 1 mole of CH_3COONa. Calculate $[H^+]$ in the resultant solution. (Given $K_a(CH_3COOH) = 1.8 \times 10^{-5}$).

Solution. $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

t = 0	0.1	1.0	1.0
On completion	0	0.9	1.1

$$[H^+] = K_a \times \dfrac{[CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \times \dfrac{0.9}{1.1} = 1.47 \times 10^{-5} \, M$$

Illustration 15*. You are given 0.1 M CH_3COOH in a beaker and to that 0.1 M solution NaOH is gradually added from a burrete. Calculate the pH of the solution in a beaker when acid is 25% neutralized. (Given pK_a (acetic acid) = 4.74)

Solution. $CH_3COOH \quad + \quad NaOH \quad \longrightarrow \quad CH_3COONa + H_2O$

0.1	0.1	0
0.1–0.025	0.1 – 0.025	0.025

$$pH = pK_a + \log \dfrac{salt}{acid} = 4.74 + \log \dfrac{0.025}{0.075} = 4.263$$
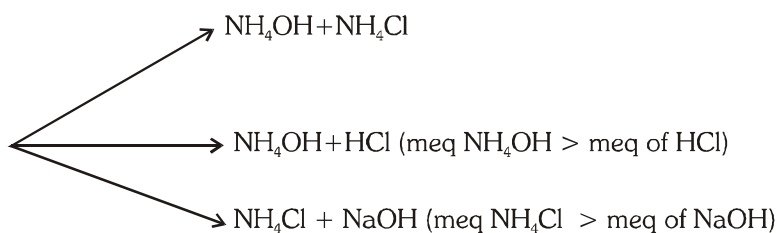
If HA is neutralized by SB then at any stage of neutralization

$$pH = pK_a + \log \frac{\alpha}{1-\alpha}, \text{ where } \alpha \text{ is \% neutralization}$$

∴   for any weak acid at his half equivalance point, $pH = pk_a$,

Similarly for a weak base, at 50% neutralization, $pOH = pk_b$.

6.2. Basic Buffer (WB + WBSA)
SL AL

For a buffer made up of weak base and its salt with a strong acid the Henderson's equation looks like this

$$NH_4OH + NH_4Cl$$

$$NH_4OH + HCl \text{ (meq } NH_4OH > \text{ meq of HCl)}$$

$$NH_4Cl + NaOH \text{ (meq } NH_4Cl > \text{ meq of NaOH)}$$

$$\boldsymbol{pOH = pK_b + log \frac{[Salt]}{[Base]}}$$

——————————— Illustrations ———————————

Illustration 16. Calculate the amount of $(NH_4)_2SO_4$ in grams which must be added to 500ml of 0.2 M NH_3 to yield a solution of pH =9.3. Given pK_b for NH_3 = 4.7

Solution. $$pOH = pK_b + \log \frac{[Cojugate\,acid]}{[Base]}$$

$$4.7 = 4.7 + \log \frac{x}{0.2} \Rightarrow x = 0.2, \text{ so concentration of } (NH_4)_2SO_4 \text{ required} = 0.1\,M$$

∴   moles of SO_4 needed = 0.05

∴   weight of $(NH_4)_2SO_4$ needed = $132 \times 0.05 = 6.6$ gm

Illustration 17*. A buffer solution of pH = 9.56 was obtained by mixing 2 mole of NH_3(eq.) and 1 mole of NH_4Cl to form 1 liter solution. To 200ml of this solution, 10 ml of 10 M NaOH is added. Caculate pH of this resulting solution.

Solution. $$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

⇒ $pOH = 14 - 9.56 = 4.44 = pK_b + \log \frac{1}{2} \Rightarrow \quad pK_b = 4.74$

In 200 ml of this solution, no. of moles NH_4Cl = 0.2 and no. of moles of NH_3(eq)= 0.4
no. of moles of NaOH added = 0.1

$$NH_4Cl + NaOH \longrightarrow NH_4OH + NaCl$$
   0.2   0.1   0.4
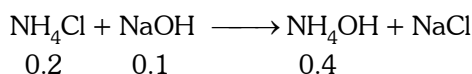
   0.1   0   0.5 $pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\frac{0.1}{0.5} = 4.04$

$$pH = 14 - 4.04 = 9.96$$

7.0 ACID-BASE TITRATION

AL

(A) **Titration of SA v/s SB :**

Volume of NaOH added	pH of solution
0 ml	1
10 ml	1.22
20 ml	1.48
30 ml	1.84
39 ml	2.84
39.9 ml	3.90
40.0 ml	7.00
40.1 ml	10.1
41 ml	11.1
50 ml	12.05
60 ml	12.30

40 ml 0.1 M HCl, **NaOH 0.1 M**
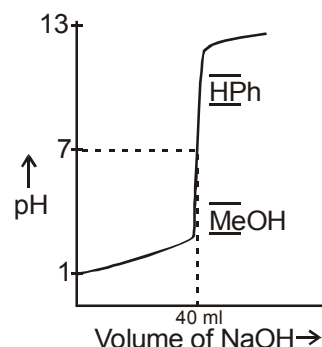
- Indicator should change it colour sharply for indication of reaction to be complete so its pH - range should lie perfectly with in sharp change to avoid experimental error.

- MeOH and HpH both can use for titration of SA and SB .

(B) **Titration of SB is WA :**

Volume of NaOH	pH value
0	2.5
5 ml	4.23
10 ml	4.7
15 ml	4.7 log 3 = 5.17
19 ml	4.7 + log 19/1 = 6
20 ml	7 + 1/2 (4.7) + 1/2 log (1/4) = 9.05
21 ml	12.4
30 ml	13.23
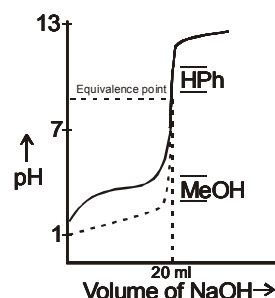
- In sharp change of titration HPh is suitable indicator.
- Initially fast change in pH is due to free ions availabel from weak acid.
- Slow down of pH change is due to Buffer formation, which is maximum at pH = pKa.
- Near equivalence point pH again increases fastly due to salt formation.
- After equiv. point pH changes very sharply due to presence of strong base.

(C) **Titration of SA + wB**
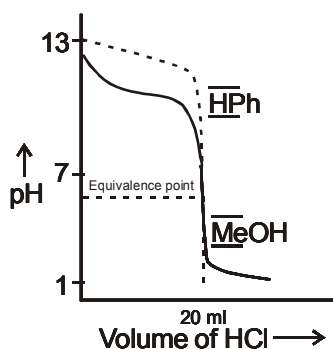
Sharp change between 4 to 7

(D) **Titration of W.A. S.B. salt + S.A.**
50 mL of 0.1 M CH_3COONa is titrated with 0.1 M HCl. Calculate pH when Vol. of HCl added is.
(a) 0 mL **(b)** 10 mL **(c)** 25 mL **(d)** 40 mL **(e)** 50 mL **(f)** 60 mL **(g)** 75 mL
pKa of CH_3COOHO = 4.74

(a) $pH = 1/2 (pK_w + pK_a + \log c)$
$= 1/2 (14 + 4.74 - 1) = 8.87$

(b) $CH_3COONa + HCl \longrightarrow NaCl + CH_3COOH$

| 5 mm | 1 mm | 0 | 0 |
| 4 mm | 0 | 1 mm | – |
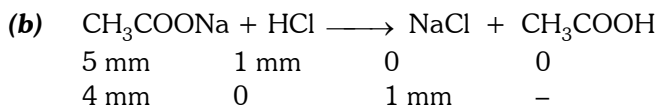
$pH = pka + \log 4$
$= 4.74 + 0.6 = 5.34$

(c) $pH = pka = 4.74$
(d) $pH = pka + \log 1/4 = 4.14$
(e) equivalent point, WA'S solution
$[CH_3COOH] = 5/100 = 1/20$

$pH = 1/2 (pka - \log C) = 1/2 (4.74 + 2 - 0.7)$

$= \dfrac{6.04}{2} = 3.02$

(f) $[HCl] = 1/100$ $pH = 2.1$

(g) $[HCl] = \dfrac{2.5}{125}$ $pH = 1.7$

(E) **W.B.S.A salt + S.B.**
(NH₄Cl) + NaOH)

$(NH_4Cl) + NaOH)$

Volume of NaOH added
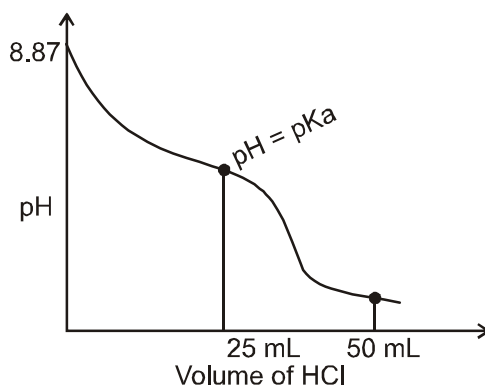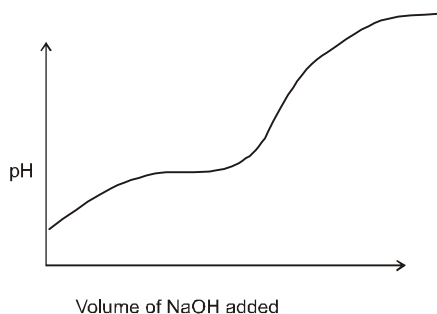
Illustrations

Illustration 18. 25 ml; 10^{-4} M NH_4OH solution is titrated against 10^{-3} M solution of HCl. Calculate the pH of solution at equivalent point. Also calculate the % of NH_4OH present in the form of NH_4^+ ion at this point.
$(K_b (NH_4OH) = 1.8 \times 10^{-5})$
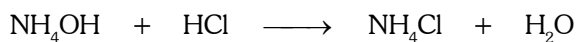
Solution. $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$
For equivalent point
$N_1V_1 = N_2V_2$
$V_2 = 2.5$ ml

$\therefore$ total vol. of solution at equivalent point
= 25 + 2.5 = 27.5 ml

$\therefore$ $[NH_4^+] = 9.7 \times 10^{-5}$ M

$$K_h = \frac{10^{-14}}{1.8 \times 10^{-5}} = ch^2$$

h = 2.47 × 10⁻³

$\therefore$ $[H^+] = ch = 2.247 \times 10^{-7}$ M

pH = 6.65   **Ans.**

% of NH_4OH as NH_4^+ = 99.7753.   **Ans.**

(F) ***Titration of Poly protic acid v/s S.B. :***

50 mL of 0.1 M H_3PO_4 agent 0.1 M NaOH. Calculate pH when vol. of NaOH added is

(a) 0 mL   **(b)** 25 mL   **(c)** 50 mL   **(d)** 75 mL   **(e)** 100 mL

(f) 125 mL   **(g)** 150 mL   **(h)** 200 mL   **(i)** 90 mL

pka₁ = 3   pka₂ = 7 , pka₃ = 11

(a)   pH = 1/2 (pka₁ – log C)
= 1/2 (3 + 1) = 2

(b)

H_3PO_4 +   NaOH $\rightleftharpoons$ NaH_2PO_4 + H_2O

t = 0 5 M mol   2.5 M mol   0   –

2.5 M mol   –   2.5 M mol

pH = pka₁ + log 1/1 = pka₁ = 3
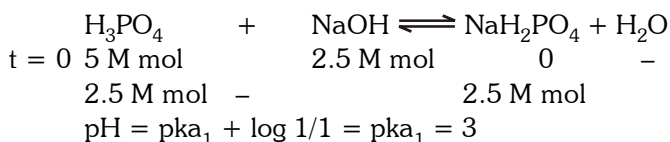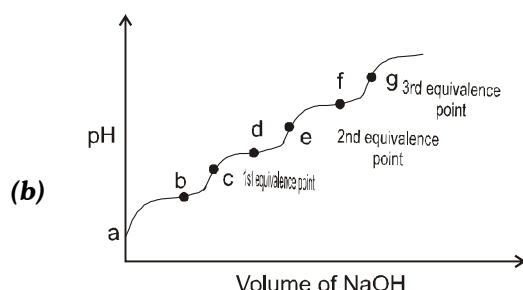
(c)   solution of $H_2PO_4^-$ amphoteric species

$$pH = \frac{pKa_1 + pKa_2}{2} = \frac{3+7}{2} = 5$$

(d) NaH_2PO_4 +   NaOH $\longrightarrow$ Na_2HPO_4 + H_2O

t = 0 5 M mol   2.5 M mol   0   –

2.5 M mol –   2.5 M mol   –

pH = log 1/1 + pka₂ = 7
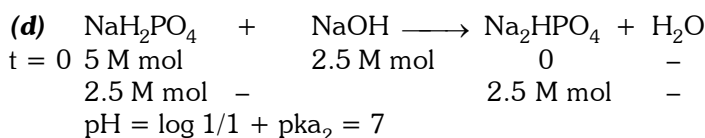
(e) HPO_4^{2-} solution (amphoteric species)

$$pH = \frac{pKa_2 + pKa_3}{2} = 9$$

(f) Na_2HPO_4 + NaOH $\longrightarrow$ Na_3PO_4 + H_2O

5   2.5   0   –

2.5   –   2.5   –

pH = pka₃ + 10 g 1/1 = 0
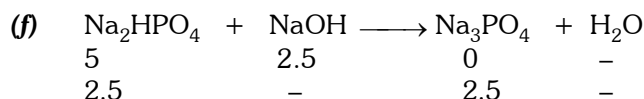
(g)   3ʳᵈ eq. pt Na_3PO_4 solution

$[Na_3PO_4] = 5/200 = 1/40$

pH = 1/2{pk�w + pk₃ + log C}

= 1/2 (14 + 11 – 2 + 0.4) = 11.7

(h) 200 mL

hydrolysis of Na_3PO_4 can be neglected in Presence of NaOH

[NaOH] = 5/250 = 1/50 pOH = 1.7

pH = 12.3

(i) 90 mL

$$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$$

	5	4	0
	1	0	4

$pH = pka_2 + \log 4 = 7.6$

Illustrations

Illustration 19. Predict graph for $(Na_2CO_3 + HCl)$. (W.A.S.B Vs S.B.)

Solution. $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$$pH = \frac{pKa_1 + pKa_2}{2} \simeq 9$$

$Na_2HCO_3 + NaCl \longrightarrow H_2CO_3 + NaCl$

$pH = 1/2 \{\log C + pka_1\} \simeq 3.5 - 4$

Volume of HCl added
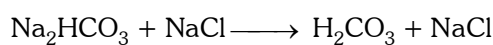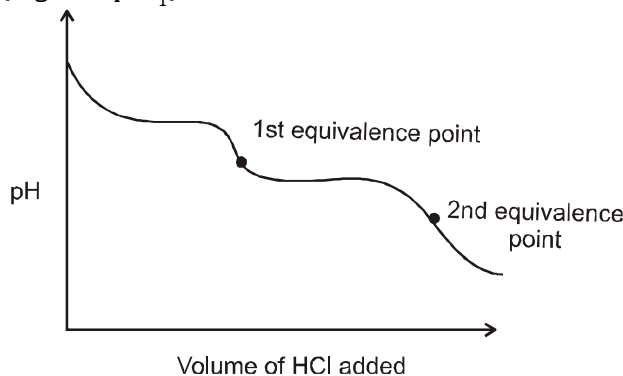
Illustration 20*. 1.06 gm of Na_2CO_3 is dissolved in 100 ml water. This solution is titrated against a 0.05 M HCl.

Calcualte the pH when.

(a) 200 ml of HCl is added $K_1 = 4.2 \times 10^{-7}$

(b) 400 ml of HCl is added $K_2 = 4.8 \times 10^{-11}$

Solution. m mole of Na_2CO_3 taken $= \dfrac{1.06}{106} \times 1000 = 10$

(a) m mole of HCl taken $= 200 \times 0.05 = 10$

$$pH = \frac{pKa_1 + pKa_2}{2} = \frac{6.38 + 10.32}{2} = 8.35 \quad \textbf{Ans.}$$

(b) m moles of HCl $= 400 \times 0.05 = 20$

$$Na_2CO_3 \;+\; 2HCl \longrightarrow H_2CO_3 \;+\; 2NaCl$$

$$H_2CO_3 \rightleftharpoons H^+ \;+\; HCO_3^-$$

0.02	x	x
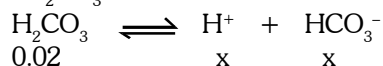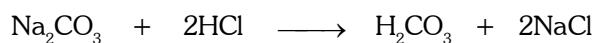
$$\frac{x^2}{0.02 - x} = 4.2 \times 10^{-7}$$

$x = 9.165 \times 10^{-5}\,M = [H^+] \Rightarrow pH = 4.04 \quad \textbf{Ans.}$

8.0 INDICATORS

Indicators are the substance, which indicates the end-point of a titration by changing their colour. They are in general, either weak organic acids or weak organic bases having characteristically different colours in the ionised and unionised forms. For example, methyl organce is a weak base (having red colour in ionised form and yellow colour in the unionised form) and phenolphthalein is a weak acid (having pink colour in the ionized form while its unionised form is colourless)

Let us consider the equilibrium between the ionised and unionsed form of an acid indicator (HIn)
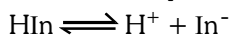
$$HIn \rightleftharpoons H^+ + In^-$$

$\therefore \quad K_{HIn} = \dfrac{[H^+][In^-]}{[HIn]}$ [K_{HIn} = indicator constant or dissociation constant of indicator]

or $\quad [H^+] = K_{HIn} \times \dfrac{[HIn]}{[In^-]}$

Taking negative logarithm of both sides

$$- \log [H^+] = \log K_{HIn} - \log \dfrac{[HIn]}{[In^-]}$$

$\therefore \quad pH = pK_{HIn} + \log \dfrac{[In^-]}{[HIn]} \qquad \Rightarrow \qquad pH = pK_{HIn} + \log \dfrac{[\text{Ionised form}]}{[\text{Unionised form}]}$

In general, the intensity of a coloured solution depends on the concentration of the colour imparting species. If the solution contains two coloured species, then the colour of the solution depends on the relative concentration of the colour imparting species. When the solution contains two coloured species as HIn and In⁻, then it is seen that the solution acquires a distinct colour of In⁻ only when the concentration of In⁻ is approximately at least 10 times greater than the concentration of HIn and vice versa.

Let us consider two cases.

Case-I :

In order for the solution to show colour due to In⁻ the minimum ratio of $\dfrac{[In^-]}{[HIn]}$ should be 10.

$\therefore \quad pH = pK_{HIn} + \log (10) = pK_{HIn} + 1$

At this stage, the percentage of the indicator in In⁻ form would be given by

$$\dfrac{[In^-]}{[In^-] + [HIn]} \times 100 = \dfrac{10}{10+1} \times 100 \approx 91.$$

Thus, nearly 91% of the indicator has been present in the ionised form (In⁻). In fact pH = pK_{HIn} + 1 is the minimum pH up to which the solution has a distinct colour characteristic of In⁻. At pH greater than this value, some more indicator will be present in the ionised form. Thus at pH $\geq pK_{Hin}$ + 1, the solution has a colour characteristic of In⁻.

Case - II:

In order for the solution to show colour due to HIn, the minimum ratio of $\dfrac{[In^-]}{[HIn]}$ should be $\dfrac{1}{10}$.

$\therefore \quad pH = pK_{HIn} + \log \dfrac{1}{10} = pK_{HIn} - 1.$

At this stage, the percentage of the indicator in In⁻ form would be given by

$$\dfrac{[In^-]}{[In^-] + [HIn]} \times 100 = \dfrac{1}{1+10} \times 100 \approx 9.1$$

Thus, nearly 9.1% of the indicator has been present in the ionised from (In⁻) and ≈ 91% of the indicator is present in the uionzed from (HIn). In factr pH = pK_{HIn} − 1 is the maximum pH up to which the solution has a distinct colour characteristic of HIn. At pH smaller than this value, some more indicator will be present in the unionised form. Thus at pH < pK_{HIn} = 1, the solution has a colour characteristic of HIn.

─────────── Illustrations ───────────

Illustration 21*. In indicator HIn has a standard ionisation constant of 10^{-10}. The acid form of the indicator is yellow and the alkaline form is red. The yellow colour is visible when the ratio of yellow form to red form is 30 to 1 and the red colour is predominant when the ratio of red form to yellow form is 2 to 1. What is the pH range of indicator. (log2 = 0.3, log3 = 0.48)
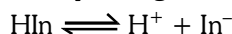
Solution. $\qquad HIn \rightleftharpoons H^+ + In^-$

$$K_{In} = \dfrac{[H^+] \ [In^-]}{[HIn]}$$

When yellow : red = 30 : 1

$\Rightarrow \quad [H^+]_1 = 10^{-10} \times \dfrac{[HIn]}{[In^-]} = 30 \times 10^{-10} \quad \Rightarrow \quad pH_1 = 8.52$

When red : yellow = 2 : 1

$10^{-10} = [H^+]_2 \left(\dfrac{2}{1}\right). \qquad\qquad \Rightarrow \quad pH_2 = 10.3$

BEGINNER'S BOX–4

Buffer Solution, Titration curve and Indicator theory

1*. To a 50 ml. of 0.05M formic acid how much volume of 0.10M sodium formate must be added to get a buffer solution of pH = 4.0 ? (pK_a of the acid is 3.7)
(A) 40 ml.   (B) 4 ml.   (C) 50 ml.   (D) 100 ml.

2. On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralised. If pK_a of CH_3COOH is 4.7 then the pH of the resulting solution is :
(A) More than 4.7 but less than 5.0   (B) Less than 4.7 but more than 4.0
(C) More than 5.0   (D) Remains unchanged

3*. Which of the following solutions does not act as buffer :
(A) $H_3PO_4 + NaH_2PO_4$ (B) $NaHCO_3 + H_2CO_3$
(C) $NH_4Cl + HCl$ (D) $CH_3COOH + CH_3COONa$

4*. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 0.5 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre :
(A) 1 : 1   (B) 2 : 1   (C) 1 : 2   (D) 2 : 3

5. 10 ml. of a solution contains 0.1 M NH_4Cl + 0.01M NH_4OH.
Which addition would not change the pH of solution :
(A) Adding 1 ml. water   (B) Adding 5 ml. of 0.1 M NH_4Cl
(C) Adding 5 ml. of 0.1 M NH_4OH (D) Adding 10 ml. of 0.1 M NH_4Cl

6*. $\dfrac{N}{10}$ acetic acid was titrated with $\dfrac{N}{10}$ NaOH. When 25%, 50% and 75% of titration is over then the pH of the solution will be :[$K_a = 10^{-5}$]
(A) 5 + log 1/3, 5, 5 + log 3   (B) 5 + log 3, 4, 5 + log 1/3
(C) 5 – log 1/3, 5, 5 – log 3   (D) 5 – log 1/3, 4, 5 + log 1/3

7. The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In⁻) forms of the indicator by the expression :

(A) $\log \dfrac{[HIn]}{[In^-]} = pK_{In} - pH$ (B) $\log \dfrac{[HIn]}{[In^-]} = pH - pK_{In}$

(C) $\log \dfrac{[In^-]}{[HIn]} = pH + pK_{In}$ (D) $\log \dfrac{[In^-]}{[HIn]} = pK_{In} - pH$

8. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

9*. CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5}.

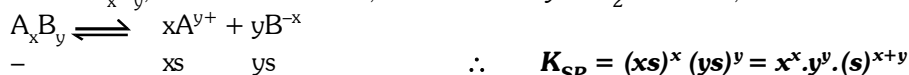## 9.0 Solubility(s) and Solubility Product(k_{sp})

SL AL

Solubility product(k_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

Following examples will illustrate the different type of solubilities and the effects of different factors or situations on solubility of a salt.
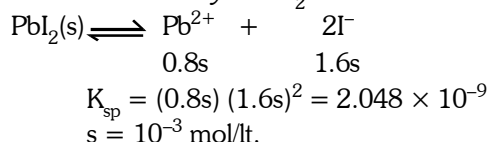
9.1. Simple Solubility

SL AL

Let the salt is A_xB_y, in solution in water, let the solubility in H_2O = 's' M, then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{-x}$$

$$- \qquad xs \qquad ys \qquad\qquad \therefore \quad K_{SP} = (xs)^x \, (ys)^y = x^x.y^y.(s)^{x+y}$$

- Calculate k_{SP} of $Li_3Na_3[AlF_6]_2$

$$K_{SP} = 3^3.3^3.2^2 \, (s)^8 = 3^6.4.(s)^8 = 2916 \, s^8$$

- Calculate solubility of PbI_2 in water at 25°C which is 80% dissociated $K_{sp}[PbI_2] = 2.048 \times 10^{-9}$

$$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$$

$$\qquad\qquad 0.8s \qquad 1.6s$$

$$K_{sp} = (0.8s) \, (1.6s)^2 = 2.048 \times 10^{-9}$$

$$s = 10^{-3} \, mol/lt.$$

9.2. Effect of common ions on solubility

SL AL

Because of the presence of common ion the solubility of the salt decreases.

- If K_{sp} of $SrF_2 = 8 \times 10^{-10}$. Calculate its solubility in 0.1 M NaF solution.

  If x be the solubility of SrF_2 in presence of NaF, then

$$SrF_2 \rightleftharpoons Sr^{2+} + 2F^- \qquad\qquad NaF \longrightarrow Na^+ + F^-$$

$$\qquad x \qquad 2x \qquad\qquad\qquad 0.1 \qquad 0 \quad 0$$

$$\qquad x \qquad (2x + 0.1) \qquad\qquad 0 \qquad 0.1 \quad (0.1 + 2x)$$
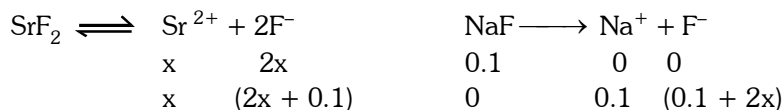
$$K_{sp} = x \, (2x + 0.1)^2 = 8 \times 10^{-10}.$$

Neglecting 2x with respect to 0.1, as we have solubility of SrF_2 in pure water in the range of 10^{-3}, in presence of common ions from NaF the solubility will get further decreased so we can easily neglect F^- ions from SrF_2, then we will have

$$\Rightarrow \quad \frac{K_{sp}}{[F^-]^2} = [Sr^{2+}] \quad \Rightarrow \frac{K_{SP}}{(0.1)^2} = x = \text{solubility of } SrF_2 = 8 \times 10^{-8}$$

9.3. Calculation of simultaneous Solubility

AL

- The ratio of solubility products of barium sulphate and barium chromate is 1 : 2.4. When pure water is saturated with both the solids simultaneously the total $[Ba^{2+}]$ is found to be 1.85×10^{-5}. Caculate K_{sp} of the compounds.

  Let the solubilities of the salts be x and y respectively, then

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-} \qquad\qquad BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{-2}$$

$$\qquad\qquad x+y \qquad x \qquad\qquad\qquad\qquad x + y \qquad y$$
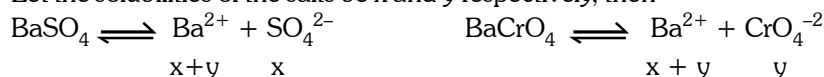
$$x + y = 1.85 \times 10^{-5}$$

$$K_{sp1} = x \, (x+y) \qquad\qquad\qquad\qquad K_{sp2} = y \, (x+y)$$

$$\frac{1}{2.4} = \frac{x}{y} \qquad y = 2.4x$$

$$x = \frac{1.8 \times 10^{-5}}{3.4}$$

$$\Rightarrow \quad K_{sp1} = \frac{(1.85)^2}{3.4} \times 10^{-10} = 1 \times 10^{-10} \text{ and } K_{sp2} = 2.4 \times 10^{-10}$$

9.4 Condition of precipitation

AL

For precipitation ionic product should be greater than K_{SP}

- You are given 10^{-5} M NaCl solution and 10^{-8} M $AgNO_3$ solution, they are mixed in 1 : 1 volume ratio, predict whether AgCl will be precipitated or not, if solubility product of AgCl is $= 10^{-10}$ mole per litre.

Ionic product $= \dfrac{10^{-5}}{2} \times \dfrac{10^{-8}}{2} = 25 \times 10^{-15} < K_{sp}$

Hence no precipitation will take place.

9.5. Selective Precipitation

AL

- 2×10^{-4} moles of Mn^{2+} and Cu^{2+} each is present in one litre solution of 10^{-3} M $HClO_4$, which is saturated with H_2S. Whether or not each of the ions will be precipitaed? Given that concentration of H_2S in its saturated solution is $= 0.1$ M, net dissociation constant of $H_2S = 10^{-21}$,
K_{sp} for MnS $= 2.5 \times 10^{-10}$ and K_{sp} for (CuS) $= 8.5 \times 10^{-36}$

$$
\begin{array}{cccc}
H_2S & \rightleftharpoons & 2H^+ & + & S^{2-} \\
10^{-1} & & 10^{-3} & & x
\end{array}
$$

$$K = \frac{x \times (10^{-3})^2}{[H_2S]} = 10^{-21} \quad \Rightarrow [S^{2-}] = 10^{-16} M$$

Ionic Product of CuS $= [Cu^{2+}][S^{2-}] = 2 \times 10^{-4} \times 10^{-16} = 2 \times 10^{-20} > K_{SP}$ of CuS
Ionic Product of MnS $= 2 \times 10^{-20} < K_{SP}$ of MnS
CuS will be precipitated

9.6. Solubility in appropriate buffer solutions

AL

Appropriate buffer means that the components of buffer should not interfere with the salt or only H^+ or OH^- ions should be interacting with the ions of the salt.

——————————— Illustrations ———————————

Illustration 22. The Solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate its solubility in buffer solution of pH = 8

Solution. Pb $(OH)_2$ solubility in water $= 6.7 \times 10^{-6}$, $K_{sp} = 4s^3 = 4 \times 300 \times 10^{-18} = 1.2 \times 10^{-15}$
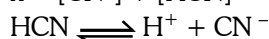$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$
Let $[Pb^{2+}] \quad = x$, then $\qquad K_{sp} = x [OH^-]^2$
$1.2 \times 10^{-15} \quad = x \times 10^{-12} \Rightarrow \quad x = 1.2 \times 10^{-3}$ M
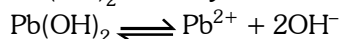
Illustration 23*. Calculate solubility of AgCN in a buffer solution of pH = 3, given that K_{sp}(AgCN) $= 1.2 \times 10^{-15}$, K_a for HCN $= 4.8 \times 10^{-10}$.

Solution. let the new solubility be $= x$
$[Ag^+] = x = [CN^-]$, but some of CN^- ions will react with H^+ ions from the buffer so,
$x = [CN^-] + [HCN]$
$HCN \rightleftharpoons H^+ + CN^-$

$$K_a = 4.8 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} \quad \Rightarrow \quad [HCN] = \frac{10^{-3}[CN^-]}{4.8 \times 10^{-10}} = \frac{[CN^-] \times 10^7}{4.8}$$

$$x = \frac{[CN^-] \times 10^7}{4.8} + CN^- \qquad \text{(CN– concentration can be neglegted in comparison to first term.)}$$

$$K_{sp} = x \cdot \frac{4.8x}{10^7} = 1.2 \times 10^{-15} \qquad \Rightarrow \qquad x = 5 \times 10^{-5}$$

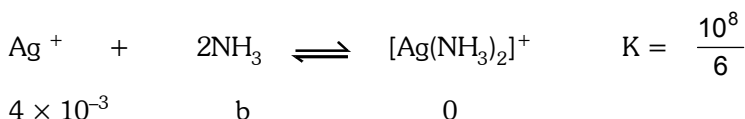## 9.7. Effect on solubility because of complex formation

AL

*   What must be the concentration of aq. NH_3(eq.) which must be added to a solution containing 4×10^{-3} M Ag^+ and 0.001 M NaCl, to prevent the precipitation of AgCl. Given that $K_{SP}(AgCl) = 1.8 \times 10^{-10}$ and the formation constant of $[Ag(NH_3)_2]^+$ is $K_{formation} = \dfrac{10^8}{6}$.

    Calculate silver ion concentration which can be allowed to remain in the solution,
    $1.8 \times 10^{-10} = [Ag^+] [Cl^-]$

    $$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} \text{ M, This quantity is so small that almost all the } Ag^+ \text{ ion will be consumed.}$$

    $Ag^+ \qquad + \qquad 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \qquad K = \dfrac{10^8}{6}$

    $4 \times 10^{-3} \qquad\qquad b \qquad\qquad 0$

    $1.8 \times 10^{-7} \quad (b - 8 \times 10^{-3}) \qquad 4 \times 10^{-3} \qquad K = \dfrac{10^8}{6} = \dfrac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2}$

    $\Rightarrow \quad b = 0.0445$

9.8 Amphoterism

AL

The hydroxides of certain metals can function as both bases and acids.

eg. $Zn(OH)_2$, $Al(OH)_3$, $Sn(OH)_2$, $Cr(OH)_3$
$Zn(OH)_2$ (s) $\rightleftharpoons$ Zn^{2+} (aq.) $+$ $2OH^-$ (aq.)
$Zn(OH)_2$ (s) $+$ $2OH^-$ (aq.) $\rightleftharpoons$ $Zn(OH)_4^{2-}$ (aq.)
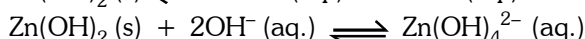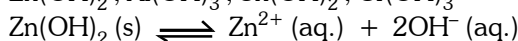
If the $[OH^-]$ is very small, then Zn^{2+} is present in high concentration.
On the other hand at high hydroxide concentration $Zn(OH)_4^{2-}$ is present in high concentration.
In other words, solubility at $Zn(OH)_2$ is greater in an acidic or basic solution than in neutral water.

(a) At what minimum concentration OH^- will 10^{-3} mole of $Zn(OH)_2$ go into solution as $Zn(OH)_4^{2-}$ in 1 L solution.
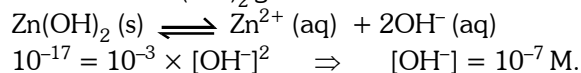
(b) At what maximum concentration of OH^- with 10^{-3} moles of $Zn(OH)_2$ go into solution as Zn^{2+} in 1 L solution.

Given : $Zn(OH)_4^{-2}$ (aq.) $\rightleftharpoons$ Zn^{2+} (aq) $+ 4OH^-$ (aq) $\qquad K = 10^{-15}$
$\qquad\qquad Zn(OH)_2$ (s) $\rightleftharpoons$ Zn^{2+} (aq) $+ 2OH^-$ (aq) $\qquad K_{SP} = 10^{-17}$
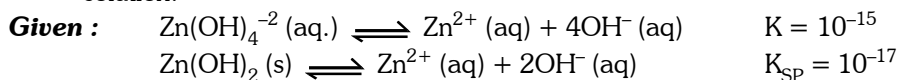
(a) If 10^{-3} mole $Zn(OH)_2$ go into $Zn(OH)_4^{2-}$.
$Zn(OH)_2$ (s) $+ 2OH^-$ (aq) $\rightleftharpoons$ $Zn(OH)_4^{2-}$ (aq)

$$10^{-2} = \frac{10^{-3}}{[OH^-]^2} \qquad \Rightarrow \qquad [OH^-] = 0.316 \text{ M}$$

(b) If 10^{-3} mole $Zn(OH)_2$ go into Zn^{2+}.
$Zn(OH)_2$ (s) $\rightleftharpoons$ Zn^{2+} (aq) $+ 2OH^-$ (aq)
$10^{-17} = 10^{-3} \times [OH^-]^2 \qquad \Rightarrow \qquad [OH^-] = 10^{-7}$ M.

BEGINNER'S BOX–5

Solubility Equilibrium

1*. Arrange in increasing order of solubility of AgBr in solutions given

(i) 0.1 M NH_3 (ii) 0.1 M $AgNO_3$ (iii) 0.2 M NaBr   (iv) pure water

(A) (iii) < (ii) < (iv) < (i)   (B) (iii) < (ii) < (i) < (iv)

(C) (iii) < (ii) = (i) < (iv)   (D) (ii) < (iii) < (iv) < (i)

2. Which of the following is most soluble in water?

(A) MnS (K_{sp} = 8×10^{-37})   (B) ZnS (K_{sp} = 7×10^{-16})

(C) Bi_2S_3 (K_{sp} = 1×10^{-72})   (D) $Ag_3(PO_4)$ (K_{sp} = 1.8×10^{-18})

3. When equal volumes of the following solutions are mixed, precipitation of

AgCl (K_{sp} = 1.8×10^{-10}) will occur only with:

(A) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)   (B) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(C) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)   (D) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

4*. The best explanation for the solubility of MnS in dilute HCl is that :

(A) Solubility product of $MnCl_2$ is less than that of MnS

(B) Concentration of Mn^{2+} is lowered by the formation of complex ions with chloride ions

(C) Concentration of sulphide ions is lowered by oxidation to free sulphur

(D) Concentration of sulphide ions is lowered by formation of weak acid H_2S

5. At 25^0C, the solubility product values of AgCl and AgCNS are 1.7 x 10^{-10} and 1.0 x 10^{-12} respectively. When water is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution.

6*. The K_{sp} value for $Gd(OH)_3$ is 2.7×10^{-23}, the pH at which $Gd(OH)_3$ begins to precipitate is (log 3 = 0.48)

(A) 6.08   (B) 5.08   (C) 8.48   (D) 4.08

7. If the solubility of AgCl (formula mass=143) in water at 25°C is 1.43×10^{-4} gm./100 ml. of solution then the value of K_{sp} will be :

(A) 1×10^{-5} (B) 2×10^{-5} (C) 1×10^{-10} (D) 2×10^{-10}

8. The solubility of $PbSO_4$ water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$.

GOLDEN KEY POINTS

- A strong electrolyte is defined as a substance which dissociates almost completely into ions in aqueous solution and hence is a very good conductor of electricity e.g., NaOH, KOH, HCl, H_2SO_4, NaCl, KNO_3 etc.

- A weak electrolyte is defined as a substance which dissociates to a small extent in aqueous solution and hence conducts electricity also to a small extent e.g. NH_4OH, CH_3COOH etc.

- Degree of dissociation :- The fraction of the total amount of an electrolyte which dissociates into ions is called the degree of dissociation (α),

  i.e. $\alpha = \dfrac{\text{Number of moles dissociated}}{\text{Number of moles taken}}$

- According to Arrhenius concept of acids and bases, an acid is a substance which gives H^+ ions in the aqueous solution whereas a base is a substance which gives OH^- ions in the aqueous solution.

- According to Bronsted-Lowry concept of acids and bases, an acid is a substance which can give a proton and a base is a substance which accepts a proton.

- According to Lewis concept of acids and bases, an acid is a substance which can accept a lone pair of electrons whereas a base is a substance which can donate a lone pair of electrons.

- ***Types of Lewis bases***

  (i) Neutral molecules containing a lone pair of electrons on the central atom like : NH_3, $R\overset{..}{\underset{..}{O}}H$, $H_2\overset{..}{O}$: etc.

  (ii) All negative ions like F^-, Cl^-, Br^-, I^-, OH^- etc.

- ***Types of Lewis acids***
  (i) Molecules having central atom with incomplete octet e.g. BF_3, $AlCl_3$ etc.
  (ii) Simple cations e.g. Ag^+, Cu^{2+}, Fe^{3+} etc.
  (iii) Molecules having central atom with empty d-orbitals e.g. $SnCl_4$, SiF_4, PF_5 etc.
  (iv) Molecules containing multiple bonds between different atoms e.g. $O = C = O$.

- According to Ostwald's dilution law, for the solution of a weak electrolyte with concentration C, mol L^{-1} and α as the degree of dissociation,

  $$K_a = \dfrac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \qquad \text{or} \qquad \alpha = \sqrt{K_a/C} = \sqrt{K_a V}$$

- Relative strength of two weak acids is given by $\dfrac{\text{Strength of acid } HA_1}{\text{Strength of acid } HA_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

- Ionic product of water, $K_w = [H^+][OH^-]$ or $[H_3O^+][OH^-]$. Its value at 25°C = 10^{-14}

- $pH = -\log[H_3O^+]$, $pOH = -\log[OH^-]$, $pK_a = -\log K_a$, $pK_b = -\log K_b$

- As $K_w = [H^+][OH^-] = 10^{-14}$ therefore $pK_w = pH + pOH = 14$.

	Salt	*h*	*pH*
●	SA+SB	No hydrolysis	pH = 7 Neutral
●	SA + WB	$K_h = \dfrac{k_w}{k_b}$	$pH = \dfrac{1}{2}(Pk_w - pK_b - \log_{10} C)$
●	SB + WA	$K_h = \dfrac{K_w}{k_a}$	$pH = \dfrac{1}{2}(Pk_w + pK_a + \log_{10} C)$
●	WA + WB	$K_h = \dfrac{K_w}{K_a \cdot K_b}$	$pH = \dfrac{1}{2}(pK_w + pK_a - pK_b)$

- **For Acidic Buffer solution**

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

- **For Basic Buffer solution**

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

- **For Best Buffer action** $\boxed{pH = pK_a}$, $\boxed{pOH = pK_b}$

  Range

  $pH = pK_a \pm 1$

  $pOH = pK_b \pm 1$

- **For Indicator** $pH = pK_{In} + \log \frac{[Ionised\ form]}{[Unionised\ form]}$

- Solubility product of a sparingly soluble salt $A_x B_y$ is given by
  $$K_{sp} = [A^{y+}]^x \times [B^{x-}]^y$$
  e.g. for AgCl, $K_{sp} = [Ag^+] [Cl^-]$, for $Ca_3(PO_4)_2$, $K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$ etc.

- If two solutions are mixed in which ions can combine to form a precipitate, concentration of ions in the solution after mixing are calculated. Then ionic product is calculated using the same expression as for K_{sp}. If ionic product > solubility product, a precipitate is formed.

- To calculate the solubility of a salt like AgCl in the presence of a strong electrolyte like NaCl, total $[Cl^-]$ is calculated (Cl^- ions from AgCl being negligible). Knowing K_{sp}, $[Ag^+]$ can be calculated.

SOME WORKED OUT EXAMPLES

Illustration 1.

Stomach acid is a solution of HCl with concentration of 2.2×10^{-3} M. what is the pH of stomach acid :

(A) 3.92   (B) 2.65   (C) 4.92   (D) 1.92

Solution.   ***(B)***

HCl is 100 % ionised so

$[H_3O^+] = 2.2 \times 10^{-3}$ M

$pH = -\log(2.2 \times 10^{-3}$ M$)$ or pH = 2.65

Illustration 2.

Calculate the $[H_3O^+]$ of blood, the pH of which is 7.2 (slightly basic).

(A) 5×10^{-8} M   (B) 6.3×10^{-8} M   (C) 5×10^{-9} M   (D) 4×10^{-7} M

Solution.   ***(B)***

As pH = 7.2 so $[H_3O^+] = $ antilog $(-7.2) = 6.3 \times 10^{-8}$ M

Illustration 3.

The pH of an aqueous solution at 25°C made up to 0.3 M, with respect to NaOH and 0.5 M, with respect to acetic acid ($pK_a = 4.76$) would be nearly :

(A) 4.25   (B) 4.93   (C) 4.75   (D) 5.05

Solution.   ***(B)***

$$pH = pK_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

0.3 M NaOH will react with acid to form 0.3 M CH_3COONa and therefore CH_3COOH concentration will be reduced to 0.2 M.

$$pH = 4.76 - \log\frac{0.2}{0.3} = 4.93$$

Illustration 4.

The pH of a solution of NH_3 is 5.806. If its concentration is 0.95 M then what is the value of its dissociation constant ? :

(A) anti log [28 + log (0.95) – 23.242]   (B) anti log [11.612 – log (0.95) – 28]

(C) anti log [11.612 – log (0.95) – 14]   (D) anti log [14 + log (0.95) – 11.612]

Solution.   ***(B)***

Since pH = 14 – pOH and $pOH = \dfrac{1}{2} pK_b - \dfrac{1}{2} \log C$

or $pH = 14 - \dfrac{1}{2}pK_b + \dfrac{1}{2}\log C$

or $pK_b = 2 (14 + \dfrac{1}{2} \log C - pH)$

or $K_b = $ antilog [11.612 – log (0.95) – 28]

Illustration 5.

The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration :

(A) 10^{-9} M   (B) 10^{-8} M   (C) 10^{-7} M   (D) 10^{-6} M

Solution.   ***(D)***

$[Ba^{2+}] [SO_4^{2-}] = 1.5 \times 10^{-9}$ (K_{sp}) and $[Ba^{2+}] = 0.01$ M

so   Required $[SO_4^{2-}] = \dfrac{1.5 \times 10^{-9}}{0.01} = 1.5 \times 10^{-7}$

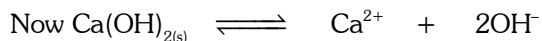so $[H_2SO_4] > 1.5 \times 10^{-7}$ for precipitation of $BaSO_4$.

Illustration 6*.

pH of a saturated solution of $Ca(OH)_2$ is 12. Its solubility product is :

(A) 10^{-6} (B) 4×10^{-6} (C) 5×10^{-7} (D) None of these

Solution. **(C)**

pH = 12   so $[OH^-] = 10^{-2}$ M

Now $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+} + 2OH^-$

5×10^{-3}M 10^{-2} M

so $K_{sp} = [Ca^{2+}][OH^-]^2$

$= (5 \times 10^{-3})(10^{-2})^2 = 5 \times 10^{-7}$

Illustration 7*.

A sample of 100 ml of 0.10 M acid HA ($K_a = 1 \times 10^{-7}$) is titrated with standard 0.10 M KOH. How many mL of KOH will have to be added when the pH in the titration flask will be 7.00 ?

(A) 0   (B) 10   (C) 100   (D) 50

Solution. **(D)**

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$7 = 7 + \log \frac{[N_2 V_2]}{[N_1 V_1 - N_2 V_2]}$$

$$1 = \frac{0.1 \times V_2}{0.1 \times 100 - 0.1 \times V_2}$$

or $10 - 0.1\,V_2 = 0.1\,V_2$

or $V_2 = 50$ mL

Illustration 8*.

When pure water is saturated with $CaCO_3$ and CaC_2O_4, the concentration of calcium ion in the solution under equilibrium is 8×10^{-5} M. If the ratio of the solubility product of $CaCO_3$ to that of CaC_2O_4 is 3, what is the solubility product of $CaCO_3$ in pure water?

(A) 4.80×10^{-8} (B) 9.60×10^{-9} (C) 9.60×10^{-8} (D) 4.80×10^{-9}

Solution.

$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$ $CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$

  x   x   y   y

(x+y)   x   (x+y)   y
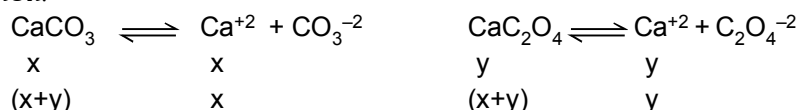
$$\frac{K_{SP}(CaCO_3)}{K_{SP}(CaC_2O_4)} = \frac{x}{y} = 3 \quad \Rightarrow \quad x = 3y$$

(x + y) $= 8 \times 10^{-5}$

(3y + y) $= 8 \times 10^{-5} \Rightarrow y = 2 \times 10^{-5}$ $x = 6 \times 10^{-5}$

$K_{SP}(CaCO_3) =$ $[Ca^{+2}][CO_3^{-2}]$

            $= $ $8 \times 10^{-5} \times 6 \times 10^{-5}$

            $= $ 48×10^{-10}

$K_{SP}(CaCO_3) =$ 4.8×10^{-9}

Illustration 9.

The solution of a salt of a weak acid and weak base will have pH :

($K_b = 10^{-4}$; $K_a = 10^{-6}$)

(A) 7   (B) 8   (C) 6   (D) 4

Solution. **(B)**

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7 + 3 - 2 = 8$$

Illustration 10.

Determine the effect on the concentrations of NH_3, NH_4^+ and OH^- when small amounts of each of the following is added to a solution of NH_3 in water.

(A) HCl   (B) NH_3 (C) NaOH   (D) NH_4Cl

(E) KNO_3

Solution.

The equilibria of NH_3 in water will be

$$NH_3 + H_2O \rightleftharpoons NH_4^+ \text{ (aq.)} + OH^- \text{ (aq.)}$$

(A) If HCl is added it will furnish H^+ and Cl^- ions as it is a strong electrolyte. Now H^+ will form H_2O with OH^- ions (neutralisation) so $[NH_3]$ will decrease, $[NH_4^+]$ and $[OH^-]$ increase since equilibria will shift in forward direction.

(B) If more NH_3 is added, then $[NH_3]$, $[NH_4^+]$ and $[OH^-]$ will increase.

(C) If NaOH is added it will furnish $[Na^+]$ and $[OH^-]$ ions since it is a strong electrolyte and $[OH^-]$ will suppress the ionisation of weak base NH_3 so $[NH_3]$ increases, $[NH_4^+]$ decreases and $[OH^-]$ increases.

(D) NH_4Cl will also apply common ion effect on NH_4OH but now $[NH_3]$ increases, $[NH_4^+]$ increases but $[OH^-]$ decreases.

(E) NO effect expected.

Illustration 11.

The pH of 0.0516 M solution of HCN is 2.34, what is K_a for HCN ?

Solution.

For weak acid.

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C$$

$$2.34 = \frac{1}{2} pK_a - \frac{1}{2} \log (0.0516)$$

$$pK_a = 3.3926 \quad \text{or} \quad K_a = \text{anti log } (-3.3926)$$
$$K_a = 4.04 \times 10^{-4}$$

Illustration 12*.

A buffer with pH 10 is to prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1 M NH_4OH. ($K_b = 1.8 \times 10^{-5}$) :

Solution.

Handerson equation for base buffer may be given as :

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$14 - pH = pK_b + \log \frac{[Salt]}{[Base]} \quad \text{.......(i)}$$

Given, pH $= 10$

[Base] $= [NH_4OH] = 1$ M

$pK_b = -\log K_b$
$= -\log [1.8 \times 10^{-5}] = 4.7447$

Hence, from Eq. (i), we get

$$14 - 10 = 4.7447 + \log \frac{[Salt]}{1}$$

[Salt] $= 0.18$ M

No. of moles of $NH_4Cl = 0.18$

Illustration 13.

Fluoroacetic acid has a K_a of 3.6×10^{-3}. What concentration of the acid is needed so that $[H^+]$ is 2.0×10^{-3} ?

Solution.

$$HC_2H_2FO_2 + H_2O \rightleftharpoons C_2H_2FO_2^- + H_3O^+$$
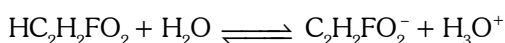
$$K_a = \frac{[H_3O^+][C_2H_2FO_2^-]}{[HC_2H_2FO_2]} = \frac{(2.0 \times 10^{-3})^2}{[HC_2H_2FO_2]} = 3.6 \times 10^{-3}$$

Thus $[HC_2H_2FO_2] = \dfrac{(2.0 \times 10^{-3})^2}{(3.6 \times 10^{-3})} = 1.11 \times 10^{-3}$ M remaining in solution.

Total concentration
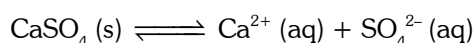$$= (2.0 \times 10^{-3}) + (1.1 \times 10^{-3}) = 3.1 \times 10^{-3} \, M$$

Illustration 14.

A solution is prepared by mixing 200 mL of 0.025 $CaCl_2$ and 400 mL of 0.15 M Na_2SO_4. Should $CaSO_4$ precipitate from a solution ?

Given $K_{sp} = 2.4 \times 10^{-5}$

Solution.

The equation for the equilibrium is

$$CaSO_4 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)}$$

and the solubility product expression is

$$K_{sp} = [Ca^{2+}] [SO_4^{2-}] = 2.4 \times 10^{-5}$$

If we assume that the volumes of the solutions that are mixed are additive, the final solution will have a volume of 600 ml. This total volume contains the equivalent of 200 mL of $CaCl_2$, so the concentration of Ca^{2+} ions is

$$[Ca^{2+}] = \left(\frac{200 \, mL \, CaCl_2 \, solution}{600 \, mL \, total \, volume} \right) \times (0.025 \, M) = 8.33 \times 10^{-3} \, M$$ and the concentration of SO_4^{2-} ions is

$$[SO_4^{2-}] = \left(\frac{400 \, mL \, Na_2SO_4 \, solution}{600 \, mL \, total \, volume} \right) \times (0.15 \, M) = 0.1 \, M$$

The ionic product is

$$[Ca^{2+}] [SO_4^{2-}] = (8.33 \times 10^{-3}) (1.0 \times 10^{-1}) = 8.33 \times 10^{-4}$$

Which is larger than K_{sp}, so $CaSO_4$ should precipitate from the solution.

Illustration 15.

Calculate the pH of a solution of 0.10 M acetic acid. Calculate the pH after 100 mL of this solution is treated with 50.0 mL of 0.10 M NaOH. $(K_a CH_3COOH = 1.8 \times 10^{-5})$

Solution.

$$HC_2H_3O_2 + H_2O \longrightarrow H_3O^+ + C_2H_3O_2^-$$
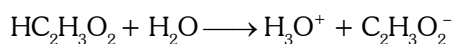
$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

Before treatment :
$$[H_3O^+] = [C_2H_3O_2^-] = X$$
$$[HC_2H_3O_2] = 0.10 - X \approx 0.10$$

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5} \text{ thus}$$

$$x = 1.35 \times 10^{-3} = [H_3O^+] \text{ and pH} = 2.87$$
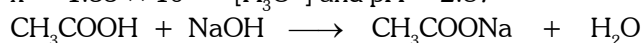
$$
\begin{array}{llll}
CH_3COOH & + \; NaOH & \longrightarrow \quad CH_3COONa & + \quad H_2O \\
100 \times 0.1 & 50 \times 0.1 & - & - \\
= 10 & = 5 & - & - \\
5 & 0 & 5 & - \\
\end{array}
$$

this is the buffer solution

$$pH = pk_a + \log \frac{[salt]}{[acid]} = 4.74 + \log \frac{[5]}{[5]} = 4.74$$

Illustration 16.

Ionic product of water and ionization constant of acetic acid at 25°C are 1×10^{-14} and 1.75×10^{-5} respectively. Calculate the hydrolysis constant of sodium acetate and its degree of hydrolysis in 10^{-3} M solution. Also calculate the pH of the solution ?

Solution.

CH_3COONa is salt of weak acid and strong base ; its degree of hydrolysis may be calculated using the formula :

$$h = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{\left(\frac{K_w}{CK_a}\right)} \qquad \textbf{...(i)}$$

Hence, from Eq. (i)

$$h = \sqrt{\frac{10^{-14}}{10^{-3} \times 1.75 \times 10^{-5}}} = 7.55 \times 10^{-4}$$

$$K_h \text{ (hydrolysis constant)} = \frac{K_w}{K_a} = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

pH after salt hydrolysis may be calculated as -

$$pH = \frac{1}{2} [pK_w + pK_a + \log C] \qquad \textbf{...(ii)}$$

$pK_w = -\log K_w = -\log 10^{-14} = 14$
$pK_a = -\log K_a = -\log (1.75 \times 10^{-5}) = 4.7569$
$\log C = \log 10^{-3} = -3$

Substituting the values in Eq.(ii), we get

$$pH = \frac{1}{2} [14 + 4.7569 - 3]$$

or   pH   = 7.88

Illustration 17*.

If $[Cd^{2+}] = [Zn^{2+}] = 0.1$ M initially, what $[H^+]$ must be maintained in a saturated H_2S (0.1 M) to precipitate CdS but not ZnS ?

K_{sp} (CdS) $= 8 \times 10^{-27}$
K_{sp} (ZnS) $= 1 \times 10^{-21}$
K_a (H_2S) $= 1.1 \times 10^{-21}$

Solution.

In order to prevent precipitation of ZnS,

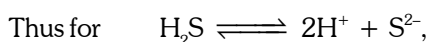$[Zn^{2+}] [S^{2-}] < K_{sp}$ (ZnS) $= 1 \times 10^{-21}$
(Ionic product)

or $(0.1).[S^{2-}] < 1 \times 10^{-21}$

or $[S^{2-}] < 1 \times 10^{-20}$

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x.

Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$,

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

or $x = [H^+] = 0.1$ M.

∴   No ZnS will precipitate at a concentration of H^+ greater than 0.1 M.

Illustration 18.

10^{-6} M HCI is diluted to 100 times. Its pH is:

(A) 6.0   (B) 8.0   (C) 6.95   (D) 9.5

Solution.

New concentration of; $HCI = \dfrac{10^{-6}}{100} = 10^{-8}$ M

$[H^+] = 10^{-7} + 10^{-8}$ (approximately)

(Little less than 10^{-7} from water).

Illustration 19.

In an attempted determination of the solubility product constant of $T\ell_2S$, the solubility of this compound in pure CO_2 free water was determined as 6.3×10^{-6} mol/L. Assume that the dissolved sulphide hydrolysis almost completely to HS^- and that the further hydrolysis to H_2S can be neglected. What is the computed K_{sp}? ($K_2 = 1.0 \times 10^{-14}$)

Solution.

$T\ell_2S \rightleftharpoons 2T\ell^+ + S^{2-}$, $K_{sp} = [T\ell^+]^2 [S^{2-}]$

$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$
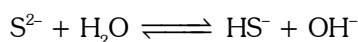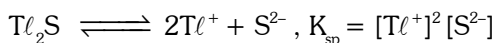
$K_h = \dfrac{K_w}{K_2} = \dfrac{1.0 \times 10^{-14}}{1.0 \times 10^{-14}} = 1.0$

$[T\ell^+] = 2(6.3 \times 10^{-6})$ M, $[S^{-2}] = 6.3 \times 10^{-6}$ M, and since $[HS^-] = [S^{-2}]$

$K_h = \dfrac{(6.3 \times 10^{-6})^2}{[S^{-2}]} = 1.0$

$[S^{2-}] = (6.3 \times 10^{-6})^2$

$K_{sp} = (6.3 \times 10^{-6})^2 [2(6.3 \times 10^{-6})]^2$

     $= 6.3 \times 10^{-21}$

Illustration 20*.

To reduce $[Cu^{2+}]$ to 10^{-12} how much NH_3 should be added to a solution of 0.0010 M $Cu(NO_3)_2$? Neglect the amount of copper in complexes containing fewer than 4 ammonia molecules per copper atom. ($K_d Cu(NH_3)_4^{2+} = 1 \times 10^{-12}$)

Solution.

$Cu(NH_3)_4^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$
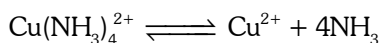
$K_d = \dfrac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 1.0 \times 10^{-12}$

since the sum of the concentration of copper in the complex and in the free ionic state must equal 0.0010 mol/L, and since the amount of the free ion is very small, the concentration of the complex is taken to be 0.0010 mol/L.

Let $x^4 = [NH_3]$

Then $\dfrac{(10^{-12})(x^4)}{0.0010} = 1.0 \times 10^{-3}$

or $x^4 = 1.0 \times 10^{-2}$

or $x = 0.178$

The concentration of NH_3 at equilibrium is 0.178 mol/L. The amount of NH_3 used up in forming 0.0010 mol/L of complex is 0.0040 mol/L, an amount negligible compared with the amount remaining at equilibrium. Hence the amount of NH_3 to be added is 0.178 mol/L.

Illustration 21.

The volume of the water needed to dissolve 1 g of $BaSO_4$ ($K_{SP} = 1.1 \times 10^{-10}$) at 25°C is:

(A) 280 litre   (B) 410 litre   (C) 205 litre   (D) None of these

Solution.

Solubility of $BaSO_4 = \sqrt{K_{SP}} = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$ M

∴   wt. of $BaSO_4 = 1.05 \times 10^{-5} \times 233 = 244.37 \times 10^{-5}$ g/litre.

∴   Volume of water needed to dissolve 1g $BaSO_4$ is equal to $\dfrac{1}{244.37 \times 10^{-5}} = 410$ litre1

Illustration 22.

Calculate pH of the following mixtures. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$:

(a)   50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH

(b)   50 mL of 0.10 M NaOH + 50 mL of 0.10 M CH_3COOH

Solution.

(a) $CH_3COOH \ + \ NaOH \longrightarrow CH_3COONa \ + \ H_2O$
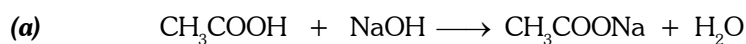
Initial	50×0.1	50×0.05	0	0
Millimoles	= 5	2.5		

Millimoles
after reaction   2.5   0   2.5   2.5

The solution consists of CH_3COOH and CH_3COONa and thus for buffer

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

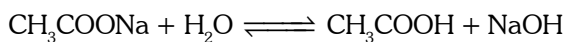$$\Rightarrow \quad pH = -\log 1.8 \times 10^{-5} + \log \frac{2.5/100}{2.5/100} \Rightarrow pH = 4.7447$$

(b) $CH_3COOH \ + \ NaOH \rightarrow CH_3COONa \ + \ H_2O$
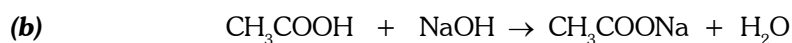
Initial millimoles	50×0.1	50×0.1	0	0
	= 5	= 5	0	0
Final millimoles	0	0	5	5

Finally concentration of $CH_3COONa = \dfrac{5}{100}$, and pH is decided by salt hydrolysis.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

C   0   0

C(1 – h)   Ch   Ch

$$[OH^-] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w \times C}{K_a}} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \times \frac{5}{100}} = 5.27 \times 10^{-6} M$$

$$[H^+] = \frac{10^{-14}}{5.27 \times 10^{-6}} = \frac{10^{-8}}{5.27} = 0.189 \times 10^{-8} \text{ or } pH = 8.72$$

Illustration 23.

Should $Mg(OH)_2$ precipitate from a solution that is 0.001 M $MgCl_2$ if the solution is also made 0.10 M in $NH_3 [K_{sp[Mg(OH)_2]} = 1.8 \times 10^{-11}, K_{b(NH_4OH)} = 1.8 \times 10^{-5}]$

Solution.

$[OH^-]$ in 0.10 M $NH_4OH = \sqrt{K_bC}$ (Ostwald's dilution law)

$$= \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} M$$

$\Rightarrow \quad [Mg^{2+}] = 0.001$ M

Ionic product $= [Mg^{2+}][OH^-]^2 = (0.001) \times (1.34 \times 10^{-3})^2$

$$= \textbf{1.8} \times \textbf{10}^{-9} > \textbf{\textit{K}}_{\textbf{\textit{sp}}}$$

As, Ionic product is greater than K_{sp} of Mg $(OH)_2$, hence precipitation should occur.

Illustration 24.

Calculate the pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colour when indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ions are 60% present.

Solution.

For indicator dissociation equilibrium

$$HI_n \rightleftharpoons H^+ + I_n^-$$
$$\text{Colour A} \qquad \text{Colour B}$$
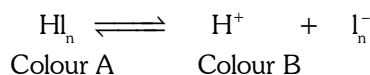
$$K_{In} = \frac{[H^+][I_n^-]}{[HI_n]}$$

The mid - point of the colour change of an indicator HI_n is the point at which

$[In^-] = [HI_n]$, $K_{In} = [H^+] = 1 \times 10^{-5}$

$\therefore \quad pH = 5$

Thus, at pH = 5 the indicator will change its colour.

$$K_{In} = \frac{[H^+][I_n^-]}{[HI_n]} \Rightarrow 1 \times 10^{-5} = \frac{[H^+] \times 60/100}{20/100}$$

$\therefore \quad [H^+] = 0.666 \times 10^{-5}$

$\therefore \quad pH = \textbf{5.1760}$

Illustration 25.

A solution has 0.1 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. $K_{sp[Mg(OH)_2]} = 18.0 \times 10^{-12}$ and ionisation constant of NH_3 is 1.8×10^{-5}.
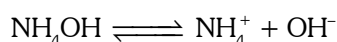
Solution.

The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ can be obtained by $K_{sp} = [Mg^{2+}][OH^-]^2$

$\Rightarrow \quad 18.0 \times 10^{-12} = (0.1) \times [OH^-]^2$

$\therefore \quad [OH^-] = 1.34 \times 10^{-5}$ M

Thus, solution having $[OH^-] = 1.34 \times 10^{-5}$ M will not show precipitation of $Mg(OH)_2$ in 0.1 M Mg^{2+}. These hydroxyl ions are to be derived by basic buffer of NH_4Cl and NH_4OH.

$$pH = pK_b + \log \frac{[Salt]}{[Base]} \Rightarrow pH = pK_b + \log \frac{[NH_4^+]}{[NH_4OH]}$$
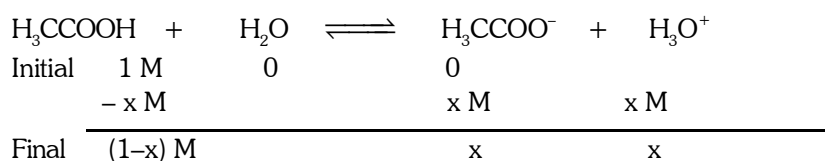
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In presence of $[NH_4Cl]$, all the NH_4^+ ions provided by NH_4Cl as due to common ion effect, dissociation of NH_4OH will be suppressed.

$$-\log [OH^-] = -\log 1.8 \times 10^{-5} + \log \frac{[NH_4^+]}{[0.05]}$$

$\therefore \quad [NH_4^+] = 0.067$ M or $[NH_4Cl] = 0.067$ M

Illustration 26.

What is pH of 1 M CH_3COOH solution? To what volume must one litre of this solution be diluted so that the pH of resulting solution will be twice the original value. Given : $K_a = 1.8 \times 10^{-5}$

Solution.

	H_3CCOOH	+	H_2O	$\rightleftharpoons$	H_3CCOO^-	+	H_3O^+
Initial	1 M		0		0		
	– x M				x M		x M
Final	(1–x) M				x		x

$$K_a = \frac{x^2}{1-x} \approx \frac{x^2}{1} \therefore x = \sqrt{K_a} = 4.2 \times 10^{-3} = [H_3O^+]$$
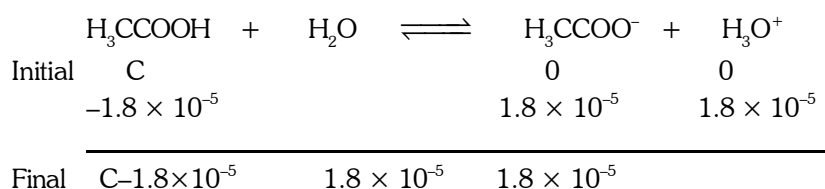
$pH = -\log [H_3O^+] = -\log \{4.2 \times 10^{-3}\} = 3 - \log 4.2 = 2.37$

Now, let 1 L of 1 M AcOH solution be diluted to V L to double the pH and the conc. of diluted solution be C.

New pH = 2 × Old pH = 2 × 2.37 = 4.74

$pH = -\log [H_3O^+] = 4.74$

$\therefore \quad [H_3O^+] = 1.8 \times 10^{-5}$

	H_3CCOOH	+	H_2O	$\rightleftharpoons$	H_3CCOO^-	+	H_3O^+
Initial	C				0		0
	-1.8×10^{-5}				1.8×10^{-5}		1.8×10^{-5}
Final	$C-1.8\times10^{-5}$				1.8×10^{-5}		1.8×10^{-5}

$$K_a = \frac{[CH_3COO^-] \times [H_3O^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{C - 1.8 \times 10^{-5}}$$

$\therefore \quad C = 3.6 \times 10^{-5} M$

On dilution,

$M_1V_1 = M_2V_2$

$1 M \times 1 L = 3.6 \times 10^{-5} M \times V_2$

$\therefore \quad V_2 = 2.78 \times 10^4 L$

Illustration 27*.

A sample of AgCl was treated with 10 mL of 1.7 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate solubility product of AgCl. $K_{sp(Ag2CO3)} = 8.2 \times 10^{-12}$

Solution.

$[CO_3^{2-}] = [Na_2CO_3] = 1.7 M$

At eqm., $[Cl^-] = [NaCl] = \dfrac{0.0026}{35.5} = 7.32 \times 10^{-5} M$

	$2AgCl (s)$	+	Na_2CO_3	$\rightleftharpoons$	$Ag_2CO_3 (s)$	+	$2NaCl$
Initial			1.7 M				0
At eqm.			$(1.7 - 7.32 \times 10^{-5})$				$7.32 \times 10^{-5} M$
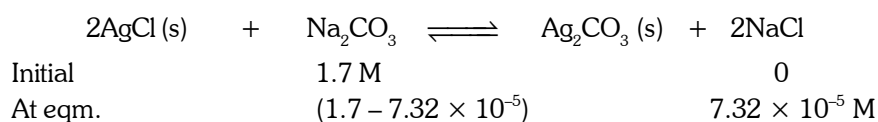
$[Ag^+]^2 [CO_3^{2-}] = K_{sp(Ag2CO3)}$

$$\therefore \quad [Ag^+] = \sqrt{\frac{K_{sp(Ag2CO3)}}{[CO_3^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.7}} = 2.1963 \times 10^{-6} M$$

$\therefore \quad K_{sp(AgCl)} = [Ag^+][Cl^-] = (2.1963 \times 10^{-6}) \times (7.32 \times 10^{-5}) = 1.61 \times 10^{-10}$

Illustration 28*.

Given $Ag^+(NH_3)_2 \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 8.2 \times 10^{-8}$ and $K_{sp(AgCl)} = 2.378 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

Solution.

$[Ag(NH_3)_2]^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq)$
$\qquad\qquad\qquad\qquad x + y \qquad 2x$

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$\qquad\qquad\quad x + y \qquad y$
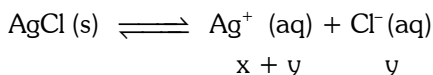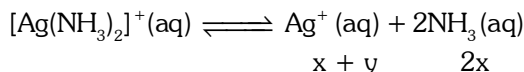
In case of simultaneous solubility, Ag^+ remains same in both the equilibrium

$$K_c = \frac{(x+y) \times (2x)^2}{[Ag(NH_3)_2]^+} \qquad \text{...(1)}$$

$$K_{sp} = (x+y) \times y \qquad \text{...(2)}$$

$$\therefore \quad \frac{K_c}{K_{sp}} = \frac{(2x)^2}{[Ag(NH_3)_2]^+ \times y} \quad \text{Given, } [NH_3] = 2x = 1 \text{ M}$$

$[Ag(NH_3)_2]^+ = [Cl^-] = y$ because Ag^+ obtained from AgCl passes in $[Ag(NH_3)_2]^+$ state.

$$\frac{K_c}{K_{sp}} = \frac{1}{y \times y} \Rightarrow y^2 = \frac{2.378 \times 10^{-10}}{8.2 \times 10^{-8}} = 0.29 \times 10^{-2} \therefore y = 0.539 \times 10^{-1} = 0.0539 \text{ M}$$

That is, $[Ag(NH_3)_2]^+ = 0.539$ M

Illustration 29*.

How many moles of NH_3 must be added to 1 litre of 0.1 M $AgNO_3$ solution to reduce Ag^+ concentration to 2×10^{-7} M. $K_d[Ag(NH_3)_2]^+ = 7.2 \times 10^{-8}$

Solution.

As $K_f[Ag(NH_3)_2]^+ = \dfrac{1}{7.2 \times 10^{-8}}$ = very-very large

Hence, almost all Ag^+ ions will be converted to $[Ag(NH_3)_2]^+$

$\therefore \quad [Ag(NH_3)_2]^+ \approx 0.1$ M
$\qquad [Ag^+] = 2 \times 10^{-7}$

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+} \Rightarrow 7.2 \times 10^{-8} = \frac{2 \times 10^{-7} \times [NH_3]^2}{0.1}$$

$[NH_3] = 0.189$ M
It is the concentration of free NH_3.
$[NH_3]_{total} = [NH_3]_{free} + [NH_3]_{complexed} = 0.189 + 2 \times 0.1 = 0.389$ M

Illustration 30.

(i) What mass of Pb^{2+} ion is left in solution when 50 mL of 0.2 M $Pb(NO_3)_2$ is added to 50.0 mL of 1.5 M NaCl ? ($K_{sp}PbCl_2 = 1.7 \times 10^{-4}$)

(ii) 0.16 g of N_2H_4 is dissolved in water and the total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water at this dilution. The K_b for N_2H_4 is 9.0×10^{-6} M.

Solution.

(i) Millimoles of Pb^{2+} before precipitation = $50 \times 0.2 = 10$

Millimoles of Cl^- before precipitation = $50 \times 1.5 = 75$

Assuming complete precipitation of $PbCl_2$ followed by establishment of equilibrium.

Millimoles of Cl^- left after precipitation = $75 - 20 = 55$ in 100 mL.
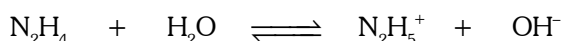
After precipitation $[Cl^-]$ = 0.55 M

That means, we have to find out solubility of $PbCl_2$ in 0.55 M Cl^- ion solution.

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-, \quad K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$[Pb^{2+}] = \frac{K_{sp}}{[Cl^-]^2} = \frac{1.7 \times 10^{-4}}{(0.55)^2} = 5.6 \times 10^{-4} M$$

Mass of Pb^{2+} in solution = $\dfrac{5.6 \times 10^{-4}}{1000} \times 100 \times 208 = 1165$ mg

(ii) $[N_2H_4] = \dfrac{0.16}{32} \times \dfrac{1000}{500} = 0.01$ M

$$
\begin{array}{ccccccc}
N_2H_4 & + & H_2O & \rightleftharpoons & N_2H_5^+ & + & OH^- \\
1 & & & & 0 & & 0 \\
(1-\alpha) & & & & \alpha & & \alpha
\end{array}
$$

$K_b = C\alpha^2,$

$$\alpha^2 = \frac{K_b}{C} = \frac{9.0 \times 10^{-6}}{0.01} = 9 \times 10^{-4}$$

$\Rightarrow \quad \alpha = \sqrt{9.0 \times 10^{-4}} = 3 \times 10^{-2} = 3 \%$

Illustration 31.

If very small amount of phenolphthalein is added to 0.15 M solution of sodium benzoate, what fraction of the indicator will exist in the coloured form ?

$K_{a(Benzoic\ acid)} = 6.2 \times 10^{-5}$

$K_{w(H_2O)} = 1 \times 10^{-14}$

$K_{In(Phenolphthalein)} = 3.16 \times 10^{-10}$

Solution.

Formula for pH of solution due to hydrolysis of C_6H_5COONa

$$pH = \frac{1}{2}[pK_w + pK_a + \log C] = \frac{1}{2}[14 - \log 6.2 \times 10^{-5} + \log 0.15] = 8.6918$$
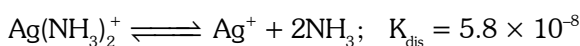
Formula for pH of indicator

$$pH = pK_{In} + \log\frac{[In^-]}{[H_{In}]} \Rightarrow 8.6918 = -\log(3.16 \times 10^{-10}) + \log\frac{[In^-]}{[HIn]}$$

$\therefore \quad \dfrac{[In^-]}{[H_{In}]} = 0.16$ (Fraction of indicator in coloured form = 0.16)

Illustration 32.

What will be the Ag^+ ion concentration in a solution of 0.2 M solution of $[Ag(NH_3)_2]^+$?

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3; \quad K_{dis} = 5.8 \times 10^{-8}$$

Solution.

Let, concentration of Ag^+ at equilibrium be C

$\therefore \quad [NH_3] = 2C$

$$K_{dis} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

$\Rightarrow \quad 5.8 \times 10^{-8} = \dfrac{C \times 4C^2}{0.2}$

$\therefore \quad C = 0.0014$ M.

ANSWERS

BEGINNER'S BOX-1

1.   (A) H_2SO_4 (aq) + NH_3 (aq) $\rightleftharpoons$ NH_4^+ (aq) + HSO_4^- (aq)   (forward)

        (B) HCO_3^- (aq) + SO_4^{2-} (aq) $\rightleftharpoons$ HSO_4^- (aq) + CO_3^{2-} (aq)   (backward)

2.   (a) HSO_4^-, $R\overset{\oplus}{N}H_3$, NH_3, $C_2H_5\overset{\overset{\displaystyle\oplus}{|}}{\underset{\underset{\displaystyle H}{|}}{O}}C_2H_5$, HF

        (b) NO_2^-, O^{2-}, HCO_3^-, ClO_4^-

        (c) H_2S & S^{2-}, NH_4^+ & NH_2^-, $C_2H_5\overset{\oplus}{O}H_2$ & $C_2H_5O^-$, H_3O^+ & OH^-

BEGINNER'S BOX-2

1.   (A)   **2.**   (C)   **3.**   (D)   **4.**   (D)   **5.** 6.022×10^7

6.   4.87   **7.**   Acidic – (vi), (vii) ;   Basic – (i), (iv) ;   Amphiprotic – (ii), (iii), (v)

8. $[H^+] = 8 \times 10^{-3}\,M$, $[HCOO^-] = 3 \times 10^{-3}\,M$, $[OCN^-] = 5 \times 10^{-3}\,M$

BEGINNER'S BOX-3

1.   (B)   **2.**   (C)   **3.**   (D)   **4.** $[OH^-] = 6.664 \times 10^{-6}$

5. $K_b = 6.25 \times 10^{-10}$ **6.** $\dfrac{6.36 + 10.36}{2} = 8.34$

7.   0.625%, pH = 7

BEGINNER'S BOX-4

1.   (C)   **2.**   (A)   **3.**   (C)   **4.**   (A)   **5.**   (A)   **6.**   (A)   **7.**   (A)   **8.**   9.56

9.   (i) 2.85   (ii) 4.096   (iii) 4.52   (iv) 4.69   (v) 5.301   (vi) 8.699

BEGINNER'S BOX-5

1.   (A)   **2.**   (D)   **3.**   (A)   **4.**   (D)   **5.** 1.7×10^2, $1.308 \times 10^{-5}\,M$ **6.**   (C)

7.   (C)   **8.** 1.6×10^{-8}

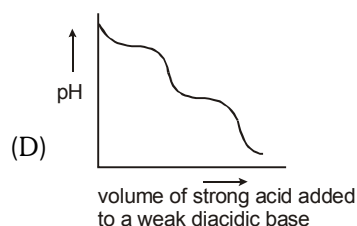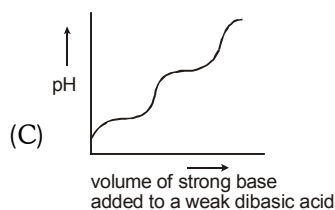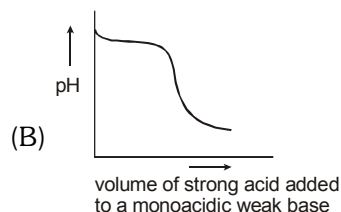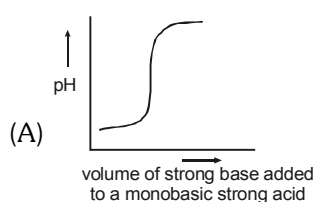**EXERCISE – 1** | **MCQ (SINGLE CHOICE CORRECT)**

1*. Which of the following expressions is not true ?

(A) $[H^+] = [OH^-] = \sqrt{K_W}$ for a neutral solution at all temperatures.

(B) $[H^+] > \sqrt{K_W}$ & $[OH^-] < \sqrt{K_W}$ for an acidic solution

(C) $[H^+] < \sqrt{K_W}$ & $[OH^-] > \sqrt{K_W}$ for an alkaline solution

(D) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures .

2. pOH of H_2O is 7.0 at 298 K . If water is heated at 350 K, which of the following should be true?

(A) pOH will decrease

(B) pOH will increase

(C) pOH will remain 7.0

(D) concentration of H^+ ions will increase but that of OH^- will decrease

3. Which of the following solution will have a pH exactly equal to 8 ?

(A) 10^{-8} M HCl solution at 25°C   (B) 10^{-8} M H^+ solution at 25°C

(C) 2×10^{-6} M $Ba(OH)_2$ solution at 25°C   (D) 10^{-6} M NaOH solution at 50°C

4. An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be:

(A) 9   (B) Between 6 and 7   (C) 7   (D) Unpredictable

5. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :

(A) 1.74×10^{-5} (B) 3.52×10^{-3} (C) 6.75×10^{-4} (D) 5.38×10^{-2}

6. At what molar concentration of HCl will its aqueous solution have an $[H^+]$ to which equal contributions come from HCl and H_2O.

(A) $\sqrt{60} \times 10^{-7}$ M   (B) $\sqrt{50} \times 10^{-8}$ M   (C) $\sqrt{40} \times 10^{-9}$ M   (D) $\sqrt{30} \times 10^{-8}$

7. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be :

(A) 5.0×10^{-5} (B) 5.0×10^{15} (C) 5.0×10^{-15} (D) 0.2×10^5

8. Degree of Hydrolysis of $\dfrac{N}{100}$ solution of KCN is (Given Ka = 1.4×10^{-9})

(A) 2.7×10^{-3} (B) 2.7×10^{-2} (C) 2.7×10^{-4} (D) 2.7×10^{-5}

9. A solution of $FeCl_3$ in water acts as acidic due to :

(A) Acidic impurities   (B) Ionisation   (C) Hydrolysis of Fe^{3+} (D) Dissociation

10*. A solution contains 0.2M NH_4OH and 0.2M NH_4Cl. If 1.0 ml of 0.001 M HCl is added to it. What will be the $[OH^-]$ of the resulting solution $[K_b = 2 \times 10^{-5}]$:

(A) 2×10^{-5} (B) 5×10^{-10} (C) 2×10^{-3} (D) None of these

11. Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl. K_b for $NH_3 = 1.8 \times 10^{-5}$:

(A) 8.1187   (B) 9.8117   (C) 8.8117   (D) None of these

12*. K_a, for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5M KCN solution required to be added to 10ml. of 2M HCN solution is-

(A) 4 ml   (B) 7.95 ml   (C) 2 ml   (D) 9.3 ml

13. Half of the formic acid solution is neutralised on addition of a KOH solution to it. If K_a (HCOOH) $= 2 \times 10^{-4}$ then pH of the solution is : (log $2 = 0.3010$)

(A) 3.6990   (B) 10.3010   (C) 3.85   (D) 4.3010

14*. We have acidic buffer of CH_3COONa and CH_3COOH. One or more of the following operations will not change pH :

I : diluting the mixture ten times

II : adding some HCl

III : adding some NaOH

IV : adding equal moles of CH_3COONa and CH_3COOH into the buffer

Select correct alternate :

(A) I, II, III, IV   (B) II, III   (C) I, IV   (D) II, IV

15. An acid-base indicator has a $K_a = 1.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue.

(A) 1.20   (B) 0.80   (C) 0.20   (D) 1.40

16. Phenolphthalein does not act as an indicator for the titration between :

(A) KOH and H_2SO_4 (B) NaOH and CH_3COOH

(C) Oxalic acid and $KMnO_4$ (D) $Ba(OH)_2$ and HCl

17. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

(A) 10^{-4} M Ca^{3+} + 10^{-4} M F^- (B) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(C) 10^{-5} M Ca^{2+} + 10^{-3} M F^- (D) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

18*. 50 litre of a solution containing 10^{-5} mole of Ag^+ is mixed with 50 litre of a 2×10^{-7} M HBr solution. $[Ag^+]$ in resultant solution is : [Given : K_{sp} (AgBr) $= 5 \times 10^{-13}$]

(A) 10^{-5} M   (B) 10^{-6} M   (C) 10^{-7} M   (D) None of these

19*. Let the solubilities of AgCl in H_2O, 0.01 M $CaCl_2$, 0.01 M NaCl & 0.05 M $AgNO_3$ be S_1, S_2, S_3 & S_4 respectively what is the correct relationship between these quantities . Neglect any complexation.

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 > S_2 = S_3 > S_4$ (C) $S_1 > S_3 > S_2 > S_4$ (D) $S_4 > S_2 > S_3 > S_1$

20. If the solubility of lithium sodium hexafluoride aluminate, $Li_3Na_3(AlF_6)_2$ is 'S' mol lt^{-1}, its solubility product is equal to

(A) S^8 (B) $12\,S^8$ (C) $18\,S^8$ (D) $2916\,S^8$

21. What is the solubility of $Al(OH)_3$, $K_{sp} = 1 \times 10^{-33}$, in a solution having pH $= 4$.

(A) 10^{-3} M   (B) 10^{-6} M   (C) 10^{-4} M   (D) 10^{-10} M

22. Solubility of AgBr will be minimum in :

(A) Pure water   (B) 0.1 M $CaBr_2$ (C) 0.1 M NaBr   (D) 0.1 M $AgNO_3$

23. Solubility product of $Mg(OH)_2$ is 1×10^{-11}. At what pH, precipitation of $Mg(OH)_2$ will begin from 0.1 M Mg^{2+} solution :

(A) 9   (B) 5   (C) 3   (D) 7

24. A certain acid-base indicator is red in acid solution and blue in basic solution 75% of the indicator is present in the solution in its blue form at pH $= 5$. Calculate the pH at which the indicator shows 90% red form?

(A) 3.56   (B) 5.47   (C) 2.5   (D) 7.4

25*. What % of the carbon in the $H_2CO_3 - HCO_3^-$ buffer should be in the form of HCO_3^- so as to have a neutral solution? ($K_a = 4 \times 10^{-7}$)

(A) 20 %   (B) 40 %   (C) 60 %   (D) 80%

26*. A well is dug in a bed of rock containing fluorspar (CaF_2). If the well contains 20000 L of water, what is the amount of F^- in it ? $K_{sp} = 4 \times 10^{-11}$ ($10^{1/3} = 2.15$)

(A) 4.3 mol   (B) 6.8 mol   (C) 8.6 mol   (D) 13.6 mol

EXERCISE – 2 | MCQ (ONE OR MORE CHOICE CORRECT)

1*. Which one is the correct graph for the corresponding acid base titration?

(A)
volume of strong base added
to a monobasic strong acid

(B)
volume of strong acid added
to a monoacidic weak base

(C)
volume of strong base
added to a weak dibasic acid

(D)
volume of strong acid added
to a weak diacidic base

2. Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions.
(A) pH = 2 HCl & pH = 12 NaOH
(B) pH = 2 HCl & pH = 4 HCl
(C) pH = 2 HCN & pH = 12 NaOH (K_a of HCN = 10^{-10})
(D) pH = 5 CH_3COOH & pH = 9 NH_3(aq), K_a (CH_3COOH) = K_b (NH_3 (aq)

3. 100 ml of 0.5M hydrazoic acid (HN_3, K_a = 3.6 x 10^{-4}) and 400ml of 0.1M cyanic acid (HOCN, K_a = 8 x 10^{-4}) are mixed. which of the following is (are) true for the final solution?
(A) $[H^+]$ = 10^{-2} 　　　　　　　　　　　　　(B) $[N_3^-]$ = 3.6 x 10^{-3}
(C) $[OCN^-]$ = 4.571 x 10^{-3} 　　　　　　　(D) $[H^+]$ = 1.4 x 10^{-2} 　　　(E) none of these

4*. K_a values for HA, HB and HD are 10^{-5}, 10^{-7} and 10^{-9} respectively. Which of the following will be correct for decimolar aqueous solutions of NaA, NaB and NaD at 25^0C?
(A) $(pH)_{NaA}$ < $(pH)_{NaB}$ 　　　　　　　(B) $(pH)_{NaD}$ < $(pH)_{NaB}$
(C) $(pH)_{NaA}$ < $(pH)_{NaD}$ 　　　　　　　(D) $(pH)_{NaB}$ = 7

5*. Titration curves for 0.1M solutions of three weak acids HA_1, HA_2 and HA_3 with ionization constants K_1, K_2 and K_3 respectively are plotted as shown in the figure. Which of the following is/are true?

(A) K_2 = $(K_1 + K_3)/2$

(B) K_1 < K_3

(C) K_1 > K_2

(D) K_2 > K_3
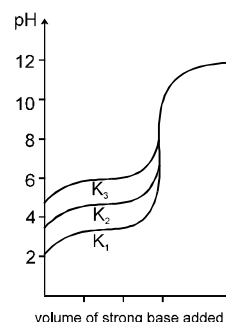
6. A 1 litre solution of pH = 1 diluted upto 10 times. What volume of a solution with pH = 2 is to be added in diluted solution so that pH does not change :
(A) 1 litre 　　　　　　(B) 10 litre 　　　　　　(C) 100 litre 　　　　　　(D) 25 litre

7. The solubility of a sparingly soluble salt A. B_y in water at 25°C 1.4 × 10^{-4} M. The solubility product is 1.1 × 10^{-11}. The possibilities are :
(A) x = 1, y = 2 　　　(B) x = 2, y = 1 　　　(C) x = 1, y = 3 　　　(D) x = 3, y = 1

8*. Which of the following solutions when added to 1L of a 0.1 M CH_3COOH solution will cause no change in either the degree of dissociation of CH_3COOH or the pH of the solution. $K_a = 1.8 \times 10^{-5}$ for CH_3COOH?

(A) 3 mM HCOOH ($K_a = 6 \times 10^{-4}$) (B) 0.1 M CH_3COONa

(C) 1.34 mM HCl (D) 0.1 M CH_3COOH

9*. Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio x : y has pH = (pH),. Buffer solution B of the same acid and its sodium salt in the concentration ratio y : x has pH = $(pH)_2$. If $(pH)_2$— (pH), =1 unit and (pH), + $(pH)_2$ = 9.5 units, then

(A) $pK_a = 4.75$ (B) $\dfrac{x}{y} = 2.36$ (C) $\dfrac{x}{y} = 3.162$ (D) $pK_a = 5.25$

10*. Which of the following aqueous solutions, when added to 100 ml of 0.1 M HCl(aq) will cause no change in its pH ? Assume volumes to be additive.

(A) 100 ml distilled water (B) 100 ml of 0.1 M HNO_3

(C) 50 ml of 0.2 M HCl (D) 100 ml of 0.1 M $AgNO_3$

Match the Column

11. Match the effect of addition of 0.1 M KOH to 0.1 M, 50 ml H_3PO_4 Ka_1, Ka_2 Ka_3 are the I, II, III ionisation constant of H_3PO_4 :

	Column-I		*Column-II*
(A)	75 ml of KOH	(p)	$pH = pKa_1$
(B)	25 ml of KOH	(q)	$pH = pKa_2$
(C)	150 ml of KOH	(r)	$pH = \dfrac{p^Ka_2 + P^Ka_3}{2}$
(D)	100 ml of KOH	(s)	$pH = 7 + \dfrac{1}{2}[p^Ka_3 + \log C]$

12*. If we mix equal volume of two solution. Match the following :

	Column I		*Column II*
(A)	0.2 M KOH + 0.5 M HCOOH	(p)	0.7
(B)	0.1 M NaCl + 0.1 M $NaNO_3$	(q)	between 1 to 7
(C)	0.1 NI NH_4Cl + 0.1 M NaOH	(r)	7
(D)	0.5 M HCl + 0.1 M NH_4OH	(s)	greater than 7

13*. K_1 and K_2 are first and second ionisation constant of H_2CrO_4, K_3 is dissociation constant for NH_3. Match the following:

	Column I		*Column II*
(A)	0.1 M H_2CrO_4	(p)	$pH = 7 + 1/2pK_2 — 1/2pK_3$
(B)	0.1 M $KHCrO_4$	(q)	$pH = 7 + 1/2pK_2 + 1/2\log C$
(C)	0.1 M $(NH_4)_2 CrO_4$	(r)	$pH = 1/2pK_1 — 1/2\log C$
(D)	0.1 M K_2CrO_4	(s)	$pH = 1/2(pK_1 + pK_2)$

Comprehension Based Questions

Comprehension-1

The solubility product of a soluble salt A_xB_y is given by: $K_{sp} = [A^{y+}]^x [B^{x-}]^y$. As soon as the product of concentration of A^{y+} and B^{x-} becomes more than its K_{sp}, the salt begins to precipitate. It may practically be noticed that AgCl is fairly soluble in water and its solubility decreases dramatically in 0.1 M NaCl or 0.1 M $AgNO_3$ solution. It may, therefore, be concluded that in presence of a common ion, the solubility of salt decreases.

14*. K_{sp} of SrF_2 in water is 8×10^{-10}. The solubility of SrF_2 in 0.1 M NaF aqueous solution is

(A) 8×10^{-10} (B) 2×10^{-3} (C) 2.7×10^{-10} (D) 8×10^{-8}

15*. Equal volume of the following two solutions are mixed. The one in which $CaSO_4$ ($K_{sp} = 2.4 \times 10^{-5}$) is precipitated is

(A) 0.02 M $CaCl_2$ + 0.0004 M Na_2SO_4 (B) 0.01 M $CaCl_2$ + 0.0004 M Na_2SO_4

(C) 0.02 M $CaCl_2$ + 0.0002 M Na_2SO_4 (D) 0.03 M $CaCl_2$ + 0.004 M Na_2SO_4

16*. The pH of a saturated solution of $Mg(OH)_2$ is (K_{sp} $Mg(OH)_2 = 1 \times 10^{-11}$).

Given : $\sqrt{2.5} = 1.35$ & $\log 2.7 = 0.431$

(A) 9 (B) 3.87 (C) 10.43 (D) 5

Comprehension-2

Buffer solution resists the change in PH value upon addition of small amount of acid or base. pH of Buffer solution is related with Henderson equation for acid Buffer as

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

For base buffer

$$pOH = PK_b + \log\frac{[Salt]}{[Base]}$$

The ionic product or auto protolysis constant of H_2O is $K_W = 10^{-14}$ at 25° its value increases with temperature.

17. Which among the following mixture acts as buffer?

(A) $HCl + CH_3COOH$ (B) $NaH_2PO_4 + Na_2HPO_4$

(C) $NaOH + NH_4OH$ (D) $HCN + NaCl$

18. How many moles of $(NH_4)_2SO_4$ must be added to 500 mL of 0.2 M NH_3 to yield a solution of pH = 8.3 (Given PK_b of $NH_3 = 4.7$)

(A) 5×10^{-3} (B) 0.5 (C) 6.6 (D) 1.32

19. The autoprotolysis constant (K_W) of H_2O at 90° is $10^{-12}M^2$. What is the pH of water at this temperature ?

(A) 7 (B) 8 (C) 6 (D) 12

Comprehension-3

Acid Buffer is mixture of weak acid and its salt with strong base and its buffer capacity has maximum range of PKa ±1. Similarly for Base Buffer capacity has maximum range of PKb ±1.

20*. 3 mole of NH_4OH and 1 mole of $(NH_4)_3PO_4$ is mixed in 10 litre solution. If PKb for $NH_4OH = 4.76$. Then pH of Buffer mixture is –

(A) 9.24 (B) 4.76 (C) 10.26 (D) 7.24

21*. The incorrect statement is

(A) An acid buffer mixture may have pH less or more than 7

(B) 5 mole of NH_4CN and 5 mole of HCN mixture acts as acid buffer and pH = PKa of HCN.

(C) 10 mole of NH_4OH and 2.5 mole of H_2SO_4 acts a basic buffer mixture and pH = pKa of NH_4^+

(D) A basic buffer always has pH greater than 7

22*. If 1 mole of HCl is added to 3 mole of NH_4OH. Then pH of mixture is (PKa of $NH_4^+ = 9.24$)

(A) 9.24 (B) 9.54 (C) 4.26 (D) 4.56

EXERCISE – 3   **SUBJECTIVE**

1.   **(i)** K_w for H_2O is 9.62×10^{-14} at 60°C. What is pH of water at 60°C.
       (ii)   What is the nature of solution at 60°C whose
               (a) pH = 6.7   (b) pH = 6.35

2*.   Calculate pH of following solutions :
      (a) 0.1 M HCl   (b) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
      (c) 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)   (d) 10^{-8} M HCl
      (e) 10^{-10} M NaOH   (f) 10^{-6} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
      (g) 10^{-8} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
      (h) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times.
      (i) 10^{-3} mole of KOH dissolved in 100 L of water.
      (j) Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution

3.   Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted 100 times.
     [Given $K_a = 10^{-5}$ M]

4.   Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective

     solution of acids.[Given $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$; $K_{a(HCN)} = 6.2 \times 10^{-10}$]

5.   Calculate [H^+] and [$CHCl_2COO^-$] in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$.
     Take ($K_a = 2.55 \times 10^{-2}$).

6.   Calculate [H^+], [CH_3COO^-] and [$C_7H_5O_2^-$] in a solution that is 0.02 M in acetic acid and 0.01M in benzoic
     acid. K_a(acetic) = 1.8×10^{-5} , K_a (benzoic) = 6.4×10^{-5}.
     [H^+] = 10^{-3}M   [$CH_3 COO^-$] = 3.6×10^{-4} [$C_7H_5 O_2^-$] = 6.4×10^{-4}M

7.   Calculate the pH of a 0.15 M aquesous solution of $AlCl_3$. Given : log 2 = 0.3, log 3 = 0.48
     [$Al(H_2O)_6$]$^{3+}$ + H_2O (ℓ) $\rightleftharpoons$ [$Al(H_2O)_5 OH$]$^{2+}$ (aq) + H_3O^+ (aq), $K_a = 1.5 \times 10^{-5}$

8.   Calculate the extent of hydrolysis & the pH of 0.02 M CH_3COONH_4.
     [K_b (NH_3) = 1.8×10^{-5}, K_a(CH_3COOH) = 1.8×10^{-5}]

9*.   Calculate the pH of 1.0×10^{-3} M sodium phenolate, $NaOC_6H_5$. K_a for HOC_6H_5 is 1.05×10^{-10}.

10.   Calculate the percent hydrolysis in a 0.06 M solution of KCN. [K_a(HCN) = 6×10^{-10}]

11.   The artificial sweetener saccharin is a weak organic acid that can be represented by HSac. On adding in a drink,
     it ionizes to give H^+ ions & Sac^- ions. Calculate [Sac^-] ions if 0.002 mole of saccharin is added in a 250 mL
     glass of black tea containing lemon juice having an initial pH of 2.0. K_a (HSac) = 2 x 10^{-12}

12.   Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a
     solution of 0.1 M NaOH. K_a for the acid = 1.9×10^{-5}.

13*. The equivalent point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of
     a 0.10M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH
     solution. What is the dissociation constant of the acid?

14.   The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more
     soluble? Explain your answer fully.

15*. A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the
     solution is [$K_{sp} = 1.2 \times 10^{-11}$]
     (a) 10^{-5} mol/L   (b) 10^{-3} mol/L ?

16.   Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

17.   Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1×10^{-12}, K_{sp}(AgBr) = 5×10^{-13}.

18*. Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2. K_{sp}(MgF_2) = 9.5×10^{-9},
     K_{sp}(SrF_2) = 4×10^{-9}.

EXERCISE – 4 | RECAP OF AIEEE/JEE (MAIN)

1. The solubility of $Mg(OH)_2$ is x mole/lit. then its solubility product is- **[AIEEE-2002]**

(A) x^3 (B) $5x^3$ (C) $4x^3$ (D) $2x^2$

2. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be **[AIEEE-2003]**

(A) 1×10^{-15} (B) 1×10^{-10} (C) 4×10^{-15} (D) 4×10^{-10}

3*. The molar solubility in mol L^{-1} of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP}. 's' is given in terms of K_{SP} by relation : **[AIEEE-2004]**

(A) $s = (K_{SP} / 128)^{1/4}$ (B) $s = (128K_{SP})^{1/4}$ (C) $s = (256K_{SP})^{1/5}$ (D) $s = (K_{SP}/256)^{1/5}$

4. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be - **[AIEEE-2005]**

(A) 3.88×10^6 (B) 3.98×10^8 (C) 3.98×10^{-6} (D) 3.68×10^{-6}

5. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is - **[AIEEE-2005]**

(A) 1.0×10^{-4} M   (B) 2.0×10^{-6} M   (C) 4.0×10^{-10} M   (D) 1.6×10^{-4} M

6*. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is - **[AIEEE-2007]**

$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution ?

(A) 28.3×10^{-2} g   (B) 2.83×10^{-3} g   (C) 1.0×10^{-7} g   (D) 1.0×10^{-4} g

7. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt. BA, will be - **[AIEEE-2008]**

(A) 9.58   (B) 4.79   (C) 7.01   (D) 9.22

8*. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{SP} for $Ba\,CO_3 = 5.1 \times 10^{-9}$) **[AIEEE-2009]**

(A) 8.1×10^{-8} M   (B) 8.1×10^{-7} M   (C) 4.1×10^{-5} M   (D) 5.1×10^{-5} M

9*. At 25° C, the solubility producct of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE–2010]**

(A) 8   (B) 9   (C) 10   (D) 11

10*. In aqueous solution the ionization constants for carbonic acid are

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid :- **[AIEEE–2010]**

(A) The concentration of H^+ is double that of CO_3^{2-}

(B) The concentration of CO_3^{2-} is 0.034 M

(C) The concentration of CO_3^{2-} is greater than that of HCO_3^-

(D) The concentrations of H^+ and HCO_3^- are approximately equal

11*. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :-

[AIEEE–2010]

(A) 5.0×10^{-8} g (B) 1.2×10^{-10} g (C) 1.2×10^{-9} g (D) 6.2×10^{-5} g

12. An acid HA ionises as

$HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be :- **[AIEEE–2011]**

(A) 1×10^{-10} (B) 5 (C) 5×10^{-8} (D) 1×10^{-5}

13. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is :- **[AIEEE–2011]**

(A) $\sqrt[2]{1.6 \times 10^{-30}}$ (B) $\sqrt[4]{1.6 \times 10^{-30}}$ (C) $\sqrt[4]{1.6 \times 10^{-30} / 27}$ (D) $1.6 \times 10^{-30}/27$

14. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, Ka of this acid is

[AIEEE–2012]

(A) 1×10^{-7} (B) 3×10^{-7} (C) 1×10^{-3} (D) 1×10^{-5}

15*. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[AIEEE–2013]**

(A) 0.1 L (B) 0.9 L (C) 2.0 L (D) 9.0 L

16. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+}, precipitate of $BaCO_3$ begins to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **[JEE-MAIN–2013]**

(A) 5.1×10^{-5} M (B) 8.1×10^{-7}M (C) 4.1×10^{-5} M (D) 7.1×10^{-8}M

17. NaOH is a strong base. What will be pH of 5.0×10^{-2}M NaOH solution ? (log2 = 0.3) **[JEE-MAIN–2013]**

(A) 13.70 (B) 13.00 (C) 14.00 (D) 12.70

18. Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts Hg_2Cl_2, $Cr_2(SO_4)_3$, $BaSO_4$ and $CrCl_3$ respectively ? **[JEE-MAIN–2013]**

(A) $\left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}, \left(\dfrac{K_{sp}}{108}\right)^{\frac{1}{3}}, \left(K_{sp}\right)^{\frac{1}{2}}, \left(\dfrac{K_{sp}}{27}\right)^{\frac{1}{4}}$ (B) $\left(K_{sp}\right)^{\frac{1}{2}}, \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}, \left(\dfrac{K_{sp}}{27}\right)^{\frac{1}{4}}, \left(\dfrac{K_{sp}}{108}\right)^{\frac{1}{3}}$

(C) $\left(K_{sp}\right)^{\frac{1}{2}}, \left(\dfrac{K_{sp}}{108}\right)^{\frac{1}{3}}, \left(\dfrac{K_{sp}}{27}\right)^{\frac{1}{4}}, \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}$ (D) $\left(\dfrac{K_{sp}}{108}\right)^{\frac{1}{3}}, \left(\dfrac{K_{sp}}{27}\right)^{\frac{1}{4}}, \left(K_{sp}\right)^{\frac{1}{2}}, \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}$

19. What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL? *(Ka = 1.75 × 10⁻⁵, pKa = 4.76)* **[JEE-MAIN–2013]**

(A) 4.76 < pH < 5.0 (B) pH < 4.70

(C) pH of solution will be equal to pH of acetic acid (D) pH = 4.70

20. In some solutions, the concentration of H_3O^+ remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as :- **[JEE-MAIN–2014]**

(A) Colloidal solutions (B) True solutions (C) Ideal solutions (D) Buffer solutions

21. Zirconium phosphate $[Zr_3(PO_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ? **[JEE-MAIN–2014]**

(A) $S = \{K_{sp}/144\}^{1/7}$ (B) $S = \{K_{sp}/(6912)^{1/7}\}$ (C) $S = (K_{sp}/6912)^{1/7}$ (D) $S = \{K_{sp}/6912\}^7$

22. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is **[JEE-MAIN–2017]**

(A) 7.2   (B) 6.9   (C) 7.0   (D) 1.0

23. Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is 10^{-5}, the ratio of salt to acid concentration in the buffer solution will be : **[JEE-MAIN–2017]**

(A) 4 : 5   (B) 1 : 10   (C) 10 : 1   (D) 5 : 4

24. 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be :- **[JEE-MAIN–2017]**

(A) 8.25   (B) 4.75   (C) 9.25   (D) 3.75

25. Which of the following salts is the most basic in aqueous solution ? **[JEE-MAIN–2018]**

(A) CH_3COOK (B) $FeCl_3$ (C) $Pb(CH_3COO)_2$ (D) $Al(CN)_3$

26. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? **[JEE-MAIN–2018]**

Base	Acid	End point
(1) Strong	Strong	Pinkish red to yellow
(B) Weak	Strong	Yellow to pinkish red
(C) Strong	Strong	Pink to colourless
(D) Weak	Strong	Colourless to pink

27. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : **[JEE-MAIN–2018]**

(A) 3×10^{-20} (B) 6×10^{-21} (C) 5×10^{-19} (D) 5×10^{-8}

28. A aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+} ? **[JEE-MAIN–2018]**

(A) 2×10^{-9} M   (B) 1.1×10^{-9} M   (C) 1.0×10^{-10} M   (D) 5×10^{-9} M

29. Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? **[JEE-MAIN–2018]**

(A) $75mL \dfrac{M}{5} HCl + 25mL \dfrac{M}{5} NaOH$ (B) $100mL \dfrac{M}{10} HCl + 100mL \dfrac{M}{10} NaOH$

(C) $55mL \dfrac{M}{10} HCl + 45mL \dfrac{M}{10} NaOH$ (D) $60mL \dfrac{M}{10} HCl + 40mL \dfrac{M}{10} NaOH$

30. The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$; atomic mass of Pb = 207 u) is : **[JEE-MAIN–2018]**

(A) 0.36 L   (B) 0.18 L   (C) 17.98 L   (D) 1.798 L

31. 20 mL of 0.1 MH_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is : [pk_b of NH_4OH = 4.7]. **[JEE-MAIN-2019]**

(A) 9.4   (B) 5.0   (C) 9.0   (D) 5.2

32. A mixture of 100 m mol of $Ca(OH)_2$ and 2g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively, are : (Molar mass of $Ca(OH)_2$, Na_2SO_4 and $CaSO_4$ are 74, 143 and 136 g mol^{-1}, respectively; K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6}) **[JEE-MAIN-2019]**

(A) 1.9 g, 0.14 mol L^{-1} (B) 13.6 g, 0.14 mol L^{-1} (C) 1.9 g, 0.28 mol L^{-1} (D) 13.6 g, 0.28 mol L^{-1}

33. If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1M $AgNO_3$ is : **[JEE-MAIN-2019]**

(A) 8×10^{-12} M   (B) 8×10^{-10} M   (C) 8×10^{-11} M   (D) 8×10^{-13}

34. If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct **[JEE-MAIN-2019]**

(A) $S = \left(\dfrac{K_{sp}}{929} \right)^{1/9}$ (B) $S = \left(\dfrac{K_{sp}}{216} \right)^{1/7}$ (C) $S = \left(\dfrac{K_{sp}}{144} \right)^{1/6}$ (D) $S = \left(\dfrac{K_{sp}}{6912} \right)^{1/7}$

35. In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titraction mixture in this experiment? **[JEE-MAIN-2019]**
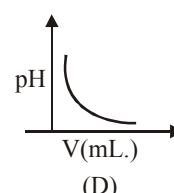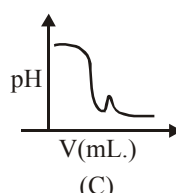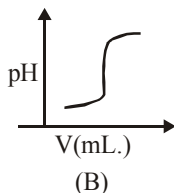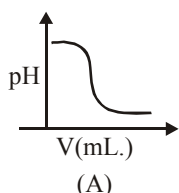
(A) (A)   (B) (C)   (C) (D)   (D) (B)

36. Consider the following statements **[JEE-MAIN-2019]**

(a) The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

(b) Ionic product of water is temperature dependent.

(c) A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.

(d) The Le Chatelier's principle is not applicable to common-ion effect.

the correct statement are :

(A) (a), (b) and (d)   (B) (a), (b) and (c)   (C) (a) and (b)   (D) (b) and (c)

37. The pH of a 0.02M NH_4Cl solution will be [given $K_b(NH_4OH) = 10^{-5}$ and log2 = 0.301] **[JEE-MAIN-2019]**

(A) 4.65   (B) 5.35   (C) 4.35   (D) 2.65

38. What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution ? Given that, solubility product of $Al(OH)_3 = 2.4 \times 10^{-24}$: **[JEE-MAIN-2019]**

(B) 12×10^{-23} (B) 12×10^{-21} (C) 3×10^{-19} (D) 3×10^{-22}

39. The molar solubility of $Cd(OH)_2$ is 1.84×10^{-5} M in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is : **[JEE-MAIN-2019]**

(A) 6.23×10^{-11} M   (B) 1.84×10^{-9} M   (C) $\dfrac{2.49}{1.84} \times 10^{-9}$ M   (D) 2.49×10^{-10} M

| EXERCISE – 5 | RECAP OF IIT-JEE/JEE (ADVANCED) |

1. The species present in solution when CO_2 is dissolved in water :

(A) CO_2, H_2CO_3, HCO_3^-, CO_3^{2-} (B) H_2CO_3, CO_3^{2-} **[JEE 2006]**

(C) CO_3^{2-}, HCO_3^- (D) CO_2, H_2CO_3

2. Solubility product constants (K_{SP}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order:

(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ **[JEE 2008]**

(C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

3*. 2.5 mL of $\dfrac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\dfrac{2}{15}$ M HCl in water at 25°C.

The concentration of H^+ at equivalence point is   **[JEE 2008]**

($K_w = 1 \times 10^{-14}$ at 25°C)

(A) 3.7×10^{-13} M   (B) 3.2×10^{-7} M   (C) 3.2×10^{-2} M   (D) 2.7×10^{-2} M

4. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is   **[JEE 2009]**

5*. In 1 L saturated solution of AgCl [K_{sp}(AgCl) $= 1.6 \times 10^{-10}$], 0.1 mol of CuCl

[K_{sp}(CuCl) $= 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of 'x' is.   **[JEE 2011]**

6. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is   **[JEE 2013]**

(A) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 1.1×10^{-12} (D) 1.1×10^{-9}

7*. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is   **[JEE 2013]**

(A) 1×10^{-4} (B) 1×10^{-5} (C) 1×10^{-6} (D) 1×10^{-3}

Comprehension (Q.8 to Q.9)

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt.2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt.1) where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions are 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

8. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is   **[JEE 2015]**

(A) 1.0   (B) 10.0   (C) 24.5   (D) 51.4

9. The pH of the solution after Expt. 2 is   **[JEE 2015]**

(A) 2.8   (B) 4.7   (C) 5.0   (D) 7.0

10. The solubility of a salt of weak acid(AB) at pH 3 is $Y \times 10^{-3}$ mol L^{-1}. The value of Y is___.

(Given that the value of solubility product of AB (K_{sp}) $= 2 \times 10^{-10}$ and the value of ionization constant of HB(K_a) $= 1 \times 10^{-8}$)   **[JEE 2018]**

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	A	B	B	C	B	C	B	C	A	C	C	A	C	A
Que.	16	17	18	19	20	21	22	23	24	25	26				
Ans.	C	B	C	C	D	A	B	A	A	D	C				

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	ABCD	AD	AB	AC	CD	ABCD	AB	CD	AC	B

- **Match the Column**
  11. (A – q), (B – p), (C – s), (D – r)   **12*.** (A – q), (B – r), (C – s), (D – p)
  13*. (A – r), (B – s), (C – p), (D – q)

- **Comprehension Based Questions**

Comprehension 1 :	**14.** (D)	**15.** (D)	**16.** (C)
Comprehension 2 :	**17.** (B)	**18.** (B)	**19.** (C)
Comprehension 3 :	**20.** (A)	**21.** (D)	**22.** (B)

EXERCISE-3

1. **(i) 6.51 (ii) (a) Basic (b) Acidic**

(i) $[H^+] = \sqrt{K_w}$

(ii) pH scale is from 0 to pK_w.

2*. **(a) 1   (b) 2.87   (c) 11.13   (d) 6.97   (e) 6.996   (f) 6.01   (g) 6.97**
(h) 11.30   (i) 9   (j) 3
Use formula $pH = -\log[H^+]$
In case of weak monoprotic acid

$$[H^+] = C\alpha \text{ where } K_a = \frac{C\alpha^2}{1-\alpha}$$

3. **Ans. 10**

$$\alpha = \sqrt{\frac{K_a}{C}} \text{ if } \alpha << 1$$

$$\therefore \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{C_2}{C_1}}$$

4. **Ans. 170.4**

α for weak acid of type HA = $\sqrt{\dfrac{K_a}{C}}$

5. **$[H^+] = 1.612 \times 10^{-2}$ M $[CH Cl_2 COO^-] = 6.126 \times 10^{-3}$M**

$[H^+] = 0.01 + x$ and $K_a = \dfrac{(0.01+x) \times x}{(0.01-x)}$

where

$$CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$$
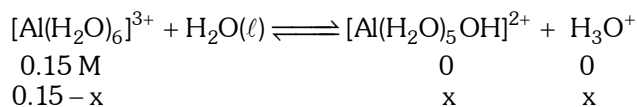$$0.01 - x \qquad\qquad x \qquad\qquad 0.01 + x$$
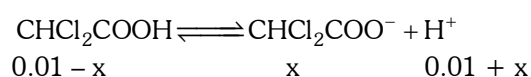
6. $[H^+] = 10^{-3}M$ $[CH_3 COO^-] = 3.6 \times 10^{-4}$ $[C_7H_5 O_2^-] = 6.4 \times 10^{-4}M$

For mixture of two weak acids HA and HB

$$[H^+] = \sqrt{Ka_1 C_1 + Ka_2 C_2}$$

7. **pH = 2.82**

$[Al(H_2O)_6]^{3+} + H_2O(\ell) \rightleftharpoons [Al(H_2O)_5 OH]^{2+} + H_3O^+$

0.15 M	0	0
0.15 – x	x	x

$\therefore \quad Ka = 1.5 \times 10^{-5} = \dfrac{x \times x}{0.15 - x}$

8. **0.56 % and pH = 7**

For salt of WA and WB

$h = \sqrt{K_h}$ where $K_h = \dfrac{Kw}{K_a K_b}$

9*. **10.43**

For C_6H_8ONa, anionic hydrolysis occur

$pH = 7 + \dfrac{1}{2} pKa + \dfrac{1}{2} \log C$

10. **1.667%**

For anionic hydrolysis

$h = \sqrt{\dfrac{K_h}{C}}$ where $K_h = \dfrac{K_w}{K_a}$

11. **[Sac⁻] = 1.6 × 10⁻¹² M**

For H Sac

$K_a = \dfrac{[H^+][Sac^-]}{[HSac]}$

$\therefore$
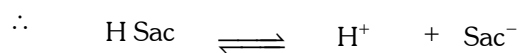
	H Sac	$\rightleftharpoons$	H⁺	+	Sac⁻
t = 0	0.008M		0.01M		0
teq	0.008 – x		0.01 + x		x

12. **5.12 × 10⁻⁶ M**

At equivalence point in titration of CH_3COOH and NaOH, only CH_3COONa exist

$\therefore \quad [OH^-] = Ch$ where $h = \sqrt{\dfrac{K_h}{C}}$ and $K_h = \dfrac{K_w}{K_a}$

13*. **2.37 × 10⁻⁶**

At equivalence point
$40 \times [Acid] = 35 \times 0.1$

After addition of 20 ml NaOH, it will from acid buffer having $pH = pKa + \log \dfrac{[salt]}{[Acid]}$

14. **QX₂ is more soluble**

For MX $K_{sp} = S^2$

For QX_2 $K_{sp} = 4S^3$

15*. *(a) No ppt.   (b) ppt.*

Precipitation will occurs when $Q > K_{sp}$

16. 1.6×10^{-3}
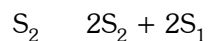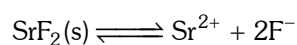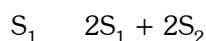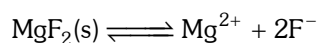
For PbI_2 $Ksp = 4S^3$

17. $4 \times 10^{-7} M\ AgBr$

Let solubility of Ag SCN and Ag Br and S_1 and S_2 respectively

Then $1.1 \times 10^{-12} = S_1(S_1 + S_2)$

$5 \times 10^{-13} = S_2 (S_1 + S_2)$

18*. $[F^-] = 3 \times 10^{-3} M$

$$MgF_2(s) \rightleftharpoons Mg^{2+} + 2F^-$$

$$S_1 \qquad 2S_1 + 2S_2$$

$$SrF_2(s) \rightleftharpoons Sr^{2+} + 2F^-$$

$$S_2 \qquad 2S_2 + 2S_1$$

$\therefore$ $9.5 \times 10^{-9} = S_1(2S_1 + 2S_2)^2$

$4 \times 10^{-9} = S_2(2S_1 + 2S_2)^2$

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	C	D	C	A	B	C	D	D	D	C	A	C	D	D
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	A	D	A	A	D	C	B	C	C	A	B	A	B	A	B
Que.	31	32	33	34	35	36	37	38	39						
Ans.	C	C	B	D	A	B	B	D	D						

EXERCISE-5

1.	(A)	**2.**	(D)	**3*.**	(C)	**4.**	(8)	**5*.**	(7)
6.	(B)	**7*.**	(A)	**8.**	(A)	**9.**	(B)	**10.**	(4.47)

THERMODYNAMICS

Recap of Early Classes

In the previous chapter gaseous state, we studied about the behaviour of ideal and real gases, which will be a very important feed for this chapter. In this chapter, we would like to answer some of the important questions through thermodynamics, like: How do we determine the energy changes involved in a chemical reaction process? Will it occur or not? What drives a chemical reaction/process? To what extent do the chemical reactionsproceed?

Index

THERMODYNAMICS

1.0 WHAT IS THERMODYNAMICS ?

[SL] [AL]

Thermodynamics is the branch of science that describes the behaviour of matter and the transformation between different forms of energy on a macroscopic scale. Thermodynamics describes a system in terms of its bulk properties. Only a few such variable are needed to describe the system, and the variables are generally directly accessible through measurements. A thermodynamic description of matter does not make reference to its structure and behaviour at the microscopic level.

2.0 THE LAWS OF THERMODYNAMICS

[SL] [AL]

The law's of thermodynamics is the law of observation. No one has ever observed that any thing goes in contrary to thermodynamics law. So we elevate this observation to the status of thermodynamic law. The real justification of this comes when things we derive using this law turn's out to be true that is verified by experiments.

3.0 APPLICATION OF THERMODYNAMICS

[SL] [AL]

(i) It provides relationship between heat, work and measurable properties of matter.

(ii) It predicts direction of natural change - like what circumstances are best for rusting of iron.

(iii) It predicts up to what extent a chemical reaction can proceed in forward direction.

  Example : How much ammonia (NH_3) can be formed from N_2 and H_2 in a closed container.

(iv) It help in understanding why different phases of matter exist - and provide simple relationship between various measurable properties of system (thermodynamical variables) :

4.0 BASIC DEFINITIONS

[SL] [AL]

(i) ***System :*** Part of universe under investigation is called system.

(ii) ***Surrounding :*** Anything out side the system is called surrounding.

(iii) ***Types of system :***

  (a) ***Closed system :*** A system which can exchange only energy with surrounding.

  (b) ***Open system :*** A system which can exchange both energy and matter with surrounding.

  (c) ***Isolated system :*** A system which cannot exchange matter or energy with surrounding.

(iv) ***Homogeneous system :*** System consist of single phase. eg. pure solid, a pure liquid, a solution, or a mixture of gases.

(v) ***Heterogenous system :*** A system consisting of many ***phases***. eg. system of two immiscible liquids, two or more solids, a liquid in contact with its vapour etc. are example of heterogenous system.

(vi) ***Boundary :*** The interface between system and surrounding is called boundary. Across the boundary, energy and mass are transferred between system and surroundings. Boundary can be real or hypothetical.

(vii) ***Wall :*** A real boundary is called wall.

  Types of walls:

  (a) Rigid wall : The wall is immovable $\Rightarrow w_{PV} = 0$.

  (b) Non Rigid wall : The wall is movable $\Rightarrow w_{PV} \neq 0$.

  (c) Adiabatic wall : The heat exchange across the wall is q = 0.

  (d) Diathermic wall : The heat can be exchanged across the wall $\Rightarrow q \neq 0$.

(viii) ***Phase :*** By the term phase we mean a homogeneous and physically distinct part of a system which is bounded by a surface and can be separated out physically from the other parts of the system.

(ix) ***The state of a system*** : We specify the state of a system - say, a sample of material - by specifying the values of all the variables describing the system. If the system is a sample of a pure substance this would mean specifying the values of the temperature, T, the pressure, p, the volume, V, and the number of moles of the substance, n.

(x) **State variables :** To define a thermodynamics states of a system, we have to specify the values of certain mesurable quantities. These are called thermodynamic variable or state variable.

A system can be completely defined by four variables namely pressure, temperature, volume and composition. A system is said to be in a certain definite state when all of its properties have definite values. ***Between two fixed states the change in the value of state function is same irrespective of the path connecting the two states.***

(xi) **Path function or path dependent quantities :** The value of path function depends upon path connecting two states . There can be infinite vaules of path function between two states depending upon path or process.

Path functions are also called **indefinite quantities** since between two fixed state the value of path function is not fixed. **Heat** and **Work** are two important path dependent quantities with which we deal in this chapter.

(xii) **Extensive and Intensive variables :** Propterties which depend on the amount of the substance (or substances) present in the system are called extensive propterties. e.g. Mass, volume, heat capacity, internal energy, entropy, Gibb's free energy (G), surface area etc. These properties will change with change in the amount of matter present in the system. It is important to note that the total value of an extensive property of a system is equal to the sum of the values of different parts into which the system is divided.

Intensive properties : Properties which are independent of the amount of substance (or substances) present in the system are called intensive properties, e.g. pressure, density, temperature, viscosity, surface tension, refractive index, emf, chemical potential, sp. heat etc, These are intensive properties.

An extensive property can be converted into intensive property by defining it per unit of another extensive property.

Ex. Concentration = mole / volume

Density = mass / volume

heat capacity = heat absorbed / rise in temperature

While mole, mass, heat are extensive properties, concentration, density and heat capacity are intensive properties.

(xiii) **Thermodynamic equilibria** : Thermodynamic generally deals the equilibrium state of the system in which the state variable are uniform and constant throughout the whole system. The term thermodynamic equilibrium implies the existence of three different types of equilibria in the system. These are :

(*a*) **Mechanical equilibrium** : When there is no macroscopic movement within the system itself or of the system with respect to surroundings, the system is said to be in a state of mechanical equilibrium.

(*b*) **Chemical equilibrium :** When the system consists of more than one substance and the composition of the system does not vary with time, the system is said to be in chemical equilibrium. The chemical composition of a system at equilibrium must be uniform and there should be no **net** chemical reaction taking place.

(*c*) **Thermal equilibrium :** When the temperature throughout the entire system is the same as that of the surroundings then the system is said to be in thermal equilibrium.

(xiv) **Equation of state** : An equation that relates the variables T, p, V, and n to each other is called the "equation of state." The most general form for an equation of state is.

$$f (p, V, T, n) = 0.$$

(*a*) **The ideal gas equation of state** : The best known equation of state for a gas is the "ideal gas equation of state". It is usually written in the form,

$$pV = nRT$$

This equation contains a constant, R, called the gas constant.

(*b*) **The vander Walls equation of state for real gases** : The vander Walls equation of state is,

$$(p + a\frac{n^2}{V^2})(V - nb) = nRT$$

Notice that the vander Walls equation of state differs from the ideal gas by the addition of two adjustable parameters, a, and b (among other things).

Note : *Equation of state for liquid and solids are also defined empirically.*

5.0 SOME THERMODYNAMIC PROCESSES

(i) **Isothermal process :** A process in which temperature of the system remains constant is called isothermal process.

(ii) **Isobaric process :** A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.
Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at contant pressure (1 atm.)

(iii) **Adiabatic process :** A process in which no heat exchange takes place is called adiabatic process. Adiatatic process occurs in isolated systems.

(iv) **Isochoric process :** The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed vessel.

(v) **Cyclic process :** If a system after completing a series of different process returns to its initial state then overall process is called cyclic process.
In cyclic process all the state variables remains constant because initial state becomes final state in cyclic process.
Ex. $\Delta H = 0$, $\Delta E = 0$, $\Delta P.E. = 0$

(vi) **Polytropic processes :** It is defined as a process in which $PV^n = $ constant $= k$
All of the above mentioned processes can be performed in two ways , **reversibly and irreversibly**

(vii) **Reversible process :** When the difference between driving force and opposing force is very small and the process is carried out infinitesimally slowly, then the process is called reversible process. The reversible process is carried out in such a manner that at any moment of the change the directon of process can be reversed by making a small change in driving force.A reversible process is also called quasi static process. During a reversilbe process, the system and surrounding remain in equilibrium throught the process.
The reversible proceses are idealized processes which cannot be actually carried out, but neverthless they are very important because they help in calculation of change in state function in the process.In other words the reversible processes are **hypothetical processes.**

(viii) **Irreversible process :** Any process which does not take place in the above manner and difference between driving force and the opposing force is quite large is called irreversible process.All natural processes are example of irreversible process.

6.0 HEAT AND WORK

Heat and work both are modes of energy transfer between system and surroundings.

Heat flows due to **temperature gradient** while work is done due to imbalance of **generalized force.**

Due to imbalance of generalized force(intersive property) generalized displacement (extensive property) is produced. The product of generalized force and generalized displacement is work.

Work done on the system can be reversible and irrervisible depending on magnitude of imbalance of generalized force. Heat is also transfered between system and surrounding in two ways – reversible and irreversible. Reverssible heating means heating an object from T_i to T_f using infinite heat reservoirs. Irreverssible heat transfer means heat transfer across temp difference ΔT. Heating an object from 100 K to 1000 K by using heat reservoir of temperature 1000 K is an example of irreverssible heating. While heating an object from 100 to 1000 K using reservoir of temp 100 + dT, 100 + 2dT, ... 1000 – dT, 1000 K is an example of reversible heating. You can clearly see reversible heating is hypothetical concept.

(i) **Work :**
PV-work : Consider a clylinder fitted with a frictionless piston, which enclosed n mole of an ideal gas. Let an external force F pushes the piston inside producing displacement in piston.Let distance of piston from a fixed point is x and distance of bottom of piston at the same fixed point is ℓ. This means the volume of cylinder $= (\ell - x)A$
where A is area of cross section of piston.
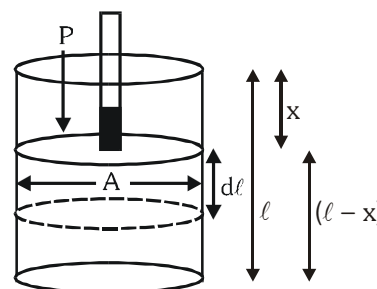
For a small displacement dx due to force F , **work done on the system**.

$$dw = F.dx$$

Also $P = \dfrac{F}{A}$

$F = PA$

$dW = PA.dx$

$V = (\ell - x)\,A$

$\Rightarrow \quad dV = -A\,.\,dx$

$\Rightarrow \quad dW = -P_{ext.}\,dV$

Note: *During expansion dV is +ive and hence sign of w is -ive since work is done by the system and -ive sign representing decrese in energy content of system. During compression, the sign of dV is -ive which gives +ive value of w representing the increase in energy content of system during compression.*

    Sign conventions : According to latest sign conventions

        Work done is taken negative if it is done by the system since energy of system is decreased.

    Ex.   Expansion of gas.

        Work done is taken positive if it is done on the system, since energy of system is increased.
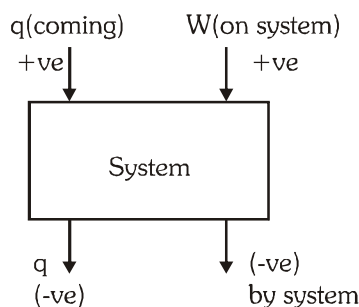
    $\therefore \quad W = -P_{ex}.\Delta V$

(ii)   **Heat** : Heat is defined as the amount of energy which flows between system and surrounding because of temperature difference.

Note : *Heat always flows from high temperature to low temperature .*

- **Sign convention**
  - Heat is taken negative when it goes out of the system.
  - Heat is taken positive when it comes inside the system.

(iii)   **Difference between heat and work :** When a gas is supplied some heat, its molecules move faster and with greater randomness in different directions.

But when work is done on the same system gas molecules are compressed and move initially in direction of force as they get condensed.

So heat is random form of energy while work is organised from of energy.

BEGINNER'S BOX–1

Basic definitions

**1.**   Predict sign of work done in following reactions at constant pressure.

	Initial state		Final state
(i)	H_2O (g)	$\longrightarrow$	H_2O (*l*)
(ii)	H_2O (s)	$\longrightarrow$	H_2O (g)
(iii)	H_2O (*l*)	$\longrightarrow$	H_2O (s)
(iv)	$CaCO_3$ (s)	$\longrightarrow$	CaO (s) + CO_2 (g)

2.   Water expands when it freezes. Determine amount of work, in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

3. Which one of the following quantity is dependent on path ?

(A) molar internal energy   (B) volume   (C) w   (D) q + w

4. In thermodynamics, a process is called reversible when :-
(A) surroundings and system change into each other
(B) there is no boundary between system and surroundings
(C) the surrounding are always in equilibrium with the system
(D) the system changes into the surroundings spontaneously

5*. Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV) Intensive properties are :
(A) I, II   (B) I, II, III   (C) I, III, IV   (D) all of these

6*. A cyclic process ABCD is shown in PV diagram for an ideal gas. Which of the following diagram represents the same process?
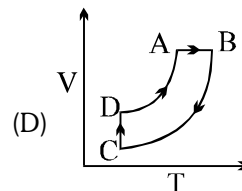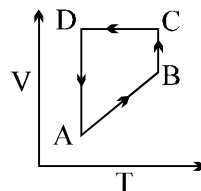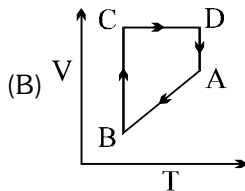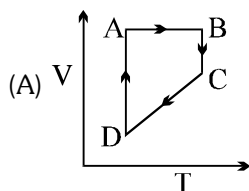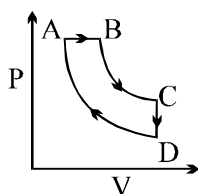
7*. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :
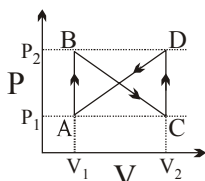
(A) zero   (B) positive   (C) negative   (D) we cannot predict

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7.0 THE INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS
SL **AL**

The first law of thermodynamics is based on experience that energy can be neither created nor destroyed, if both the system and the surroundings are taken into account.Suppose a blocks of mass 'M' is moving in gravitational field with velocity v. **The total energy of blocks (in earth frame of reference) is given as :**

E = K + V + U : (K = kinetic energy, V = potential energy, U = internal energy) Where K & V are the marocscopic (not molecular) kinetic and potential energies of the body (due to motion of the body as a whole and the presence of fields act on the body). A thermodynamic system is studies generally at rest so K = 0. If effect of gravitation field (or any other fields) is also ignored then we left with E = U. Thus U (internal energy) is energy of system. If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy U_A.

Suppose by a process the system is taken from state A to state B. In the process 'q' heat is absorbed by system and w work is done on the system. Thus in the state 'B' total internal energy of system become

$$U_B = U_A + q + w.$$
$$U_B - U_A = q + w$$

$\Rightarrow$ $\boxed{\Delta U = q + w}$
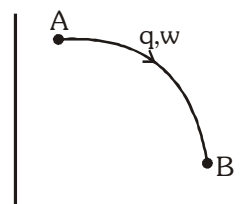
This is mathematical statement of first law.

First law of thermodynamics states that energy is conserved. Direct consequence of this statement is U that is state function. This implies that between any two fixed states, there can be infinite processes or paths, but ΔU in all processes will remain the same.

Consider a system taken from state A to B by n different paths.
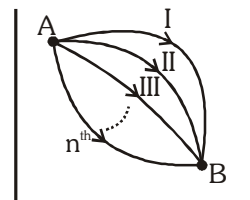
$\Rightarrow$ from first law

$U_B - U_A = q_1 + w_1 = q_2 + w_2 = ... \ q_i + w_i$

Here q_i, w_i are heat and work involve in respective processes.

Note that heat and work involve in all the process are different but ΔU is same. This mean heat and work are indefinite quantities while ΔU is a definite quantity.

$\Rightarrow$ ***Some other statement of first law :***

$$\sum_{\substack{cyclic \\ process}} \Delta U = 0 \ = \ or \ \oint dU = 0 \quad \text{\{Integral of dU over cyclic path is zero.\}}$$

7.1 First law of thermodynamics applied to close system involving only PV work
SL AL

For system involving only PV work first law mathematical statement can be written in differential from as:

$\boxed{dU = dq - PdV}$

7.2 The microscopic nature of First law of thermodynamics
SL AL

The internal energy of the gas confined in a container is defined relative to a coordinate system fixed on the container. Viewed at a microscopic level, the internal energy can take on a number of forms such as.

- The kinetic energy of the molecules ;
- The potential energy of the constituents of the system ; for example, a crystal consisting of dipolar molecules will experience a change in its potential energy as an electric field is applied to the system ;
- The internal energy stored in the form of molecular vibrations and rotations;
- The internal energy stored in the form of chemical bonds that can be released through a chemical reaction.
- The total of all these forms of energy for the system of interest is given the symbol U and is called the internal energy.
- Hence total internal energy of a system can be written as
  $U = U_{translational} + U_{rotational} + U_{vibrational} + U_{intermolecular} + U_{electronic} + U_{relativistic}$ of these $U_{relativistic}$ and $U_{eletronic}$ is unaffected by ordinary heating. So basically the kinetic energy terms and $U_{intermolecur}$ accommodate heat provided to the system . Hence heat capacity of a sample depends upon these four terms.
- For an ideal gas, $U_{intermolecular}$ is equal to zero, because of absence of intermolecular force of attraction in ideal gas. $U_{intermolecular}$ have large and negative value in solids and liquids.
- For an ideal gas U is only function of temperature *e.g.* $U = F(T) + Constant$
- Due to absence of pressure or volume terms in ideal gas internal energy, U is independent of pressure and volume of theoretical ideal gas.

7.3 Enthalpy
SL AL

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function ***Enthalpy*** (H) as :

$\quad$ H = U + PV (By definition)

or $\quad \Delta H = \Delta U + \Delta(PV)$ $\quad\quad$ ***...(i)***

or $\quad \Delta H = \Delta U + P\Delta V$ (at constant pressure). Combining with first law, equation (1) becomes

$\quad \Delta H = q_p$

7.4 Heat exchange at constant volume and constant pressure (q_p and q_v)
SL AL

For an isochoric process in a system involving only PV work,

$$\Delta U = q_v$$

This result is valid for all the substance under isochoric conditions (when only PV work is involved) Also from the previous article it is clear that

$$\Delta H = q_p$$

This result is valid for all the substance involving isobaric process(when only PV work is involved)

Hence heat exchanged at constant pressure and volume are important ***definite quantities***

7.5 Heat capacity
SL AL

The heat capacity of a system may be defined as the amount of heat required to raise the temperature of the system by one degree.

If δq is the small quantity of heat added to the system, let the temperature of the system rises by dT, then heat capacity C of the system is given by

$$C = \frac{dq}{dT} \qquad \text{...(i)}$$

In case of gases we have two types of heat capacity i.e. heat capacity at constant volume and heat capacity at constant pressure.

(a) ***Heat capacity at constant volume(C_v) :***

Molar heat capacity at constant volume is defined by the relation

$$C_V = \frac{dq_v}{dT} \qquad \text{...(ii)}$$

For first law of thermodynamics

$$dU = dq - dw$$

But $\qquad dw = P\,dV$

$\therefore \qquad dU = dq - P\,dV \qquad \text{...(iii)}$

At constant volume

$$dU = dq_v$$

$\therefore \qquad$ Heat capacity at constant volume C_v is given by

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v \qquad \text{...(iv)}$$

It may be defined as the rate of change of internal energy with temperature at constant volume.

(b) ***Heat capacity at constant pressure(C_p) :***

When pressure is maintained constant, equation (i) takes the form

$$C_P = \frac{\delta q_v}{dT} \qquad \text{...(v)}$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$
$$[\because H = U + PV \text{ At constant P, } dH = dU + PdV]$$

$\therefore \qquad \delta q_p = dH \qquad \text{....(vi)}$

Heat capacity at constant pressure C_p is given by

$$C_p = \frac{\delta d_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{...(vii)}$$

It is the rate of change of enthalpy with temperature at constant pressure.

Hence heat capacity of a system at constant volume C_v is equal to the increase in internal energy of the system per degree rise of temperature at constant volume. Similarly heat capacity at constant pressure C_p is numerically equally to the increase in enthalpy of the system per degree rise of temperature.

For 1 mole of an ideal gas, heat capacity at constant pressure i.e. C_p is greater than the heat capacity at constant volume i.e., C_v,

$$C_p > C_v$$

These are called molar heat capacities

i.e,
$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

and
$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Note: *For ideal gases, since U and H are only function of temperature, hence subscript P and V from C_p and C_v*

equation can be droped , which means $C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)$ which means $C_p = \left(\frac{\partial H}{\partial T}\right)$

hence for any process involving ideal gas $dH = C_p dT$

similarily for change in internal energy involving ideal gas, the subscript V from the expression of C_v can be dropped. Hence, $dU = w\, C_v dT$ for all process involving ideal gases.

Hence ΔH and ΔU is equal to zero for isothermal process involving ideal gases.

— Illustrations —

Illustration 1. 10 dm^3 of O_2 at 101.325 kP$_a$ and 298 K is heated to 348 K. Calculate the heat absorbed, ΔH and ΔU of this process at

(a) at constant volume
(b) at constant volume
Given : $C_P/JK^{-1}\, mol^{-1} = 25.72 + 0.013\, (T/K) - 3.86 \times 10^{-6}\, (T/K)^2$
Assume ideal behaviour.

Solution. Amount of the gas, $n = \dfrac{PV}{RT}$

or $\quad n = \dfrac{(101.325)(10)}{(8.314)(298)} = 0.409$ mol.

(a) constant pressure

$$q_P = \Delta H = n \int_{T_1}^{T_2} C_P dT$$

Here $\quad T_2 = 348\ K,\ T_1 = 298\ K$

or $\quad q_P = 0.409\left[(25.72)(T_2 - T_1) + 0.013\left(\dfrac{T_2^2}{2} - \dfrac{T_1^2}{2}\right)? (3.86 \times 10^{-6})\left(\dfrac{T_2^3}{3} - \dfrac{T_1^3}{3}\right)\right]$

or $\quad q_P = 0.409 \times 1475.775 = 603.59$ J **Ans.**

$\Delta U = \Delta H - \Delta(PV)$
$\quad = \Delta H - P\Delta V - V\Delta P$
at constant pressure
$\Delta U = \Delta H - P\Delta V = \Delta H - nR\Delta T$
$\quad = 603.59 - 0.409 \times 8.314 \times 50$
$\quad = 433.57$ J **Ans.**

(b) At constant volume

$$q_P = \Delta H = \int_{T_1}^{T_2} nC_V dT = \int_{T_1}^{T_2} nC_P dT - \int_{T_1}^{T_2} nR\, dT$$

$\quad = 603.59 - 170.02 = 433.57$ J **Ans.**
$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 603.59$ J **Ans.**

Illustration 2*. Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in :

(a) an open beaker

(b) a closed beaker at 300 K.

Solution. **(a)** From one mole of zinc, the no. of moles of H_2 gas evolved = 1

Hence volume of hydrogen gas evolved = 22.4 litre (when P = 1 atm and T = 273 K)

$\therefore \qquad w = -P\Delta V = -1 \times 22.4$ litre atm

$$= -22.4 \times \frac{8.314}{0.082} J = -2271.14 \text{ J} \qquad \textbf{Ans.}$$

(b) For a closed system $P_{ext} = 0.$, therefore, w = 0.

7.6 Degree of freedom and equipartition principle

[AL]

According to Law of equipartition of energy (i) each translation and rotational degree of freedom in a molecule

contributes $\frac{1}{2}RT$ to the thermal energy of one mole of a gas, and (ii) each vibrational degree of freedom in a

molecule contributes RT to the thermal energy of one mole of a gas.

The degrees of freedom in a molecule are given by the ***number of coordinates*** required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z. If a molecule contains N atoms, each atom contributes these three degrees of freedom, so the molecule has a total of 3N degrees of freedom. Since three coordinates (degree of freedom) are required to represent the translational motion of the molecule, the remaining (3N – 3) coordinates represent what are called the ***internal degrees of freedom***. If the molecule is linear, it has two rotational degrees of freedom ; for a non-linear molecule, there are three rotational degrees of freedom. The remaining degrees of freedom, that is 3N – 5 for linear and 3N – 6 non - linear molecules are the vibrational degrees of freedom. Table list the degrees of freedom for several molecule.

In a monatomic molecule $\bar{E} = 3RT/2$ in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and

Type	Molecule	trans	rot	vib	Total
Monoatomic	He	3	0	0	3
Diatomic	N_2	3	2	1	6
Triatomic linear	CO_2	3	2	4	9
non-linear	H_2O	3	3	3	9

one vibrational degrees of freedom making a total of six. the thermal energy per mole would, therefore, be,

$$\bar{E} = (\frac{1}{2}RT)_{trans} + (\frac{1}{2}RT)_{rot} + (1RT)_{vib}$$

and $\quad \bar{C}_V = 3R/2 + R + R = 7R/2 = 7$ cal deg^{-1} mol^{-1}

The observed values of $\bar{C}_V$ for diatomic molecules deviate greatly from the predicted values, The fact that the value of 5 cal deg^{-1} mol^{-1}(which is close to 5R/2) is most common for simple diatomic molecules shows that vibration degrees of freedom are active only at very high temperature. The following graph shows
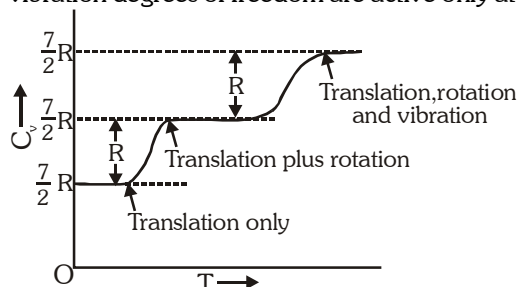
Variation of heat capacity at constant volume of a di atomic gas due to excitaton of rotational and vibrational levels.

variation of C_v with temperature highlighting the fact that with increase in temperature the vibriation modes of motion also contribute to the heat capacity

7.7 Relationship between C_p and C_v for ideal gas

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

from the first law $dH = dU + d(PV)$ for a differential change in state

if only ideal gas is involved $PV = nRT$ $dU = nC_v dT$ and $dH = nC_p dT$

substituting these results we get

$$nC_p dT = nC_v dT + nRdT$$
$$C_p = C_v + R \quad \text{valid only for ideal gas}$$

8.0 INTERNAL ENERGY AND ENTHALPY CHANGE IN PROCESS INVOLVING IDEAL GASES

8.1 Reversible isothermal process

Take an ideal gas in a cylinder fitted with a frictionless piston. The cylinder is put in a large constant temperature bath and pressure over the piston is changed infinitesimally slowly.

If external pressure is decreased by infinitesimally small value, piston will go up by infinitesimal distance 'dx' and temperature of gas inside piston decreases by dT (due to kinetic energy transfer of molecule to piston). To maintain thermal equilibrium infinitesimally small least dq will enter into the system. If the process is continued for infinite steps, the path of process is an isotherm on P.V. graph. If the gas is expanded from initial volume V_1 to final volume V_2 by gradually changing external pressure infinite steps, process is called reversible isothermal process.

Work done in reversible isothermal expansion
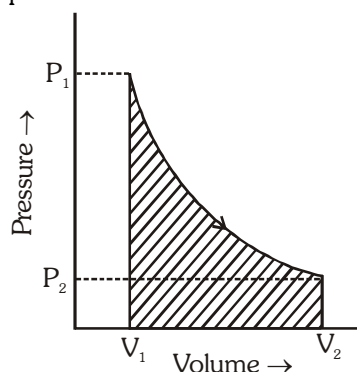
During reversible process :

$$P_{ext} = P_{int} \pm dP$$

$$\Rightarrow \quad P_{ext} = P_{int} = \frac{nRT}{V} \quad \text{for an ideal gas}$$

because $P_{int} = P_{ideal} = \dfrac{nRT}{V}$

$$dw_{rev,\ isothermal} = -PdV$$

$$\int dw = -\int \frac{nRT}{V} dV$$
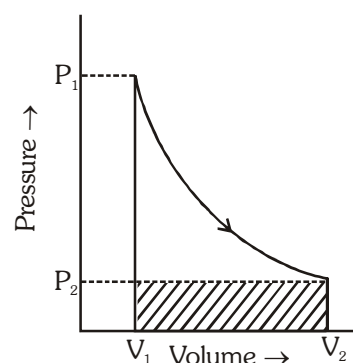
$$\boxed{w = -nRT \ln\left(\frac{V_2}{V_1}\right)}$$

8.2 Irreversible isothermal expansion

If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is distured and piston rushes out :

$$w_{irr} = -P_{ext.}\ \Delta V$$

### 8.3 Many steps Irreversible isothermal expansion and compression

(Comparison) consider an irrerversible expansion of an ideal gas from initial pressure of P_i to final pressure of P_f in four steps. The gas is allowed to expand against constant external pressure of P_1, P_2, P_3 and P_4 and finally P_f . Hence the system passes on to final state through four equilibrium states. The work done in the process is shown graphically .

The area under the isotherm is the magnitude of reversible work. Clearly the magnitude of reversible work of expansion is greater than irreversible work. As the number of intermediate steps in irrevisible expansion
is incresesed, the magnitude of work increases,
and as number of steps tend to infinity, w_{irr} tends to $w_{rev.}$ The graphical comparison of irreversible and reversible work is shown in fig. Here system is taken from initial state to the final state in four steps and isotherm represent magnitude of reversible work. Clearly, $w_{reversible}$ is less than $w_{irreversible}$. Once again as the number of steps in irreversible compression increases, work required to compress the ideal gas decreases, and as number of steps tends to infinity, the $\boldsymbol{w_{rev}} = \boldsymbol{w_{irr}}$.
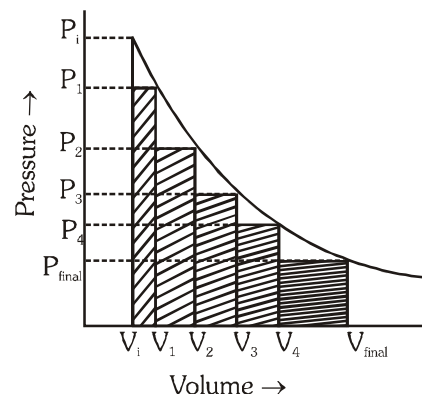
8.4 Free expansion of ideal gas
SL AL

When ideal gas is allowed to expand against zero external pressure, the process is called free expansion. W=0 for free expansion. During the free expansion, the ideal gas does not lose any energy , and hence temperature of ideal gas remains constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.
However if a real gas is allowed to expand in vaccum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas hots up upon expansion is called inversion temperature.

8.5 Stoppered expansion(kind of an irreversible expansion)
AL

In this expansion , the gas is allowed to expand against constant external pressure but the piston is stopped at certain volume when system gradually attains equilibrium. In this type of expansion , the $P_{external}$ and P_{final} are different. The stoppered expansion will help you realize that there can be infinite irreversible paths connection for any two given state at same temperature.(the same can be said about reversible paths)
the work done during stoppered expansion can be given by

$$w = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right) \qquad \text{where } P_{ext} \text{ and } P_f \text{ are different}$$

8.6 Reversible adiabatic process
SL AL

In an adiabatic process, no loss or gain of heat takes place i.e., $dq = 0$.
From first law, we have,
$$dq = dU + dw$$
Since $dq = 0$
$\therefore \quad dU = -dw$
For an ideal gas,
$$dU = C_v dT$$
$\therefore \quad C_v dT = -dw = -pdV$
or, $\quad C_v dT = -(nRT/V)dV$
or, $\quad C_v dT/T + nR\, dV/V = 0$
Intergrating the above equation between T_1 and T_2 and V_1 and V_2, the initial and final temperature and volumes, we have,

$$\int_{T_1}^{T_2} C_v \frac{\partial T}{T} + nR \int_{v_1}^{v_2} \frac{\partial V}{V} = 0$$

or $\quad C_v \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1} = 0$

Here C_v is assumed to be independent of temperature.

But, $\quad C_p - C_v = nR$

Hence, from we get

$$C_v \ln \dfrac{T_2}{T_1} + (C_p - C_v) \ln \dfrac{V_2}{V_1} = 0$$

or, $\ln \dfrac{T_2}{T_1} = \dfrac{C_p - C_v}{C_v} \ln \dfrac{V_1}{V_2}$

we put,

$\quad C_p/C_v = \gamma$

Equation may therefore be written as,

$$(\gamma - 1) \ln \dfrac{V_2}{V_1} + \ln \dfrac{T_2}{T_1} = 0$$

or $\quad \dfrac{T_1}{T_2} = \left(\dfrac{V_2}{V_1} \right)^{\gamma - 1}$

or $\quad (T_1 V_1)^{\gamma - 1} = (T_2 V_2)^{\gamma - 1} = $ constant

For an ideal gas,

$$\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2} \quad \text{or} \quad \dfrac{T_1}{T_2} = \dfrac{P_1 V_1}{P_2 V_2}$$

∴ $\quad$ from equation we have

$\quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = $ constant

In general, for a reversible adiabatic expansion

$\quad P\,V^{\gamma} = $ constant

$\quad TV^{\gamma - 1} = $ constant

$\quad TP^{1 - \gamma/\gamma} = $ constant

work done is given by either $w = nC_v(T_2 - T_1)$ or rearranging it gives $w = (P_2 V_2 - P_1 V_1)/\gamma - 1$

For an isothermal expansion, $PV = $ constant.but for an reversible adiabatic expansion $PV^{\gamma} = $ constant differentiating both PV and $PV^{\gamma - 1}$ with respect to V we get for isothermal process $dP/dV = -P/V$ while for adiabatic process $dP/dV = -\gamma (P/V)$ since γ is always >1 slope of $P V$ curve is more negative in case of adiabatic process. In figure, pressure and volume are plotted for isothermal and adiabatic cases. It is evident that a given pressure fall produces a lesser volume increase in the adiabatic case, because the temperature also falls during the adiabatic expansion.
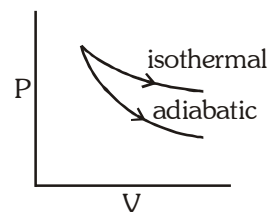
8.7 The irreversible adiabatic process

SL AL

Suppose an ideal gas is confined in a adiabatic container fitted with friction less piston. If the thermodynamic equilibrium of system is disturbed by changing external pressure suddenly by finite value and let the system come to equilibrium the process is irreversible adiabatic process. The work done (w) is given by

$\quad \Delta U = w = - P_{ext} (V_f - V_i)$

$\quad \Delta U = nC_V (T_f - T_i)$

⇒ $\quad nC_V (T_f - T_i) = - P_{ext} (V_f - V_i)$

$$nC_V (T_f - T_i) = - P_{ext} \left(\dfrac{nRT_f}{P_f} - \dfrac{nRT_i}{P_i} \right)$$

solving this equation for T_f

now $\quad w = \Delta U = nC_V (T_2 - T_1)$

$$w = \left[\dfrac{P_f V_f - P_i V_i}{\gamma - 1} \right]$$

8.8 Comparison of isothermal and adiabatic process

SL AL

Starting from same state, if system is allowed to expand to same final pressure,

$|w_{rev, isothermal}| > |w_{rev, adiabatic}|$.

In reversible isothermal process, heat is entering from surrounding, while in adiabatic process, work is done on the expansion of internal energy of system.

Starting from same initial state, if system is compressed to same final pressure, $w_{rev,adia} > w_{rev,iso}$. During adiabatic compression, the work done is getting stored in the system, and temperature of system increses, the gas become less and less compressible, and greater work is required to compress the system.

8.9 Polytropic process

AL

A process discribed by $PV^n = C$ is called polytropic process. where n is a real number.

Work done for polytropic process :

$$dw = - PdV$$

Let us suppose an ideal gas is undergoing polytropic process

$$dw = - PdV$$

$$\int dw = \int_{V_1}^{V_2} \frac{C}{V^n} dV$$

$$\Rightarrow \quad w = \frac{-C}{(-n+1)} \cdot \frac{1}{V^{n-1}} \bigg]_{V_1}^{V_2}$$

$$= \quad \frac{C}{(n-1)} \cdot \left(\frac{1}{V_2^{n-1}} - \frac{1}{V_1^{n-1}} \right)$$

$$w = \frac{C}{(n-1)} \left(\frac{P_2 V_2 - P_1 V_1}{C} \right)$$

$$\boxed{w = \left(\frac{P_2 V_2 - P_1 V_1}{n-1} \right)}$$
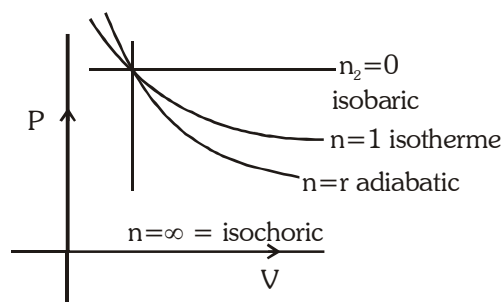
- **Heat capacity for polytropic process**

$$C = \frac{dq}{dT}$$

from first law

$$dq = dU + PdV \qquad \qquad ....(i)$$

$$\frac{dq}{dT} = \frac{nC_V dT}{dT} + \frac{nRT}{V} \cdot \frac{dV}{dT} \Rightarrow C = \frac{nC_V dT}{dT}$$

$$C = nC_V + \frac{nRT}{V} \cdot \left(\frac{dV}{dT} \right) \qquad \qquad ....(ii)$$

$$PV^n = k$$

$$V^n = \frac{k}{P} = \frac{kV}{n_g RT} \Rightarrow V^{(n-1)} = \frac{k}{n_g RT}$$

$$(n-1) V^{(n-2)} dV = \frac{-R \, dT}{n_g R T^2}$$

$$\Rightarrow \quad \frac{dV}{dT} = \frac{k}{(n-1) \left(\dfrac{k}{PV^2} \right) (PV) T}$$

$$\frac{dV}{dT} = -\left(\frac{V}{T}\right)\left(\frac{1}{n-1}\right) \qquad \qquad ...(iii)$$

substituting (iii) in equation (ii)

$$C = n_g C_V + \frac{n_g R}{1-n}$$

from 1 mole gas

$$\boxed{C = C_V + \frac{R}{1-n}}$$

BEGINNER'S BOX–2

### Thermodynamic Work and First law of thermodynamics

1*. Select the correct set of statement/s :

I.   Work done by the surrounding in case of infinite stage expansion is more than single stage expansion

II.   Irreversible work is always greater than reversible work (with sign).

III.   On an ideal gas in case of single stage expansion and compression system as well as surrounding are restored back to their original states

IV.   If gas is in thermodynamic equilibrium is taken from state A to state B, by four successive single stage expansions. Then we can plot 4 points on the P-V indicator diagram.

(A) II   (B) I, II, III, IV   (C) II, IV   (D) I, II, IV

2. If w_1, w_2, w_3 and w_3 are work done in isothermal, adiabatic, isobaric and isochoric reversible process, the correct order (for expansion) will be

(A) $w_1 > w_2 > w_3 > w_4$ (B) $w_3 > w_2 > w_1 > w_4$ (C) $w_3 > w_2 > w_4 > w_1$ (D) $w_3 > w_1 > w_2 > w_4$

3. Following graph shows a single stange expansion process, then workdone by the system is
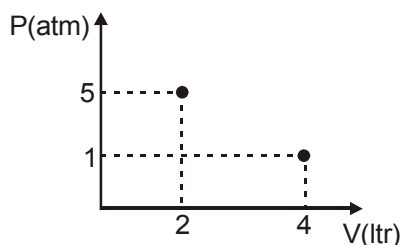
(A) – 9104 J   (B) – 202.6 J   (C) – 506 J   (D) – 101.3 J

4*. 50 Ltr. of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 Ltr. and the final pressure of the liquid is 10 atm. Find the workdone.

(A) 1L.atm   (B) 5 L.atm   (C) 500 L.atm   (D) 50 L.atm

5. In an isothermal expansion of a gaseous sample the correct relation is (consider w (work) with sign according to new IUPAC convention)

[The reversible and irreversible processes are carried out between same initial and final states.]

(A) $w_{rev} > w_{irrev}$ (B) $w_{irrev} > w_{rev}$ (C) $q_{rev} < q_{irrev}$ (D) can not be predicted

6. 1 mole of NH_3 gas at 27° C is expanded reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are -

(A) 150 K, 900 cal   (B) 150 K, 400 cal   (C) 250 K, 1000 cal   (D) 200 K, 800 cal

7*. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ($\gamma = 1.33$) from 300K and pressure 10 atm to 1 atm.

8*. A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC. Then the temperature of the states A and B are
(Given R = 8.3 joules/mol K) :

(A) T_A = 120.5 K, T_B = 120. 5K (B) T_A = 241 K, T_B = 241 K
(C) T_A = 120.5 K, T_B = 241 K (D) T_A = 241 K, T_B = 482 K
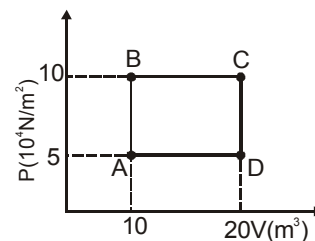
9*. When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30 J of work. (a) How much heat flows into the system along path ADB if the work done is 10 J? (b) When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much? (c) If $U_D - U_A$ = 40 J, find the heat absorbed in the process AD and DB.
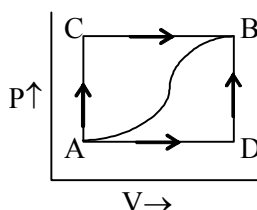
10*. Two mole of ideal diatomic gas ($C_{V,m}$ = 5/2 R) at 300 K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w, ΔH & ΔU.

11. Three moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas C_V is 27.5 JK^{-1} mol^{-1} in this temperature range. Calculate q, w, ΔU, ΔH and final V and final P.

12. The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and ΔE ?

8.10 Change in internal energy and enthalpy in chemical reactions
SL AL

Enthalpy and internal energy change in chemical reaction involve change in potential energy due to chemical change. During chemical change transformation of bonds take place. If the bonds in product are more stable, leading to decrease in potential energy of atom and molecules, the enthalpy and internal energies decreases In the process surplus energy is librated and process is called exothermic process.

During endothermic chemical process which take place absorbing energy from surrounding, the potential energy of system of chemical substance increases.

Consider a chemical reaction

aA + bB ---> cC + dD
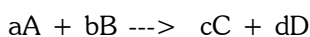
The internal energy change can be given as (Theoratically)

ΔU= cU_c + dU_d – aU_a – bU_b

where U_a , U_b , U_c , U_d etc. are molar internal enegy of respective species.

since absolute internal energies cannot be determine, U_i are determined with respect to internal energy of elements in their most stable state. The internal energies of elements in their most stable allotropic modification is arbitary taken as zero at 298K and 1 atm pressure.

also, $\Delta_r U = q_v$ for reaction taking place under constant volume and temperature condition. For the similar reaction occuring at constant pressure and temperature, enthalpy change, ΔH is given by

ΔH = cH_c + dH_d – aH_a – bH_b
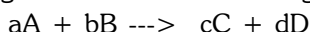
where H are enthalpies of respective species

however ΔH is equal to heat exchange during chemical process at constant pressure and temperature.

$\Delta_r H = q_p$ for reaction taking place under constant pressure and temperature conditions

8.11 Relationship between $\Delta_r H$ and $\Delta_r U$ in chemical reactions

SL AL

For a general chemical reaction given by

$aA + bB \longrightarrow cC + dD$

$\Delta_r H = cH_c + dH_d - aH_a - bH_b$ ...(i)

but $H_i = U_i + PV_i$

substituting the value of molar enthalpies of substance in equation (1) we get

$\Delta_r H = cU_c + dU_d - aU_a - bU_b + P(cV_c + dV_d - aV_a - bV_b)$

$\Delta_r H = \Delta_r U + P(V_f - V_i)$ ...(ii)

(a) If all the reactant and products are ideal gases V_c, V_d, V_a and V_b all are equal to molar volume of ideal gas e.g.

$V = RT/P$ which on substitution in previous equation gives

$\Delta_r H = \Delta_r U + (d + c - a - b)RT$

$\boldsymbol{\Delta_r H = \Delta_r U + \Delta n_g RT}$ ...(iii)

Where $\boldsymbol{\Delta n_g}$ is difference of stoichiometric cofficient of gaseous products and gaseous reactants.

(b) In case of liquid and solids present in chemical equations, their molar volumes can be ignored in comparison to molar volume of ideal gases and hence do not count stoichiometric cofficient of solid and liquids in Δn_g.

(c) In case of real gases, equation (ii) should be used.

8.12 Change in internal energy and enthalpy in phase transition

SL AL

At certain temperature under one atmospheric pressure, one phase changes into other phase by taking or releasing certain amount of Heat. The temperatrue at which this happens is called ***transition temperature*** and heat absorbed or realeased druing the process is called Enthalpy of phase transition. Heat absorbed or released during transition is exchanged at constant pressure and temperatrue and it is significant to know that the process is reversible.

Fusion : Solid ice at 273K and 1 atm pressure reversibly changes into liquid water absorbing heat which is know as latent heat of fusion.or enthalpy of fusion.

Vaporisation : Water at 373K and 1 atm pressure changes into its vapors absorbing heat known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally , isobarically and reversibly to convert water into its vapour at boiling point.

8.13 Variation of enthalpy with temperature (KIRCHHOFF'S EQUATION)

SL AL

The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in ΔH with temprature is usually small compared to the value of ΔH itself,

consider a reaction $A \longrightarrow B$ at temperature T_1 and pressure P

$$A(T_y, P) \xrightarrow{\Delta H_1} B(T_1, P)$$

$$\Delta H_4 = \int_{T_2}^{T_1} C_{p,A} dT \qquad \qquad \Delta H_3 = \int_{T_1}^{T_2} C_{p,B} dT$$

$$A(T_2, P) \xrightarrow{\Delta H_2} B(T_2, P)$$
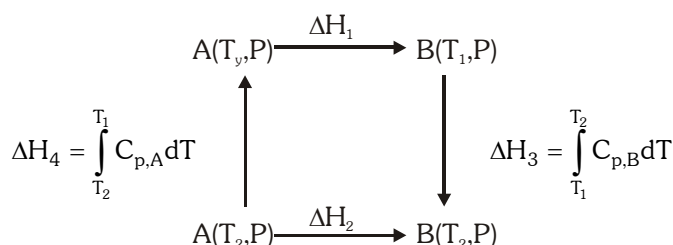
Change in enthalpy in cyclic process is equal to zero. To calculate enthalpy change (ΔH_2) at temperataure T_2 at constant pressure consider cyclic process shown in figure. It is clear

ΔH_3 = change in enthalpy of A when temperature is raised from T_1 to T_2 at constant pressure. $\Delta H_3 = \int_{T_1}^{T_2} C_{p,B} dT$

ΔH_4 = Change in enthalpy taking 1 mole of B at constant pressure from T_1 to $T_2 = \Delta H_4 = \int_{T_2}^{T_1} C_{p,A} dT$

now : $\Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_2$

$\Rightarrow \quad \Delta H_2 - \Delta H_1 = \Delta H_3 + \Delta H_4$

$\Rightarrow \quad \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p,B} - C_{p,A})dT$

$\Rightarrow \quad \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1) \qquad$ If $\Delta_r C_p$ is independent of 'temperature'

BEGINNER'S BOX–3

Enthalpy

1. The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31$ KJ. What is the ΔU ?

2*. 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 Cal/gm and latent heat of vaporisation of liquid water at 0°C is 596 Cal per gram and the volume of ice in comparison to that of water (vapour) is neglected.

3*. The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 kJmol⁻¹ What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?

4. The enthalpy of combustion of glucose is – 2808 kJmol⁻¹ at 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5 kg].
(a)   to climb a flight of stairs rising through 3M.
(b)   to climb a mountain of altitude 3000 M?
Assume that 25% of enthalpy can be converted to useful work.

5. The difference between heats of reaction at constatnt pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25° in kJ mol⁻¹ is :-
(A) –7.43 (B) +3.72 (C) –3.72 (D) +7.43

6*. The P–T graph as given below was observed for a process of an ideal gas, which of the following statement is true :

(A) w = +ve, ΔH = +ve (B) w = –ve, ΔH = –ve
(C) w = –ve, ΔH = +ve (D) w = +ve, ΔH = –ve
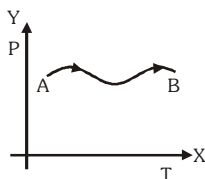
7. How much heat, in joules, must be added to 0.250 mol of Ar(g) to raise its temperature from 20°C to 36.0°C at constant pressure ?
(A) 50.0 (B) 83.2 (C) 187 (D) 200

9.0 SECOND LAW

SL AL

There are two types of processes reversible process or quasi static process in which system remains in equilibrium with surrounding through out the process.
However reversible processes can not take place on it's own - and are not natural process. Reversible process do not lead to production of disorder.

On the other hand most of the processes taking place around us are examples of irreversible process. Irreversible processes are natural processes or spontaneous processes.

Example of natural processes :

(i)   Water flowing down hill

(ii)   Heat flowing from hot body towards cold body on it's own

(iii)   mixing of two gases.

(iv)   Rusting of iron

(v)   Evaporation of water at room temperature.

(vi)   Formation of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$ gas in a closed container.

(vii)   Expansion of ideal gas in vacuum

(viii)   Burning of coal in O_2

Every natural process leads to production of disorder. (During irreversible process system moves from ordered state to disordered state).

- **The second law of thermodynamics**

   The second law of thermodynamics predict's direction of natural change. It does so with the help of a state function 'S' - called entropy. But for predicting direction of natural change another quantity $S_{surrounding}$ is also needed. $S_{surrounding}$ which is called entropy of surrounding is a path dependent quantity.

$$\boxed{\begin{aligned} dS_{system} &= \frac{dq_{rev}}{T} \\ dS_{surr} &= -\frac{dq}{T} \end{aligned}}$$

   Since S_{system} is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible. ΔS_{AB} will be same irrespective of path (A direct consequence of S_{system} being a state function).

   However, If same transition from A to B is done by different irreversible paths, $\Delta S_{surrounding}$ will be different in all processes. However if transition from $A \rightarrow B$ take place by many reversible path's, ΔS_{surr} along each path will be same because

$$-\sum_{A \rightarrow B}^{path\,1} \frac{dq_{rev}}{T} = -\Delta S_{system} = -\sum_{A \rightarrow B}^{path\,2} \frac{dq_{rev}}{T}$$

$$\Rightarrow \quad \underset{A \rightarrow B}{\Delta S_{surr}}(path\,1) = -\underset{A \rightarrow B}{\Delta S_{system}} = -\underset{A \rightarrow B}{\Delta S_{surr}}(path\,2)$$

	ΔS_{system}	$\Delta S_{surrounding}$
reversible process	$\int_A^B \dfrac{dq_{rev}}{T}$	$-\int_A^B \dfrac{dq_{rev}}{T}$
Irreversible process	$\int_A^B \dfrac{dq_{rev}}{T}$	$\int_A^B \dfrac{dq_{irrev}}{T} = -\left(\dfrac{q_{irrev}}{T}\right)_{A \rightarrow B}$

Entropy change of system and surrounding in reversible and irreversible process

Note that $\boxed{\Delta S_{surr} = -\dfrac{q_{actual}}{T}}$

The central concept of entropy is given briefly, because JEE syllabus deals with consequence of second law rather than it's derivation.

- **Prediction of spontaneity of process**

   If total entropy change in a process is positive the process must be spontaneous.

   $\Delta S_{system} + \Delta S_{surrounding} > 0$ for spontaneous change.

   The second law of thermodynamics was developed during course of development of cyclic engines. Second law was discovered while studying efficiency of steam engines. In 1824 a french engineer Sodi carnot pointed out that for a cyclic heat engine to produce continuous mechanical works, it must exchange heat with two bodies at different temperature without a cold body to discard heat, the engine can-not function continuously.

- **2ⁿᵈ law statement**

  Kelvin Statement: No Cyclic is possible in which heat is taken from a hot source and convertd completely into work.

  Clausius statement : Heat does not pass from a body at low temperature to one at high temperature without an accompanying change eleswhere.

  Another statement of 2ⁿᵈ law : Entropy of the universe increases.

10.0 EFFICIENCY OF CARNOT ENGINE

AL

Carnot has devised an engine based on reverssible steps. The efficiency of carnot engine is maximum, because it is based on reversible cycle. A Carnot engine completes a cycle in four steps.

The Carnot cycle
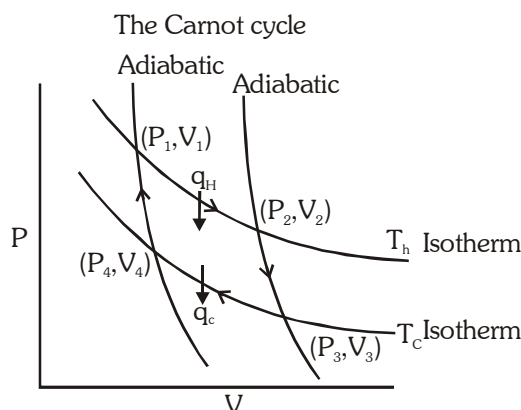
Reversible isothermal expansion from P_1, V_1 to P_2, V_2 at temp T_H

Reversible adiabatic expansion from P_2, V_2 at temp T_H to P_3, V_3 at temp T_c

Reversible isothermal compression from P_3, V_3 to P_4, V_4 at temp T_H

Reversible isothermal compression from P_4, V_4 to P_1, V_1 at temp T_c

A carnot engine rejects minimum heat to the surrounding in its operation and maximum part of heat taken form source is converted into work. Hence efficiency of carnot engine is given by

$$\eta = \frac{\left(\text{Net work done by engine in one cycle}\right)}{\text{Net heat absorbed from source}}$$

$$\eta = \frac{-w_{net}}{q_H} \qquad \text{where } w_{net} \text{ is net work done on the engine(system) in one cycle.}$$

It can be easily shown that $- w_{net} = q_H + q_C = w_{net}$

$$q_H + q_C = nRT_H \ln\frac{V_2}{V_1} + nRT_C \ln\frac{V_4}{V_3}$$

also $\begin{cases} T_C V_4^{\gamma-1} = T_h V_1^{\gamma-1} \\ T_C V_3^{\gamma-1} = T_h V_2^{\gamma-1} \end{cases} \Rightarrow \left\{ \dfrac{V_4}{V_3} = \dfrac{V_1}{V_2} \right\}$

because of reversible adiabatic process
substituting these result's

$$\boxed{\eta = \frac{T_H - T_C}{T_H} = \frac{q_H + q_C}{q_H}}$$

- Efficiency of Carnot engine only depends upon temperature of source and sink and independent of choice of working substance.

- Sum of the $\dfrac{q_{rev}}{T}$ in a cyclic process is zero.

  For the Carnot cycle $\qquad \dfrac{q_H}{T_H} + \dfrac{q_C}{T_C} = 0 \qquad \Rightarrow \qquad$ for carnot cycle $\sum \dfrac{q_{rev}}{T} = 0$

- The result in previous article is valid for any reversible cyclic process. It can be very easily varified.

Hence $\oint \dfrac{dq_{rev}}{T} = 0 \quad \Rightarrow \quad$ Sum of the $\dfrac{dq_{rev}}{T}$ over a cyclic path is zero.

now If $\oint dx = 0 \Rightarrow dx$ is differential of a state function and X is state function.

$\Rightarrow \quad dS = \dfrac{dq_{rev}}{T} =$ definite quantity

$\Rightarrow \quad \boldsymbol{S_{system}}$ *is a state function.*

11.0 CLASIUS INEQUALITY

AL

From our experience we known if any one step in carnot engine is consciously made irreversible the efficiency of carnot engine will decrease from theoretical value

$$\eta = \dfrac{q_H + q_C}{q_H} = \dfrac{T_H - T_C}{T_H}$$

$\Rightarrow \quad \dfrac{q_H}{T_H} + \dfrac{q_C}{T_C} < 0$

$\Rightarrow \quad \sum \dfrac{q_{irr}}{T} < 0$

this mathematical statement is called ***Clasius inequality.***

12.0 ENTROPY CHANGES IN SOME PROCESSES

12.1 Entropy change in isolated system (isolated system = sys + surr)

SL AL

Consider a system taken from state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to Clasius inequality, sum of q/T over the cycle must be less than zero. Hence
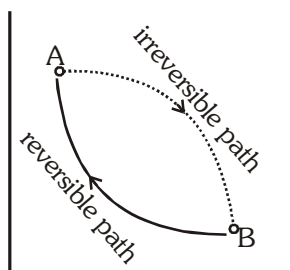
$$\sum_{A \to B} \dfrac{q_{irr}}{T} + \sum_{B \to A} \dfrac{q_{rev}}{T} \leq 0 \Rightarrow \sum_{A \to B} \dfrac{q_{irr}}{T} = - \sum_{B \to A} \dfrac{q_{rev}}{T}$$

But $- \sum_{B \to A} \dfrac{q_{rev}}{T} = \sum_{A \to B} \dfrac{q_{rev}}{T}$ since the process is reversible

for infinitesimally small change

$$\boxed{\left(\dfrac{dq}{T} \right)_{A \to B} = dS_{system\,A \to B}}$$

$\Rightarrow \quad dS_{system} - \left(\dfrac{dq}{T} \right)_{A \to B} > 0 \Rightarrow \boxed{dS_{system\,A \to B} + dS_{sur\,A \to B} > 0}$

$\Rightarrow \quad \boxed{\Delta S_{Total\,isolated\,sys} > 0}$

12.2 Entropy calculation in process involving ideal gases

SL AL

From First law

dq = dU + PdV

$\Rightarrow \quad \dfrac{dq_{rev}}{T} = \dfrac{dU}{T} + \dfrac{PdV}{T}$

But for ideal gas

$\dfrac{dU}{T} = \dfrac{nC_V dT}{T} \qquad \{\because dU = nC_V dT\}$

$$\Rightarrow \quad dS_{sys} = \frac{nC_V dT}{T} + \frac{nR}{V} dV$$

on integration gives

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1} \right) = nc_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

For isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For isochoric process

$$\Delta S = nC_V \ln \frac{T_2}{T_1}$$

For isobaric process

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

12.3 Entropy change in chemical Reaction
SL AL

From application of third law absolute entropy of every compound or element can be deduced for a general chemical reaction taking place at given condition

aA + bB ---> cC + dD
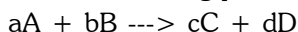
$\Delta S = \Delta S_{system}$ = entropy change of reaction

$\Rightarrow \quad = (aS_C + dS_D - aS_A - bS_B)$

where S_C, S_D, S_A and S_B are molar entropy of substance A,B, C and D under given circumtance.

12.4 Entropy change in phase transition
SL AL

(i) **Fusion :** When solid ice is heated below 273 K at external pressure of 1 atm it's temperature slowly rises. At 273 K however. its start melting into liquid without increase in temperature. The process is reversible phase transition from solid to liquid represented as :

$$H_2O \text{ (s)} \rightleftharpoons H_2O(\ell)$$
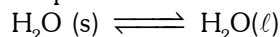
Since process is reversible (you can safely assume that phase transition at constant temperature and pressure are reversible phase transitions).

Now $\Delta S_{Total} = 0$ (since process is reversible)

$\Delta S_{system} + \Delta S_{surr} = 0$

also $\Delta S_{surrounding} = \dfrac{-\Delta H_{fusion}}{T_f}$ (here T_f = freezing point)

$$\Rightarrow \quad \Delta S_{Total} = \frac{\Delta H_{fusion}}{T_f} = 0 \quad \Rightarrow \Delta S_{fustion} = \frac{\Delta H_{fusion}}{T_f} \quad \text{entropy of fusion at Melting point.}$$

(ii) **Vapourisation :** From day to day experience you know that under atmospheric pressure, temperature of H_2O (ℓ) can not exceed 373 K. Since at 373 K liquid H_2O undergo phase transition.

$$H_2O(\ell) \rightleftharpoons H_2O(g)$$
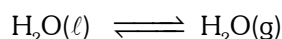
since $\Delta S_{Total} = 0$ (Process is reversible)

$\Delta S_{system} + \Delta S_{surr} = 0$

$\Delta S_{system} = \Delta S_{fusion} = S_{H_2O(g)} - S_{H_2O(\ell)}$

$\Delta S_{surrounding} = -\dfrac{\Delta H_{vap}}{T_b}$ (here T_b = melting point)

Note : *Boiling point at 1 atm pressure is called normal boiling point. There can be infinite boiling points of liquid depending upon external pressure.*

13.0 ENTROPY AND CRITERIA OF SPONTANEITY OF CHEMICAL PROCESS

SL AL

The entropy change of chemical reaction together with entropy change of surroundings determine spontaneity of a chemical process under given set of conditions.

$$\Delta S_{Total} = \Delta_r S - \frac{\Delta_r H}{T}$$

If $\Delta_r S$ = positive and very large while $\Delta_r H$ is negative and large this means $\Delta S_{Total} > 0$.

If $\Delta_r S$ = positive but small and $\Delta_r H$ is negative but having large value.

⇒ If ΔS_{Total} is +ive due to large +ive value of $\Delta_r S$, we can say reaction is entropy driven i.e increased in disorder is the driving force of reaction. ($H_2O(\ell) \longrightarrow H_2O(g)$ above 373 K at 1 atm)

⇒ Sometimes reaction go completely in forward direction inspite of negative entropy change in reaction due to large –ive value of $\Delta_r H$. These reactions are enthalpy driven.

Spontaneous and non Spontaneous

Sign of ΔH	Sign of ΔS	Comment	Example	ΔH°_{298}	ΔS°_{298}
–	+	spontaneous at all temperature	$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $C(s) + O_2(g) \longrightarrow CO_2(g)$	–185 –394	14.1 3
–	–	spontaneous at low temperature	$H_2(g) + 1/2\ O_2 \longrightarrow H_2O(\ell)$ $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	–44 –198	–119 –187
+	+	spontaneous at high temperature	$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	176 180	284 25
+	–	non spontaneous at all temperature	$3O_2 \longrightarrow 2O_3$ $2H_2O(\ell) + O_2(g) \longrightarrow 2H_2O_2(\ell)$	286 196	–137 –126

—————————— Illustrations ——————————

Illustration 3. Will ΔS be positive or negative in the following processes ? Discuss qualitatively

(a) $H_2O(s) \longrightarrow H_2O(\ell)$

(b) $H_2O(\ell) \longrightarrow H_2O(g)$

(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(d) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

(e) $2H_2(g) + N_2(g) \longrightarrow N_2H_4(\ell)$

(f) $Cl_2(g) \longrightarrow 2Cl(g)$

Solution. As we have discussed that the entropy of reaction is more if there is a change in value of $\Delta\nu_g$ (the change in the stoichiometric number of gaseous species), since the entropy of gases is much larger than the entropy of the condensed phases.

∴ for process (a) ΔS is +ve

for process (b) ΔS is +ve

for process (c) ΔS is negative

for process (d) ΔS is negative

for process (e) ΔS is negative

for process (f) ΔS is positive

BEGINNER'S BOX–4

Entropy

1. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in $J\,k^{-1}\,mol^{-1}$)

(A) 19.15   (B) – 19.15   (C) 4.7   (D) zero

2*. One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as (R = 2 calories/mol/K)

(A) $3 \ln \dfrac{298}{373} + 2 \ln 10$

(B) $5 \ln \dfrac{373}{298} + 2 \ln 10$

(C) $7 \ln \dfrac{373}{298} + 2 \ln \dfrac{1}{10}$

(D) $5 \ln \dfrac{373}{298} + 2 \ln \dfrac{1}{10}$

3*. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :
[R = 0.082 L atm mol^{-1} K^{-1} = 8.3 J mol^{-1}K^{-1}].

(A) 0   (B) $R\ell n\,(24.6)$ (C) $R\,\ell n\,(2490)$ (D) $\dfrac{3}{2}\,R\ell n\,(24.6)$

4. The enthalpy change for a given reaction at 298 K is – x J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(A) can be negative but numerically larger than x/298   (B) can be negative but numerically smaller than x/298
(C) cannot be negative   (D) cannot be positive

5. For the gas - phase decomposition,

$$PCl_5 \,(g) \underset{}{\overset{\Delta}{\rightleftharpoons}} PCl_3 \,(g) + Cl_2 \,(g) :$$
(A) $\Delta H < 0,\ \Delta S < 0$ (B) $\Delta H > 0,\ \Delta S > 0$ (C) $\Delta H > 0,\ \Delta S < 0$ (D) $\Delta H < 0,\ \Delta S > 0$

14.0 THIRD LAW OF THERMODYNAMICS

SL AL

Third law of thermodynamics helps in determining absolute entropy of substances. It is based on an assumption that entropy of every perfectly crystalline substance is zero at zero kelvin.

Kelvin. This is justified because , at absolute zero every substance is in state of lowest energy and position of every atom or molecule is defined in solid. **Hence at T=0   S = 0   Third law**

If we have sufficient heat capacity data (and the data on phase changes) we could write

$$S\,(T) = S(T = 0) + \int_0^r \frac{C_p}{T}\,dT \qquad \textit{....(i)}$$

(If there is a phase change between 0 K and T, we would have to add the entropy of the phase change.) If C_p were constant near T = 0, we would have,

$$S(T) = S(T = 0) + C_p \ln \frac{T}{0},$$

which is undefined. Fortunately, experimentally $C_p \to 0$ as $T \to 0$. For nonmetals C_p is proportional to T^3 at low temperature. For metals C_p is proportional to T^3 at low temperatures but shifts over to being proportional to T at extermely low temperatures. (The latter happens when the atomic motion "freezes out" and the heat capacity is due to the motion of the conduction electrons in the metal.)

Equation (i) could be used to calculate absolute entropies for substances if we know what the entropy is at absolute zero. Experimentally it appears that the entropy at absolute zero is the same for all substances. The third law of thermodynamics modifies this observation and sets

S (T = 0) = 0

for all elements and compounds in their most stable and perfect crystalline state at absolute zero and one atmosphere pressure. (All except for helium, which is a liquid at the lowest observable temperatures at one atmosphere.)

The advantage of this law is that it allows us to use experimental data to compute the absolute entropy of a substance. For example, suppose we want to calculate the absolute entropy of liquid water at 25°C. We would need to known the C_p of ice from 0 K to 273.15 K. We also need the heat of fusion of water at its normal melting point. With all of this data, which can be obtained partly from theory and partly from experiment, we find

$$S^\circ_{H_2O}(25°C) = 0 + \int_0^{273.15} \frac{C_p(s)}{T}dT + \frac{\Delta H_{fus}}{273.15} + \int_{273.15}^{298.15} \frac{C_p(l)}{T}dT.$$

14.1 Gibb's function

Entropy is a universal criteria of spontaneity. This means for any process if $\Delta S_{Total} > 0$ the process is spontaneous. Most of the chemical process take place at constant temperature and pressure. A very useful criteria of spontaneity of process at constant temperature and pressure is Gibb's function :

Gibb's function (G) is defined as

G = H – TS   ***...(i)***

Gibb's function and spontaneous process :

from 2nd law we known :

$$\frac{dq}{T} \le dS_{system} \;:\; \text{Less than sign for if } q = q_{irr}$$

$\Rightarrow$ dq ≤ TdS   ***...(ii)***

      dq = dV + PdV   ***...(iii)***

subsituting value of dq from equation (iii) to equation (ii)

      dV + PdV – TdS ≤ 0

$\Rightarrow$ d(H – TS)$_{P,T}$ ≤ 0

$\because$ d(H – TS)$^-_{P,T}$ = (dH – TdS – SdT)$_{P,T}$

=   (dU + PdV + VdP – TdS – SdT)$_{P,T}$ ≤ 0

$\Rightarrow$ d(H – TS)$_{P,T}$ ≤ 0

$\Rightarrow$ d(dG)$_{P,T}$ ≤ 0

14.2 Statement

During course of every spontaneous process, Gibb's function decreases. If a process is allowed to run spontaneously, eventually it attain equilibrium. At equilibrium, the Gibb's function attains minimum value. No further decrease to the value of Gibb's function is possible at equilibrium.

Hence at equilibrium. (dG)$_{T,P}$ = 0.

$\Rightarrow$ Entropy change in spontaneous process :

    $\Delta S_{system} + \Delta S_{surrounding} \ge 0$

The sign > is for spontaneous process. A state of equilibrium in a close system is attained spontaneously. As system approaches equilibrium from non-equilibrium state – S_{Total} keeps on increasing and at equilibrium S_{Total} attains its maximum value.

$\Rightarrow$ $\Delta S_{Total} = 0$ at equilibrium

    at this point   ***S_{Total} = maximum value at equilibrium in a close system***

14.3 Significance of Gibb's Function

(a)   Decrease in Gibb's function at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

    We known :

        $\Delta G = \Delta H - T\Delta S$ ***...(i)*** ; at constant T and pressure

also $\Delta H = q_p$ at constant pressure

    q_p = heat absorbed by system at constant pressure.

$\Rightarrow$ $\quad\quad\quad \Delta G = q_P - T\Delta S$ $\quad\quad\quad\quad$ ...(ii)

this gives $\quad -\dfrac{\Delta G}{T} = -\dfrac{q_P}{T} + \Delta S$

$\quad\quad\quad -\dfrac{q_P}{T} + \Delta S_{surrounding} \quad \Rightarrow \quad -\dfrac{\Delta G}{T} = (\Delta S_{surrounding} + \Delta S_{system})$

Student might get confused in

ex : $\quad\quad\quad -\dfrac{q}{T} = \Delta S_{surr.}$

ex : $\quad\quad\quad$ q $\,=$ Heat absorbed by system

$\quad\quad\quad\quad\quad$ –q $=$ Heat absorbed by surrounding

$\Rightarrow$ $\quad\quad\quad\quad$ $\boxed{-\Delta G = T(\Delta S_{Total})}$

Note equation (ii) can be written as ΔG = q – q_{rev.}

for spontaneous process (ΔG)_{T,P} < 0

$\Rightarrow$ $\quad\quad$ $q - q_{rev} < 0 \Rightarrow q_{rev} > q$

14.4 Gibbs Function and Non PV work
SL AL

Decrease in Gibb's function at constant temperature and pressure in a process gives an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electrical work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

$\quad\quad$ dU $=$ dq – PdV $=$ dw$_{non–PV}$

– dw$_{non–PV}$ = non-PV work done by the system.

$\quad\quad$ dG $\quad = $ d (H – TS)

$\quad\quad\quad\quad = $ dH – TdS – SdT

$\quad\quad$ dG $\quad = $ dU + PdV + VdP – TdS – SdT

$\quad\quad$ dG $\quad = $ dq – PdV – w$_{non,PV}$ + PdV + VdP – TdS – SdT

for a reversible change at cont. T and P

$\quad\quad\quad\quad$ dG $=$ dq$_{rev.}$ – dw$_{non}$ + VdP – TdS – SdT

since $\quad\quad\quad$ dq$_{rev}$ = TdS

$\Rightarrow$ $\quad\quad\quad\quad$ –(dG)$_{T,P}$ = dw$_{non-PV}$

Non-pV work is work done due to chemical energy transformation or due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

14.5 Gibbs Free Energy Change at Constant Temperature
SL AL

In order to derive an equation which will enable us to calculate the Gibbs free energy change of an isothermal process but with varying pressure, we may conveniently start with the equation,

$\quad\quad$ G $=$ E + PV – TS

Differentiating the above equation, we get

$\quad\quad$ dG $=$ dE + PdV + VdP – TdS – SdT

According to first law of thermodynamics,

$\quad\quad$ dQ $=$ dE + PdV

$\therefore$ $\quad$ dG $=$ dQ + VdP – TdS – SdT

Further since $\dfrac{dQ}{T} = dS$, we can replace dQ by TdS.

$\therefore$ $\quad$ dG $=$ VdP – SdT

At constant temperature, dT $= 0$

$\therefore$ $\quad$ dG $=$ VdP

or $\quad$ $\left(\dfrac{dG}{dP}\right)_r = V$

Thus Gibb's function of every substance increases on increasing pressure, but this increase is maximum for gases, compared to solids or liquids since gases have maximum molar volume. On intergrating equation $dG = VdP$ for very minute changes from state 1 to 2, we have

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

In case of one mole of a perfect gas,

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

$$\therefore \quad \Delta G = RT \int_1^2 \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$$

For n moles of a perfect gas, the free energy change is

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

14.6 Gibbs Free Energy Change at Constant Pressure

AL

From equation which is
$$dG = VdP - SdT \qquad \text{(Only for pure substances)}$$
when pressure is constant, $dP = 0$

$$\therefore \quad dG = -SdT$$

or
$$\left(\frac{dG}{dT}\right)_p = -S$$

thus Gibb's function of every substance decreases with temperature, but this decrease is maximum for gases since they have maximum state of disorder. Hence on deccreasing temperature, gas phase gain maximum stability compared to solid or liquid phase.

14.7 For Chemical Reaction

SL **AL**

$$\boxed{d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)}$$

at constant temperature, If $\Delta_r V \simeq$ constant

$$\Rightarrow \quad \int_1^2 d(\Delta_r C_p) = \Delta_r V \int_1^2 dp$$

$$\Rightarrow \quad \boxed{\Delta_r C_{p_2} - \Delta_r C_{p_1} = \Delta_r V(P_2 - P_1)}$$

only for condensed phase : equilibrium like

$$H_2O(s) \rightleftharpoons H_2O(\ell)$$

$$S(\text{Rhombic}) \rightleftharpoons S(\text{monoclinic})$$
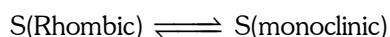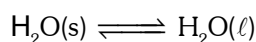
14.8 Gibbs Free Energy Change in Chemical Reactions

SL **AL**

Gibbs free energy changes have a direct relationship with the tendency of the system to proceed to a state of equilibrium. In view of this fact, it is desirable to have a knowledge of the free energy of chemical compounds so that the Gibbs free energy change of a possible reaction could be easily calculated. Standard free energies have been used for this case. A zero value of the Gibbs free energy is assigned to the free energies of the stable form of the elements at 25°C and 1 atm. pressure.

With this as reference point, free energies of compounds have been calculated which are called standard Gibbs free energies of formation. The difference in the Gibbs free energy of products and reactants in their standard states (at 25°C and 1 bar pressure) is denoted as $\Delta G°$.

In standard enthalpy and entropy values are available, $\Delta G°$ can be written from equation as,

$$\Delta G° = \Delta H° - T\Delta S°$$

14.9 Gibb's free energy in Chemical Reaction from Gibb's free Energy of Formation of Compounds
SL AL

Consider a chemical reaction,

$$aA + bB \rightarrow cC + dD$$
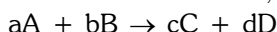
The standard Gibb's free energy change $\Delta G°$ can be computed on the basis discussed above (i.e., by assigning zero value to the Gibbs free energy of the stable form of elements at 25°C and 1 bar pressure). With this as reference, the standard Gibbs free energy of the products and reactants can be determined. The standard Gibbs free energy change for the overall reaction can be evaluted as :

$$\Delta G° = \sum G°_{f(products)} - \sum G°_{f(reactants)} = \left(c G°_c + d G°_D \right) - \left(a G°_A + b G°_B \right)$$

A negative sign of $\Delta G°$ will show that the reaction will proceed spontaneously.

note that $\Delta G°$ can be defined at any temperature, at standard pressure of 1 bar

14.10 Reversible phase transitions and Gibb's free energy change
SL AL

During reversible phase transition which occurs at transition temperatures, Gibb's function change become zero, impling the fact that these processes are reversible processes.

at 373K and 1 atm pressure $\Delta G = 0$ for $H_2O(l) \rightarrow H_2O(g)$

at 273K and 1atm pressure $\Delta G = 0$ for $H_2O(s) \rightarrow H_2O(l)$

Gibb's energy and equilibrium constant, an important topic taken up in chemical equilibrium.

Application of Gibb's function in decribing variation of vapour pressure, boiling and melting point with temperature is taken up in chemical equilibrium and liquid solutions variation of G/T with temperature , has important implication in pridicting feasibitily of process at different temperatures.This gives Famous Gibb's Helmholtz equation taken up in electrochemistry.

BEGINNER'S BOX–5

Gibb's Free energy

1. For a reaction A (g) $\rightleftharpoons$ B(g) at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of $\Delta G°$ of the reaction A $\rightarrow$ B is

    (A) RT ℓn 4   (B) – RT ℓn 4   (C) RT log 4   (D) – RT log 4

2. A reaction has $\Delta H = -33$ kJ and $\Delta S = -58 \dfrac{J}{K}$. This reaction would be :

    (A) spontaneous at all temperature   (B) non-spontaneous at all temperatures

    (C) spontaneous above a certain temperature only   (D) spontaneous below a certain temperature only

3. A reaction has $\Delta H = -33$ kJ and $\Delta S = -58$ J/K. This reaction would be :-

    (A) Spontaneous at all temperature   (B) Non-spontaneous at all temperature

    (C) Spontaneous above a certain temperature only   (D) Spontaneous below a certain temperature only

4. If $\Delta G = -177$ K cal for   (1) $2Fe(s) + \dfrac{3}{2} O_2 (g) \longrightarrow Fe_2O_3(s)$

    and $\Delta G = -19$ K cal for   (2) $4Fe_2O_3(s) + Fe(s) \longrightarrow 3Fe_3O_4(s)$

    What is the Gibbs free energy of formation of Fe_3O_4 ?

    (A) + 229.6 $\dfrac{kcal}{mol}$ (B) –242.3 $\dfrac{kcal}{mol}$ (C) –727 $\dfrac{kcal}{mol}$ (D) –229.6 $\dfrac{kcal}{mol}$

5*. For the reaction at 300 K

    A(g) + B (g) $\longrightarrow$ C (g)

    $\Delta E = -3.0$ kcal   ; $\Delta S = -10.0$ cal/K value of ΔG is ?

    (A) –600 cal   (B) –6600 cal   (C) –6000 cal   (D) none

GOLDEN KEY POINTS

- **First law of thermodynamics**

  For a finite change : $q = \Delta E - w = \Delta E - P\Delta V$

  where q is heat given to system, ΔE is change in internal energy and $-w$ is work done by the system.

  $$dq = dE - dw = dE - PdV$$

- **Work done in an irreversible process**

  $$w = -P_{ext} \times \Delta V = -P_{ext} \times (V_2 - V_1) = -P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$$

  P_{ext} is the pressure against which volume changes from V_1 to V_2

- **Work done in reversible process, i.e., Maximum work**

  Isothermal conditions

  $w_{rev} = -2.303\ nRT \log_{10}(V_2/V_1)$

  $w_{rev} = -2.303\ nRT \log_{10}(P_1/P_2)$

  w_{rev} is maximum work done.

- **Adiabatic conditions**

  $w_{rev} = [nR/(\gamma - 1)]\ [T_2 - T_1]$

  γ is poisson's ratio.

  Also for adiabatic process, following conditions hold good :

  $PV^{\gamma} = $ constant

  $T^{\gamma}P^{1-\gamma} = $ constant

  $TV^{\gamma-1} = $ constant

- **Heat capacities**

  At constant pressure $C_p = (\delta H/\delta T)_p$

  C_p is molar heat capacity at constant pressure.

  At constant volume $C_v = (\delta E/\delta T)_v$

  C_v is molar heat capacity at constant volume.

  $C_p \times c_p \times M$ and $C_v = c_v \times M$

  and $\quad C_p - C_v = R/M$

  $C_p/C_v = c_p/c_v = \gamma \quad$ (The poisson's ratio)

  c_p and c_v are specific heats at constant pressure and volume respectively.

- **Entropy**

  $\Delta S = \sum S_{products} - \sum S_{reactants}$

  $\Delta S = q_{rev}/T = 2.303\ nR \log_{10}(V_2/V_1) = 2.303\ nR \log_{10}(P_1/P_2)$

  $\Delta S_{fusion} = \Delta H_{fusion}/T$

  $\Delta S_{vap} = \Delta H_{vap}/T$

  ΔS is entropy change.

- **Free energy**

  $G = H - TS$

  $\Delta G = \Delta H - T\Delta S$ and $\Delta G° = \Delta H° - T\Delta S° \qquad$ (In standard state)

  At equilibrium, $\Delta G = 0$

  $-\Delta G° = RT \ln K_p$ (or K_C)

  $= 2.303\ RT \log_{10} K_p$ (or K_C)

  ΔG is free energy change and $\Delta G°$ is standard free energy change. K_C and K_p are equilibrium constants in terms of concentration and pressure respectively.

SOME WORKED OUT EXAMPLES

Illustration 1.

During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

Solution.

w = 200 J;   q = –140 J;

$\because$ q = ΔE + (–w); where –w is work done by the system

ΔE = q + w

ΔE = –140 + 200 = +60J

Illustration 2.

A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre. Calculate the change in internal energy.

Solution.

w = –PΔV = –1.5 × (1.0 – 0.5) = –0.75 litre atm

= –0.75 × 101.3 J = –75.975 J

$\because$ 1 litre atm = 101.3 J

Now, ΔE = 200 – 75.975 = +124.025 J

Illustration 3.

Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

Solution.

Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

w = –P_{ext} ($V_2 - V_1$)

w = –1 × ($V_2 - V_1$)

Given V_1 = 2 litre V_2 = ?T = 273 K

P_1 = 5 atm P_2 = 1 atm

$\therefore$ $P_1V_1 = P_2V_2$

$\therefore$ $V_2 = \dfrac{2 \times 5}{1}$ = 10 litre

$\therefore$ w = –1 × (10 – 2) = –8 litre atm

$\therefore$ $= -\dfrac{8 \times 1.987}{0.0821}$ calorie $= -\dfrac{8 \times 1.987 \times 4.184}{0.0821}$ J = –810.10 joule

Illustration 4.

The enthalpy of vaporisation of liquid diethyl ether –$(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS for conversion of : (a) liquid to vapour, and (b) vapour to liquid at 35°C.

Solution.

(a) $\Delta S_{vap.} = \dfrac{\Delta H_{vap.}}{T} = \dfrac{26 \times 10^3}{308}$ = +84.41 $JK^{-1}mol^{-1}$

(b) $\Delta S_{cond.} = \dfrac{\Delta H_{cond.}}{T} = -\dfrac{26 \times 10^3}{308}$ ($\because$ H_{cond} = –26 kJ)

= –84.41 JK^{-1} mol^{-1}

Illustration 5*.

Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25ºC. Lattice energy of NaCl = 777.8 kJ mol^{-1} ; ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = –774.1 kJ mol^{-1}.

Solution.

$\Delta H_{dissolution}$ = Lattice energy + Hydration energy

$\qquad$ = 777.8 – 774.1 = 3.7 kJ mol^{-1}

Now $\quad \Delta G = \Delta H - T\Delta S$

$\qquad$ = 3.7 – 298 × 0.043 = 3.7 – 12.814

$\qquad \Delta G$ = –9.114 kJ mol^{-1}

Illustration 6.

The equilibrium constant for the reaction given below is 2.0×10^{-7} at 300 K. Calculate the standard free energy change for the reaction;

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
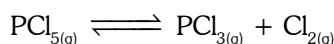
Also, calculate the standard entropy change if ΔH° = 28.40 kJ mol^{-1}.

Solution.

ΔG° = –2.303 × 8.314 × 300 log [2.0×10^{-7}]

$\qquad$ = +38479.8 J mol^{-1} = +38.48 kJ mol^{-1}

Also, $\quad \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$\therefore \qquad \Delta S^{\circ} \quad = \dfrac{\Delta H^{\circ} - \Delta G^{\circ}}{T} = \dfrac{28.40 - 38.48}{300}$ = –0.0336 kJ = –33.6 JK^{-1}

Illustration 7*.

One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :
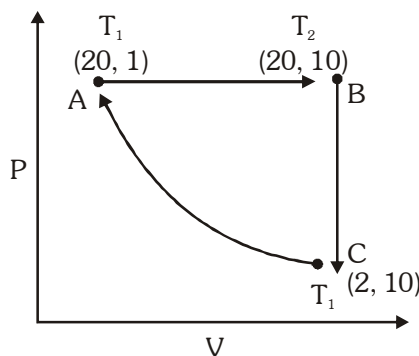
(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2.

(b) Calculate ΔE, q and w in calories, for each step and for the cycle.

Solution.

We know,

$\qquad$ Path CA – Isothermal compression

$\qquad$ Path AB – Isobaric expansion

$\qquad$ Path BC – Isochoric change

Let V_i and V_f are initial volume and final volume at respective points,

For temperature T_1 (For C) : $PV = nRT_1$

$2 \times 10 = 1 \times 0.0821 \times T_1$

$\therefore$ $T_1 = 243.60K$

For temperature T_2 (For C and B) : $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$$\dfrac{2 \times 10}{T_1} = \dfrac{20 \times 10}{T_2}$$

$\therefore$ $\dfrac{T_2}{T_1} = 10$

$\therefore$ $T_2 = 243.60 \times 10 = 2436.0 \ K$

Path CA : $w = +2.303 \ nRT_1 \log \dfrac{V_i}{V_f}$

$= 2.303 \times 1 \times 2 \times 243.6 \log \dfrac{10}{1} = +1122.02$ cal

$\Delta E = 0$ for isothermal compression ; Also $q = w$

Path AB : $w = -P(V_f - V_i)$

$= -20 \times (10 - 1) = -180$ litre atm

$= \dfrac{-180 \times 2}{0.0821} = -4384.9$ cal

Path BC : $w = -P(V_f - V_i) = 0$ ($\because V_f - V_i = 0$)

since volume is constant for monoatomic gas heat change at constant volume $= q_v = \Delta E$.

Thus for path BC $q_v = C_v \times n \times \Delta T = \Delta E$

$\therefore$ $q_v = \dfrac{3}{2} R \times 1 \times (2436 - 243.6)$

$q_v = \dfrac{3}{2} \times 2 \times 1 \times 2192.4 = 6577.2$ cal

Since process involves cooling $\therefore$ $q_v = \Delta E = -6577.2$ cal

Also in path AB, the intenal energy in state A and state C is same. Thus during path AB, an increase in internal energy equivalent of change in internal energy during path BC should take place. Thus ΔE for path AB = +6577.2 cal

Now q for path AB $= \Delta E - w_{AB} = 6577.2 + 4384.9 = 10962.1$ cal

Cycle : $\Delta E = 0$; $q = -w$ $= - [w_{Path\ CA} + w_{Path\ AB} + w_{Path\ BC}]$

$= - [+1122.02 + -4384.9 + 0]$

$\therefore$ $q = -w$

$= +3262.88$ cal

Illustration 8*.

A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The

volume ratios are $\dfrac{V_B}{V_A} = 2$ and $\dfrac{V_D}{V_A} = 4$.

If the temperature T_A at A is 27ºC, calculate :

(a) The temperature of the gas at point B.
(b) Heat absorbed or released by the gas in each process.
(c) The total work done by the gas during complete cycle.

Solution.

For the given cyclic process,
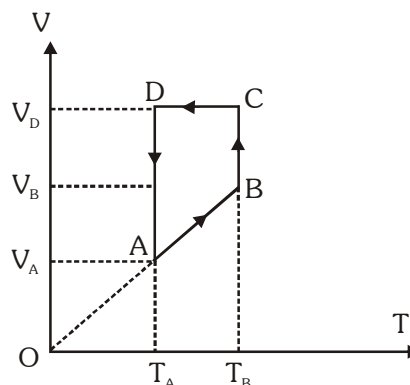
$$\frac{V_B}{V_A} = 2, \quad \frac{V_D}{V_A} = 4, \quad T_A = 300 \text{ K}$$

(a) For isobaric process AB

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\therefore \qquad T_B = T_A \times \frac{V_B}{V_A} = 300 \times 2 = 600 \text{ K}$$

(b) The following process are there in complete cycle

    (i)   A → B Isobaric expansion   (ii)   B → C Isothermal expansion

    (iii)   C → D Isochoric compression   (iv)   D → A Isothermal compression

For   (i) $q_{A \to B} = +n \times C_P \times \Delta T = +2 \times \dfrac{5}{2} \times R \times 300 = +1500 \times 2 = +3000 \text{ cal}$ (R = 2 cal)

    (ii) $q_{B \to C} = \Delta E - w$ $(\Delta E = 0)$

$\therefore \qquad q_{B \to C} = \Delta E - w = + \int PdV = +nRT \ln \dfrac{V_D}{V_B} = +2 \times 2 \times 600 \ln \dfrac{4}{2} = +1.663 + 10^3 \text{ cal}$

    (iii) $q_{C \to D} = n \times C_v \times \Delta T = 2 \times \dfrac{3}{2} \times 2 \times -300 = -1800 \text{ cal}$

    (iv) $q_{D \to A} = +nRT_A \ln \dfrac{V_A}{V_D} = +2 \times 2 \times 300 \ln \dfrac{1}{4} = -2 \times 2 \times 300 \times 1.386 = -1.663 \times 10^3 \text{ cal}$

$\therefore \qquad Q = q_{A \to B} + q_{B \to C} + q_{C \to D} + q_{D \to A} = 3000 + 1663 - 1800 - 1663 = 1200 \text{ cal}$

(c) Since the process ABCDA is a cyclic process

$\therefore \qquad \Delta E = 0 \qquad \text{or} \qquad Q = \Delta E - Q = -w \quad \text{or} \qquad Q = -1200 \text{ cal}$

i.e., work done on the system = 1200 cal

Illustration 9.

Calculate the work done when 50 g of iron reacts with hydrochloric acid in :

(i) a closed vessel of fixed volume,   (ii) an open beaker at 25°C.

Solution.

We know,

(i)   Vessel is of fixed volume, hence $\Delta V = 0$. No work is done, w = 0

(ii)   The H_2 gas formed drives back the atmosphere hence.

$$w = -P_{ext} \cdot \Delta V$$

Also $\Delta V = V_{final} - V_{initial} \simeq V_{final} \quad (\because V_{initial} = 0)$

$\therefore \qquad\qquad\qquad \Delta V = \dfrac{nRT}{P_{ext}}$

or $w = -P_{ext} \cdot \dfrac{nRT}{P_{ext}} = -nRT$

where n is the number of mole of H_2 gas obtained from n mole of $Fe_{(s)}$.

$$Fe_{(s)} = 2HCl_{(aq)} \to FeCl_{2(aq.)} + H_{2(g)}$$

1 mole   1 mole
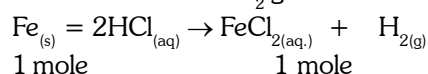
$\therefore \qquad\qquad n = \dfrac{50}{56} = 0.8929 \text{ mole}$

$\therefore \qquad\qquad w = -0.8929 \times 8.314 \times 298$

$\qquad\qquad\qquad = -2212.22 \text{ J}$

The reaction mixture in the given system does 2.212 kJ of work driving back to atmosphere.

Illustration 10.*

The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is $+0.21$ kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.

Solution.

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

Given

$$\Delta E = +0.21 \text{ kJ mol}^{-1} = 0.21 \times 10^3 \text{ J mol}^{-1}$$

$$P = \bar{1} = 1.0 \times 10^5 \text{ Pa}$$

$$\Delta V = V_{(aragonite)} - V_{(Calcite)}$$

$$= \left(\frac{100}{2.93} - \frac{100}{2.71} \right) \text{ cm}^3 \text{ mol}^{-1} \text{ of } CaCO_3$$

$$= -2.77 \text{ cm}^3 = -2.77 \times 10^{-6} \text{ m}^3$$

$\therefore$ $\Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6} = 209.72 \text{ J} = 0.20972 \text{ kJ mol}^{-1}$

Illustration 11.

For a reaction $M_2O(s) \rightarrow 2M(s) + \dfrac{1}{2} O_2(g)$; $\Delta H = 30$kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. Calculate upto which temperature, the reaction would not be spontaneous.

Solution.

Given, for the change, $\Delta H = 30 \times 10^3$ J mol^{-1}, $\Delta S = 70$ JK^{-1} mol^{-1}

For a non-spontaneous reaction

$$\Delta G = +ve$$

Since $\Delta G = \Delta H - T\Delta S$

$\therefore$ $\Delta H - T\Delta S$ should be $+ve$

or $\Delta H > T\Delta S$

or $T < \dfrac{\Delta H}{\Delta S} \Rightarrow T < \dfrac{30 \times 10^3}{70} \Rightarrow T < 428.57$ K

Illustration 12.

Predict whether the entropy change of the system in each of the following process is positive or negative.

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ (d) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
(e) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (f) Cooling of $N_2(g)$ from 20°C to –50°C

Solution.

Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than the reactants, the entropy change is probably positive. And hence, ΔS is

(a) positive   (b) negative   (c) negative   (d) negative
(e) negative   (f) negative

[***Note :*** For a given substance at a given temperature, $S_{gas} > S_{liquid} > S_{solid}$]

Illustration 13.

Calculate the boiling point of bromine from the following data :

$\Delta H°$ and $\Delta S°$ values of $Br_2(l) \rightarrow Br_2(g)$ are 30.91 kJ/mole and 93.2 J/mol. K respectively. Assume that ΔH and ΔS do not vary with temperature.

Solution.

Consider the process : $Br_2(l) \rightarrow Br_2(g)$

The b.p. of a liquid is the temperature at which the liquid and the pure gas coexist at equilibrium at 1 atm.

$\therefore$ $\Delta G = 0$

As it is given that ΔH and ΔS do not change with temperature

$$\Delta H = \Delta H° = 30.91 \text{ kJ}$$

$$\Delta S = \Delta S° = 93.2 \text{ J/K} = 0.0932 \text{ kJ/K}$$

We have, $\Delta G = \Delta H - T\Delta S = 0$

$\therefore$ $T = \dfrac{\Delta H}{\Delta S} = \dfrac{30.91}{0.0932} = 331.6$ K.

This is the temperature at which the system is in equilibrium, that is, the b.p of bromine.

Illustration 14*.

The efficiency of the Carnot engine is 1/6. On decreasing the temperature of the sink by 65K, the efficiency increases to 1/3. Find the temperature of the source and the sink.

Solution.

We have,

$\eta = \dfrac{T_2 - T_1}{T_2}$, where T_1 and T_2 are the temperatures of sink and source respectively.

$\therefore \quad \eta = \dfrac{T_2 - T_1}{T_2} = \dfrac{1}{6}$ ....(i)

Now the temperature of the sink is reduced by 65 K.

$\therefore$ temp. of the sink $= (T_1 - 65)$

$\therefore \quad \eta = \dfrac{T_2 - (T_1 - 65)}{T_2} = \dfrac{1}{3}$ ....(ii)

On solving eqns. (i) and (ii), we get,

$T_1 = 325$ K
$T_2 = 390$ K

Illustration 15*.

(a) One mole of an ideal gas expands isothermally and reversible at 25°C from a volume of 10 litres to a volume of 20 litres.
   (i) What is the change in entropy of the gas ?
   (ii) How much work is done by the gas ?
   (iii) What is q(surroundings) ?
   (iv) What is the change in the entropy of the surroundings ?
   (v) What is the change in the entropy of the system plus the surroundings ?

(b) Also answer the questions (i) to (v) if the expansion of the gas occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of 10-L volume.

Solution.

(a) (i) $\Delta S = 2.303 nR \log \dfrac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \dfrac{20}{10} = 5.76$ J/K.

   (ii) $w_{rev} = 2.303 \, nRT \log \dfrac{V_2}{V_1}$

   $= -2.303 \times 1 \times 8.314 \times 298 \times \log \dfrac{20}{10} = -1718$ J.

   (iii) For isothermal process, $\Delta E = 0$ and heat is absorbed by the gas,
   $q_{rev} = \Delta E - W = 0 - (-1718) = 1718$ J
   $\therefore \quad q_{surr} = 1718$ J. ($\because$ process is reversible)

   (iv) $\Delta S_{surr} = -\dfrac{1718}{298} = -5.76$ J/K.

   As entropy of the system increases by 5.76 J, the entropy of the surroundinig decreases by 5.76 J, since the process is carried out reversible.
   (v) $\Delta S_{sys} + \Delta S_{surr} = 0$ .... for reversible process.

(b) (i) $\Delta S = 5.76$ J/K, which is the same as above because S is a state function.
   (ii) $w = 0$. ($\because p_{ext} = 0$)
   (iii) No heat is exchanged with the surroundings.
   (iv) $\Delta S_{surr} = 0$
   (v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increases in an irreversible process.

Illustration 16.

Sulphur exists in more than one solid form. The stable form. The stable form at room temperatrure is rhombic sulphur. But above room temperature the following reaction occurs :

s (rhombic) $\longrightarrow$ s (mono clinic)
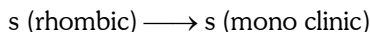
Thermodynamic measurements reveal that at 101.325 kP_a and 298 K,

$\Delta_r H = 276.144$ J mol^{-1} and $\Delta_r G = 75.312$ J mol^{-1}

(a) Compute $\Delta_r s$ at 298 K

(b) Assume that $\Delta_r H$ and $\Delta_r s$ do not vary significantly with temperature, compute T_{eq}, the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Solution.

(a) Since

$$\Delta_r G = \Delta_r H - T\Delta_r S,$$

Therefore

$$\Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144\,J\,mol^{-1} - 75.312\,J\,mol^{-1}}{298\,K} = 0.674 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) When the rhombic sulphur is in equilibrium with monoclinic sulphur, we would have

$$\Delta_r G = 0 = \Delta_r H - T_{eq} \Delta_r S$$

Thus

$$T_{eq} = \frac{\Delta_r H}{\Delta_r S} = \frac{276.144\,J\,mol^{-1}}{0.674\,J\,mol^{-1}} = 409.7 \text{ K}$$

Illustration 17.

At 1 atm and 27°C, will the vaporisation of liquid water be spontaneous ? Given $\Delta H = 9710$ cal and $\Delta s = 26$ eu.

Solution.

$H_2O(\ell) = H_2O(g)$ (P = 1 atm)
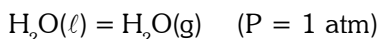
$\Delta G = \Delta H - T\Delta S = 9710 - 26 \times 300 = +1910$ cal

since ΔG is positive, at 1 atm, vaporisation is not possible. Rather the reverse process of condensation will occur.

The temperature at which the liquid and vapour will be equiv. can be obtained, by putting $\Delta G = 0$, i.e

$\Delta G = 9710 - 26T = 0$

$T = 373.4$ °C

This indeed is the boiling point of water at 1 atm.

Illustration 18.

Gases	ΔG_f° (Cal/mole)
CO	–32.80
H_2O	–54.69
CO_2	–94.26
H_2	0

Estimate the standard free energy change in the chemical reaction
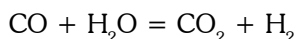
$CO + H_2O = CO_2 + H_2$

Solution.

Using the necessary data from the table

	CO	H_2O	CO_2	H_2
$\Delta G°$	– 32.8	–54.69	–94.26	0 kcal

$\therefore$ $\Delta G° = -94.26 + 0 - (-32.8) - (-54.69)$

$= -6.8$ kcal/mol

***

ANSWERS

BEGINNER'S BOX-1

1. (i) w, (ii) – w, (iii) – w, (iv) – w   **2.** – 10 J   **3.** (C)

4. (C)   **5.** (C)   **6.** (C)

7. (A)

BEGINNER'S BOX-2

1. (A)   **2.** (D)   **3.** (B)   **4.** (A)   **5.** (B)

6. (A)   **7.** – 1.683 kJ   **8.** (C)

9. (a) + 60 J (b) –70 J (c) 50J , +10 J

10. $\Delta U = w = -1247.1$; $\Delta H = -1745.94$ J

11. q = 0; w = ΔU= 4.12 kJ; ΔH = 5.37 kJ; V_f = 11.8 dm^3; P = 5.21 atm

12. q = – 65 J ; w = 20 J; ΔE = – 45 J

BEGINNER'S BOX-3

1. – 0.3024 kJ   **2.** ΔH = 12168 calories; ΔE = 11623 calories

3. ΔE= 27.91 kJ mol^{-1}, t= 514 sec.   **4.** (a) 0.47 gm, (b) 0.47 kg

5. (A)   **6.** (C)   **7**. (B)

BEGINNER'S BOX-4

1. (D)   **2.** (B)   **3.** (B)   **4.** (B)   **5.** (B)

BEGINNER'S BOX-5

1. (A)   **2.** (D)   **3.** (D)   **4.** (B)   **5.** (A)

EXERCISE – 1   **MCQ (SINGLE CHOICE CORRECT)**

1. What is the change in internal energy ΔU, for a system that does 70 joules of work as it absorbs 45 joules of heat ?
(A) 115 J   (B) 25 J   (C) –25 J   (D) –115 J

2. When 1 mol gas is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct :-
(A) $q = W = 500$ J, $\Delta U = 0$ (B) $q = \Delta U = 500$ J, $W = 0$
(C) $q = W = 500$ J, $\Delta U = 0$ (D) $\Delta U = 0$, $q = W = -500$ J,

3. Internal energy does not include
(A) vibrational energy   (B) rotational energy
(C) nuclear energy   (D) energy arising by gravitational pull

4. For a monatomic gas, the value of the ratio of $C_{p.m}$ and $C_{v.m}$ is :-

(A) $\dfrac{5}{3}$ (B) $\dfrac{7}{5}$ (C) $\dfrac{9}{7}$ (D) $\dfrac{9}{11}$

5*. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then the change in the internal energy in expanding the gas from a to c along the path abc is :-
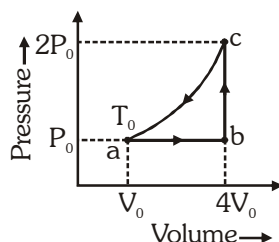
(A) $3P_0V_0$ (B) $6RT_0$ (C) $4.5RT_0$ (D) $10.5RT_0$

6. Two moles of an ideal monoatomic gas are allowed to expand adiabatically and reversibly from 300 K and 200 K. The work done in the system is ($C_v = 12.5$ J/K/mol)
(A) –12.5 kJ   (B) –2.5 kJ   (C) –6.25 kJ   (D) 500 kJ

7. The reaction $NH_2CN(s) + \dfrac{3}{2} O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O\ (\ell)$ was carried out at 300 K in a bomb calorimeter. The heat released was 743 kJ mol^{-1}. The value of ΔH_{300K} for this reaction would be :-
(A) -740.5 kJ mol^{-1} (B) -741.75 kJ mol^{-1} (C) -743.0 kJ mol^{-1} (D) -744.25 kJ mol^{-1}

8*. A block of ice at –10°C is slowly heated and converted into steam at 100°C. Which of the following curves represents the phenomenon qualitatively ?
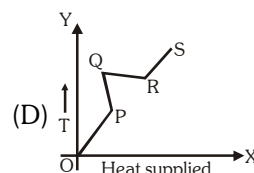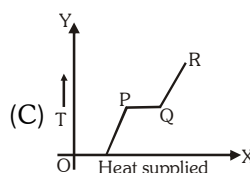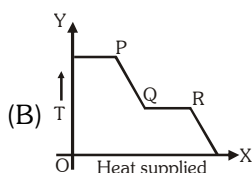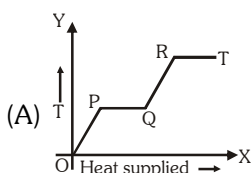
9. Molar heat capacity of water in equilibrium with ice at constant pressure is :-
(A) zero   (B) inifinity
(C) 40.45 kJ K^{-1} mol^{-1} (D) 75.48 kJ K^{-1} mol^{-1}

10. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J K^{-1} mol^{-1}) :-
(A) 19.15   (B) –19.15   (C) 4.7   (D) Zero

11. Which has maximum internal energy at 298 K ?

(A) helium gas   (B) oxygen gas   (C) ozone gas   (D) equal

12*. A cyclic process is shown in the P-T diagram.
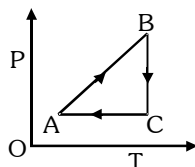
Which of the curves show the same process on V-T diagram ?
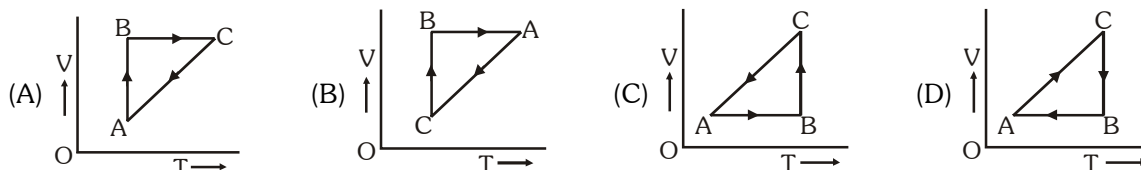
(A)   (B)   (C)   (D)

13*. q, w, ΔE and ΔH for the following process ABCD on a monoatomic gas are :-
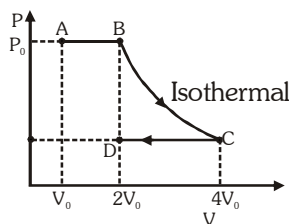
(A) $w = -2P_0V_0 \ln 2$, $q = 2P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$

(B) $w = -2P_0V_0 \ln 2$, $q = 2P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 2P_0V_0 \ln 2$

(C) $w = -P_0V_0 (1+\ln 2)$, $q = P_0V_0 (1+\ln 2)$, $\Delta E = 0$, $\Delta H = 0$

(D) $w = -P_0V_0 \ln 2$, $q = P_0V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$

14. The maximum efficiency of a heat engine operating between 100°C and 25°C is ?

(A) 20%   (B) 22.2%   (C) 25%   (D) None of these

15. A heat engine operating between 227°C and 27°C absorbs 2 kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is ?

(A) 0.4 kcal   (B) 0.8 kcal   (C) 4 kcal   (D) 8 kcal

16. For which of the following reactions. ΔS will the maximum :-

(A) $N_2(g) + 2H_2(g) \rightleftharpoons NH_3(g)$

(B) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(C) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(D) $2HI(g) \rightleftharpoons H_2(g) + I_2(s)$

17. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically ?

(A) $\frac{3}{2} R \ln \left(\frac{300}{200} \right)$ (B) $\frac{5}{2} R \ln \left(\frac{573}{273} \right)$ (C) $3R \ln \left(\frac{573}{473} \right)$ (D) $\frac{3}{2} R \ln \left(\frac{573}{473} \right)$

18. What can be concluded about the values of ΔH and ΔS from this graph ?
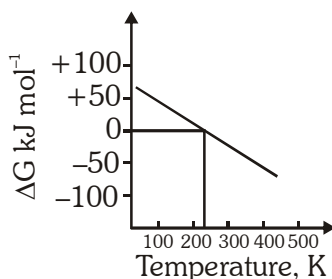
(A) $\Delta H > 0$, $\Delta S > 0$ (B) $\Delta H > 0$, $\Delta S < 0$ (C) $\Delta H < 0$, $\Delta S > 0$ (D) $\Delta H < 0$, $\Delta S < 0$

19. 1 mole of an ideal gas at 25°C is subjected to expand reversibly ten times of its initial volume. The change in entropy due to expansion is :-
(A) 19.15 JK^{-1} mole^{-1} (B) 16.15 JK^{-1} mole^{-1}
(C) 22.15 JK^{-1} mole^{-1} (D) none of these

20*. Following reaction occurs at 25°C :

$2NO$ (g, 1×10^{-5} atm) $+ Cl_2$ (g, 1×10^{-2} atm) $\rightleftharpoons$ $2NOCl$ (g, 1×10^{-2} atm).
$\Delta G°$ is :-
(A) -45.65 kJ   (B) -28.53 kJ   (C) -22.82 kJ   (D) -57.06 kJ

21. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?
(A) 80 cal   (B) 540 cal   (C) 620 cal   (D) zero

22. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?
(A) zero cal   (B) 540 cal   (C) 515.4 cal   (D) none

23. What is ΔU for the process described by figure. Heat supplied during the process q = 100 kJ.

(A) + 50 kJ

(B) – 50 kJ

(C) –150 kJ

(D) + 150 kJ

24 The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is :
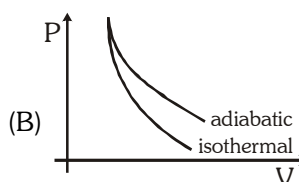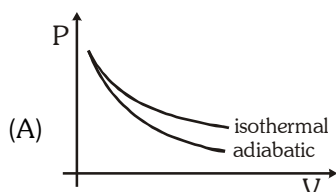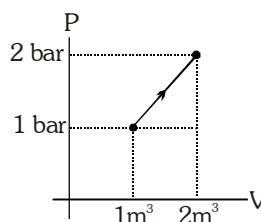
EXERCISE – 2 | **MCQ (ONE OR MORE CHOICE CORRECT)**

1. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the same change from the initial state to the final state were made by a different path, which of the following statements are correct.
(A) ΔH remain the same
(B) ΔH will depend upon the type of path
(C) Heat exchanged q will be same if the path is isobaric
(D) Heat exchanged q will be different if the path is not isobaric

2*. For which of the following processes, total entropy of universe increases.
(A) Melting one mole of ice to water at 0°C (B) Freezing one mole of water to ice at 0°C
(C) Freezing one mole of water to ice at – 10°C (D) Melting one mole of ice at 10°C into water

3*. The normal boiling point of a liquid 'A' is 350 K. ΔH_{vap} at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume ΔH_{vap} to be independent of pressure).
(A) $\Delta S_{vaporisation} > 100$ J/Kmole at 350 K and 0.5 atm (B) $\Delta S_{vaporisation} < 100$ J/K mole at 350 K and 0.5 atm
(C) $\Delta S_{vaporisation} < 100$ J/K mole at 350 K and 2 atm (D) $\Delta S_{vaporisation} = 100$ J/K mole at 350 K and 2 atm

4*. Which of the following statement(s) is/are false :

(A) $\Delta_r S$ for $\dfrac{1}{2} N_2(g) \rightarrow N(g)$ is positive

(B) ΔG_{system} is always zero for a reversible process in a closed system
(C) $\Delta G°$ for an ideal gas is a function of temperature and pressure
(D) entropy of a closed system is always maximized at equilibrium

5*. Which statement is / are correct:
(A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion.
(B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase
(C) When an ideal gas is subjected to adiabatic expansion it gets cooled
(D) Entropy increases in atomisation of dihydrogen

6. Which is / are **correct** statement.
(A) $w_{adiabatic} > w_{isothermal}$ in an ideal gas compression from same initial state to same final volume

(B) The value of γ $\left(\gamma = \dfrac{C_p}{C_v} \right)$ remains constant for diatomic gas at all temperature

(C) Entropy increases when an ideal gas expanded isothermally.
(D) $\Delta_r H$ & $\Delta_r S$ both are + ve for the decomposition of $MgCO_3$(s) .

7. In isothermal ideal gas compression:
(A) w is +ve (B) ΔH is zero (C) ΔS_{gas} is +ve (D) ΔG is +ve

8. Which one is correct about given P – V plot for 2 mole an ideal gas ?
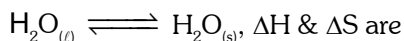**[Given CA is Isothermal process]**
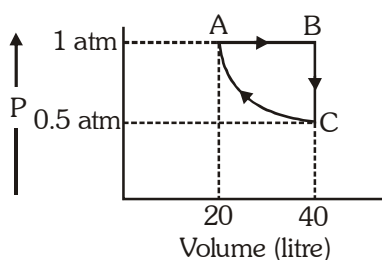
(A) $W_{AB} = -20$ L–atm (B) ΔU for Cycle = 0
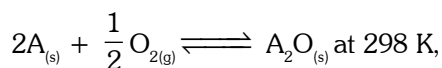(C) $\Delta S_{Cycle} = 0$ (D) $W_{CA} = +13.86$ L atm

9. Which of the following option(s) will show a decrease in Gibbs energy ?

(A) Combustiton of propane at 1 bar and 500 K.

(B) Vaprourisation of any liquid at 1 atm and above its normal boiling point.

(C) Fusion of H_2O at 1 atm and 0°C if its normal melting point is 0°C.

(D) Vaporisation of H_2O at 100°C and 1 bar if its normal boiling point is 100°C.

10. For which of the following reaction $\Delta H \neq \Delta U$:

(A) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(B) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(C) $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$

(D) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Match the Column

11*.

	Column-I (Process of reaction)		**Column-II (Positive, negative)**
(A)	For the process $H_2O_{(\ell)} \rightleftharpoons H_2O_{(s)}$, ΔH & ΔS are	(p)	–ve, +ve
(B)	For the endothermic reaction $2A_{(s)} + \dfrac{1}{2}O_{2(g)} \rightleftharpoons A_2O_{(s)}$ at 298 K, ΔS & ΔG are	(q)	+ve, –ve
(C)	C(diamond) $\rightleftharpoons$ C(graphite), favourable conditions for formation of diamond are high pressure and high temperature then ΔH_f of diamond and ΔS_f of graphite from diamond are	(r)	+ve, +ve
(D)	For the given reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, $E_{a(forward)}$ = 57.2 kJ and $E_{a(backward)}$ = 3.2 kJ, ΔH & ΔS for the given reaction	(s)	–ve, –ve
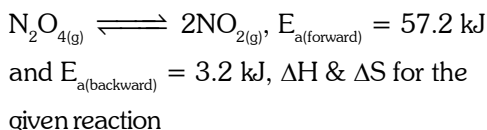
12*.

	Column-I (Process)		**Column-II (Entropy change)**
(A)	Reversible isothermal ideal gas expansion	(p)	$\Delta S_{surrounding} = 0$
(B)	Reversible adiabatic ideal gas compression	(q)	$\Delta S_{surrounding} < 0$
(C)	Adiabatic free expansion ($P_{ext} = 0$) of an ideal gas	(r)	$\Delta S_{surrounding} > 0$
(D)	Irreversible isothermal ideal gas compression	(s)	$\Delta S_{system} = 0$

EXERCISE – 3
SUBJECTIVE

1. In which of the following changes at constant pressure is work done by system on surrounding ? By the surrounding on system ?

	Initial state		*Final state*
(i)	H_2O (g)	$\longrightarrow$	$H_2O(\ell)$
(ii)	H_2O (s)	$\longrightarrow$	$H_2O(g)$
(iii)	H_2O (ℓ)	$\longrightarrow$	$H_2O(s)$
(iv)	$3H_2$ (g) + N_2(g)	$\longrightarrow$	$2NH_3$(g)
(v)	$CaCO_3$ (s)	$\longrightarrow$	CaO (s) + CO_2(g)

2. The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J which is exchanged with the surroundings. What are q, w and ΔE ?

3. The enthalpy of combustion of glucose is –2808 kJ mol^{-1} at 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5 Kg].

(a) To climb a flight of stairs rising through 3m.

(b) To climb a mountain of altitude 3000 m ?

Assume that 25% of enthalpy can be converted to useful work.

4. What is ΔE when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation, (ΔH vap.) of water at 100°C is 40.66 kJ mol^{-1}.

5. If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.

6. When the following reaction was carried out in a bomb calorimeter, ΔE is found to be –742.7 kJ/mol of NH_2CN (s) at 298 K.

$$NH_2CN(s) + \frac{3}{2} O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(\ell)$$
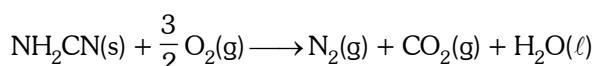
Calculate ΔH_{298} for the reaction.

7. When 1 mole of ice melt at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔE for the reaction.

8. Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

9*. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27°C in a cylinder fitted with a piston. Find the value of ΔE, q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

10*. Five moles of an ideal gas at 300K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext. pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly.

11. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

    (a)   What is final temperature

    (b)   What is work done.

        Given $\gamma = 1.33$ and $C_V = 25.08$ J mol^{-1} K^{-1} for CO_2.

12*. A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 to 248.44 K. Assume the gas behaves perfectly. Estimate the value of $C_{V,m}$.

13. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C ?

14*. One mole of an ideal monoatomic gas is carried through the cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.
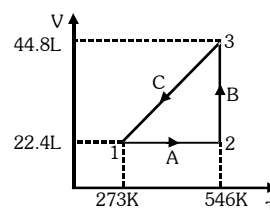
Table-1			
State	P	V	T
1			
2			
3			

Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					
overall					

15*. The standard enthalpy of formation of water liquid is –285.76 kJ at 298 K. Calculate the value at 373K. The molar heat capacities at constant pressure (C_p) in the given temperature range of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ are respectively 38.83, 29.16 and 75.312 JK^{-1}mol^{-1}.

EXERCISE – 4   **RECAP OF AIEEE/JEE (MAIN)**

1. In a irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (ΔG) and change in entropy (ΔS) satisfy the criteria :-   *[AIEEE-2003]*

(A) $(\Delta S) = 0, (\Delta G) = 0$ (B) $(\Delta S) = 0, (\Delta G) > 0$ (C) $(\Delta S) < 0, (\Delta G) < 0$ (D) $(\Delta S) > 0, (\Delta G) < 0$

2. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?   *[AIEEE-2003]*

(A) < 40 kJ   (B) Zero   (C) 40 kJ   (D) > 40 kJ

3. The enthalpy change for a reaction does not depend upon :-   *[AIEEE-2003]*

(A) The nature of intermediate reaction steps

(B) The differences in initial or final temperatures of involved substances

(C) The physical states of reactants and products

(D) Use of different reactants for the same product

4. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is :-   *[AIEEE-2003]*

(A) $\Delta G° = RT \ln K_C$ (B) $-\Delta G° = RT \ln K_C$ (C) $\Delta G = RT \ln K_C$ (D) $-\Delta G = RT \ln K_C$

5. In conversion of lime-stone to lime,

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

the values of $\Delta H°$ and $\Delta S°$ are $+179.1$ kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-   *[AIEEE-2007]*

(A) 1008 K   (B) 1200 K   (C) 845 K   (D) 1118 K

6. Identify the correct statement regarding a sponateous process :-   *[AIEEE-2007]*

(A) For a spontaneous process in an isolated system, the change in entropy is positive

(B) Endothermic processes are never spontaneous

(C) Exothermic processes are always spontaneous

(D) Lowering of energy in the reaction process is the only criterion for spontaneity

7*. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction,

$\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be   *[AIEEE-2008]*

(A) 1250 K   (B) 500 K   (C) 750 K   (D) 1000 K

8. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is :-   *[AIEEE-2011]*

(A) 32.3 J mol^{-1} K^{-1} (B) 42.3 J mol^{-1} K^{-1} (C) 38.3 J mol^{-1} K^{-1} (D) 35.8 J mol^{-1} K^{-1}

9*. The incorrect expression among the following is :-   *[AIEEE-2012]*

(A) $K = e^{-\Delta G°/RT}$ (B) $\dfrac{\Delta G_{system}}{\Delta S_{total}} = -T$

(C) In isothermal process, $W_{reversible} = -nRT \ln \dfrac{V_f}{V_i}$ (D) $\ln K = \dfrac{\Delta H° - T\Delta S°}{RT}$

10. One mole of an ideal gas is expanded isothermally and reversibly to half its initial pressure. ΔS for the process in J K^{-1} mol^{-1} is [ln 2 = 0.693 and R = 8.314, J/(mol/K)] : **[AIEEE-2012]**

(A) 10.76   (B) 6.76   (C) 8.03   (D) 5.76

11. The entropy of a sample of a certain substance increases by 0.836 JK^{-1} on adding reversibly 0.3344 J of heat at constant temperature. The temperature of the sample is :- **[AIEEE-2012]**

(A) 0.4 K   (B) 2.5 K   (C) 0.016 K   (D) 0.3 K

12*. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208J of heat. The values of q and w for the process will be :-

(R = 8.314 J/mol K) (ln 7.5 = 2.01) **[JEE Main-2013]**

(A) q = + 208 J, w = – 208 J   (B) q = – 208 J, w = – 208 J

(C) q = – 208 J, w = + 208 J   (D) q = + 208 J, w = + 208 J

13*. For complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomd calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, $\Delta_c H$, for the reaction will be: (R = 8.314 kJ mol^{-1}) **[JEE Main-2014]**

(A) – 1366.95 kJ mol^{-1} (B) – 1361.95 kJ mol^{-1} (C) – 1460.50 kJ mol^{-1} (D) – 1350.50 kJ mol^{-1}

14. The following reaction is performed at 298 K.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$ **[JEE Main-2015]**

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K ? ($K_p = 1.6 \times 10^{12}$)

(A) R(298) ℓn (1.6×10^{12}) – 86600   (B) 86600 + R(298) ℓn (1.6×10^{12})

(C) $86600 - \dfrac{\ell n(1.6 \times 10^{12})}{R(298)}$ (D) 0.5[2 × 86,600 – R(298) ℓn (1.6×10^{12})]

15. ΔU is equal to : **[JEE Main-2017]**

(A) Isothermal work   (B) Isochoric work   (C) Isobaric work   (D) Adiabatic work

16. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:- **[JEE Main-2017]**

(A) 10 J of the work will be done by the surrounding on gas.

(B) 6 J of the work will be done by the surrounding on gas.

(C) 10 J of the work will be done by the gas.

(D) 6 J of the work will be done by the gas.

17. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is : **[JEE Main-2017]**

(Given $\Delta_{fus}H$ = 6 kJ mol^{-1} at 0°C, $C_P(H_2O, l)$ = 75.3 J mol^{-1} K^{-1}, $C_P(H_2O, s)$ = 36.8 J mol^{-1} K^{-1})

(A) –6.56 kJ mol^{-1} (B) –5.81 kJ mol^{-1} (C) –6.00 kJ mol^{-1} (D) –5.44 kJ mol^{-1}

18. An ideal gas undergoes a cyclic process as shown in figure. **[JEE Main-2018]**
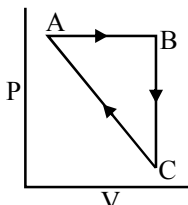
$DU_{BC} = -5 \text{ kJ mol}^{-1}$, $q_{AB} = 2 \text{ kJ mol}^{-1}$

$W_{AB} = -5 \text{ kJ mol}^{-1}$, $W_{CA} = 3 \text{ kJ mol}^{-1}$

Heat absorbed by the system during process CA is :-

(A) 18 kJ mol⁻¹ → 18 kJ mol^{-1} (B) $+5 \text{ kJ mol}^{-1}$ (C) -5 kJ mol^{-1} (D) -18 kJ mol^{-1}

19. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is :

(**Specific heat of water liquid and water vapour are 4.2 kJ K⁻¹ kg⁻¹ and 2.0 kJ K⁻¹ kg⁻¹** ; heat of liquid fusion and vapourisation of water are 344 kJ kg⁻¹ and 2491 kJ kg⁻¹, respectively).

(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583) *[JEE Main-2019]*

(A) 7.90 kJ kg⁻¹ K⁻¹ (B) 2.64 kJ kg⁻¹ K⁻¹ (C) 8.49 kJ kg⁻¹ K⁻¹ (D) 4.26 kJ kg⁻¹ K⁻¹

20. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is:

[JEE Main-2019]

(A)   (B)   (C)   (D)
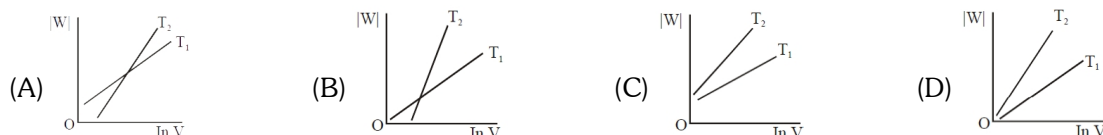
21. An ideal gas undergoes isothermal compression from 5 m³ against a constant external pressure of 4 Nm⁻². Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol⁻¹ K⁻¹, the temperature of Al increases by : *[JEE Main-2019]*

(A) $\dfrac{3}{2}K$ (B) $\dfrac{2}{3}K$ (C) 1K (D) 2 K

22. A process has $\Delta H = 200 \text{ J mol}^{-1}$ and $\Delta S = 40 \text{ JK}^{-1}\text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous : *[JEE Main-2019]*

(A) 5 K (B) 4 K (C) 20 K (D) 12 K

23. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by $\Delta_r G^\circ = A - Bt$, Where A and B are non-zero constants. Which of the following is TRUE about this reaction ?

[JEE Main-2019]

(A) Exothermic if B < 0 (B) Exothermic if A > 0 and B < 0

(C) Endothermic if A < 0 and B > 0 (D) Endothermic if A > 0

24. Two blocks of the same metal having same mass and at temperature T_1 and T_2, respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy ΔS, for this process is : *[JEE Main-2019]*

(A) $2C_p \ln\left(\dfrac{T_1 + T_2}{4T_1T_2}\right)$ (B) $2C_p \ln\left[\dfrac{(T_1 + T_2)^{\frac{1}{2}}}{T_1T_2}\right]$ (C) $C_p \ln\left[\dfrac{(T_1 + T_2)^2}{4T_1T_2}\right]$ (D) $2C_p \ln\left[\dfrac{T_1 + T_2}{2T_1T_2}\right]$

25. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as:

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}) = 120 - \dfrac{3}{8}T$$

The major component of the reaction mixture at T is : *[JEE Main-2019]*

(A) X if T = 315 K (B) X if T = 350 K (C) Y if T = 300 K (D) Y if T = 280 K

26. For diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities ?   **[JEE Main-2019]**

(A)   (B)   (C)   (D)
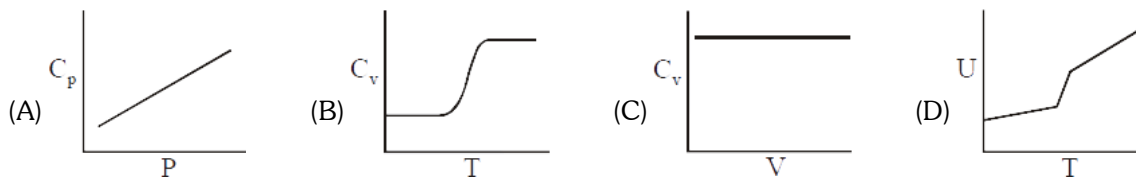
27. The combination of plots which does not represent isothermal expansion of an ideal gas is : **[JEE Main-2019]**

(a)   (b)   (c)   (d)
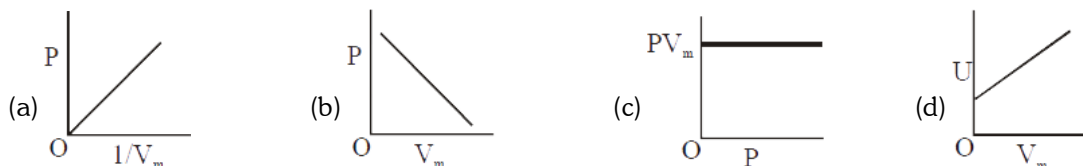
(A) (a) and (c)   (B) (a) and (d)   (C) (b) and (d)   (D) (b) and (c)

28. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero)

(A) Cyclic process : $q = -w$ (B) Isothermal process : $q = -w$

(C) Adiabatic process : $\Delta U = -w$ (D) Isochoric process : $\Delta U = q$

29. For silver, $C_p (JK^{-1}mol^{-1}) = 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300K to 1000 K at 1 atm pressure, the value of ΔH will be close to

(A) 21 kJ   (B) 16 kJ   (C) 13 kJ   (D) 62 kJ

30. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28$ JK^{-1}mol^{-1}, calculate ΔU and ΔpV for this process. (R = 8.0 JK^{-1} mol^{-1}]

(A) $\Delta U = 14$ kJ; $\Delta (pV) = 4$ kJ   (B) $\Delta U = 14$ kJ; $\Delta (pV) = 18$ kJ

(C) $\Delta U = 2.8$ kJ; $\Delta (pV) = 0.8$ kJ   (D) $\Delta U = 14$ kJ; $\Delta (pV) = 0.8$ kJ

31. Among the following, the set of parameters that represents path function, is :

(a) $q + w$ (b) q (c) w (d) H–TS

(A) (a) and (d)   (B) (b), (c) and (d)   (C) (b) and (c)   (D) (a), (b) and (c)

32. During compression of a spring the work done is 10kJ and 2kJ escaped to the surroundings as heat. The change in internal energy, ΔU(inkJ) is:

(A) 8   (B) 12   (C) – 12   (D) –8

33. A process will be spontaneous at all temperatures if :-

(A) $\Delta H > 0$ and $\Delta S < 0$ (B) $\Delta H < 0$ and $\Delta S > 0$ (C) $\Delta H > 0$ and $\Delta S > 0$ (D) $\Delta H < 0$ and $\Delta S < 0$

34. The difference between ΔH and ΔU (ΔH–ΔU), when the combustion of one mole of heptane (A) is carried out at a temperature T, is equal to:

(A) 3RT   (B) –3RT   (C) –4RT   (D) 4RT

35. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1bar. The work done in kJ is :

(A) –9.0   (B) +10.0   (C) –0.9   (D) –2.0

1. A process A $\longrightarrow$ B is difficult to occur directly instead it takes place in three successive steps :-

C $\longrightarrow$ D ΔS (A $\longrightarrow$ C) = 50 $e.u.$
     ΔS (C $\longrightarrow$ D) = 30 $e.u.$
A   B ΔS (B $\longrightarrow$ D) = 20 $e.u.$
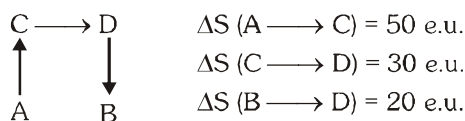
where $e.u.$ is entropy unit.

Then the entropy change ΔS for the process (A $\longrightarrow$ B) is   **[IIT-JEE-2006]**

(A) +100 $e.u.$ (B) –60 $e.u.$ (C) –100 $e.u.$ (D) +60 $e.u.$

2. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one :-

(A) 4/2 R   (B) 3/2 R   (C) 5/2 R   (D) zero   **[IIT-JEE-2006]**

3. For the reaction,   **[IIT-JEE-2006]**

$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$; $\Delta H = -560 \, kJ \, mol^{-1}$

In one litre vessel at 500 K the initial pressur is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change in internal energy. All the above gases show significant deviation from ideal behaviour. (1 Latm = 0.1 kJ)

4. For the process H_2O (l) (1 bar, 373 K) $\longrightarrow$ $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is :-   **[JEE 2007]**

(A) $\Delta G = 0$, $\Delta S = + ve$ (B) $\Delta G = 0$, $\Delta S = - ve$

(C) $\Delta G = + ve$, $\Delta S = 0$ (D) $\Delta G = - ve$, $\Delta S = +ve$

5. **Statement-1 :** There is a natural asymmetry between converting work to heat and converting heat to work.

Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.   **[JEE 2008]**

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

6. **Statement-1 :** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.   **[JEE 2008]**

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

7. Among the following, the state function(s) is (are)   **[JEE 2009]**

(A) Internal energy   (B) Irreversible expansion work

(C) Reversible expansion   (D) Molar enthalpy

8*. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d, then the integer closed to the ratio w_d / w_s is-   **[JEE 2010]**
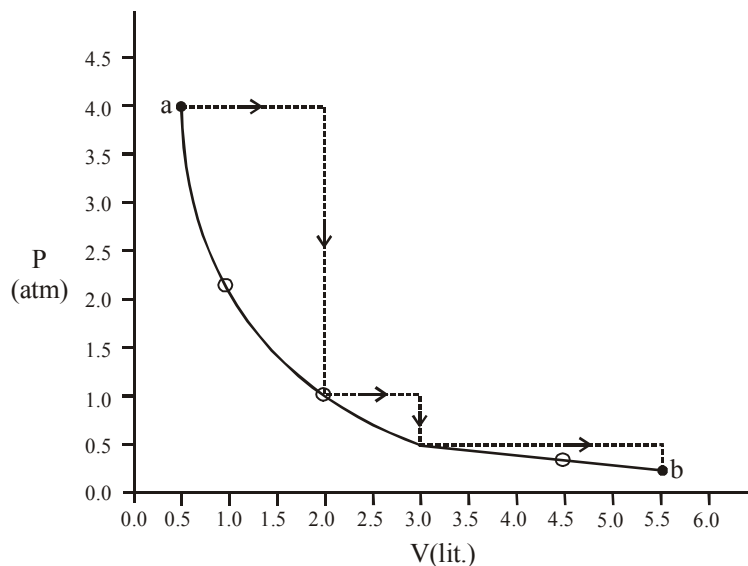
9*. Match the transformations in **Column-I** with appropriate option in **Column-II**   **[JEE 2011]**

Column-I		**Column-II**	
(A)	$CO_2(s) \rightarrow CO_2(g)$	(p)	phase transition
(B)	$CaCO_3(g) \rightarrow CaO(s) + CO_2(g)$	(q)	allotropic change
(C)	$2H\bullet \rightarrow H_2(g)$	(r)	ΔH is positive
(D)	$P_{(white, solid)} \rightarrow P_{(red,solid)}$	(s)	ΔS is positive
		(t)	ΔS is negative

10*. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ?   **[JEE 2012]**
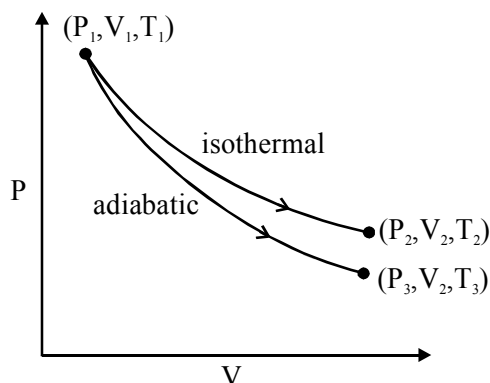
(A) $T_1 = T_2$ (B) $T_3 > T_1$ (C) $w_{isothermal} > w_{adiabatic}$ (D) $\Delta U_{isothermal} > \Delta U_{adiabatic}$

11. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done]   **[IIT-JEE 2012]**

(A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

(B) $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$

(C) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$

(D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$
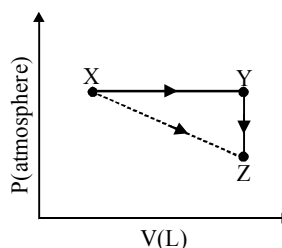
Paragraph for Question (Q.12 and 13)

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. **[IIT-JEE 2013]**
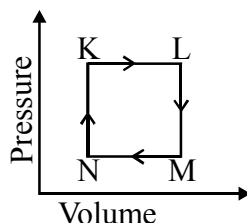
12. The pair of isochoric processes among the transformation of states is

(A) K to L and L to M   (B) L to M and N to K   (C) L to M and M to N   (D) M to N and N to K

13*. The succeeding operations that enable this transformation of states are

(A) Heating, cooling, heating, cooling   (B) cooling, heating, cooling, heating

(C) Heating, cooling, cooling, heating   (D) Cooling, heating, heating, cooling

14. For the process $H_2O(l) \rightarrow H_2O(g)$ at T = 100 °C and 1 atmosphere pressure, the correct choice is **[JEE 2014]**

(A) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} > 0$ (B) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$

(C) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} > 0$ (D) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} < 0$

15*. An ideal gas in a thermally insulated veseel at internal pressure = P_1, Volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion. **[JEE 2014]**
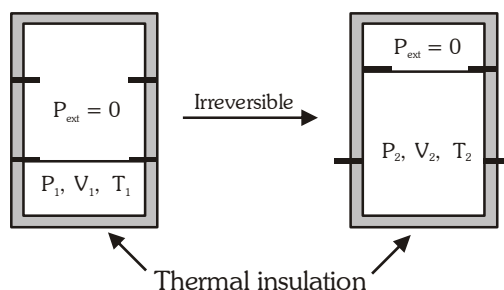
(A) q = 0   (B) $T_2 = T_1$ (C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

16*. Match the thermodynamic processes given Column I with the expressions given under Column II.

	Column I		Column II	**[JEE 2015]**
(A)	Freezing of water at 273 K and 1 atm	(P)	q = 0	
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q)	w = 0	
(C)	Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R)	$\Delta S_{sys} < 0$	
(D)	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(S)	$\Delta U = 0$	
		(T)	$\Delta G = 0$	

17*. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is **[JEE 2016]**

(A) 5.763   (B) 1.013   (C) –1.013   (D) –5.763

18*. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are)   **[JEE 2017]**

    (A) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1.

    (B) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

    (C) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.

    (D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.

19*. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

        $\Delta_f G^o$ [C(graphite)] = 0 kJ mol^{-1} $\Delta_f G^o$ [C(diamond)] = 2.9 kJ mol^{-1}

    The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is   **[JEE 2017]**

    [Useful information : 1 J = 1 kg m^2 s^{-2} ; 1 Pa = 1 kg m^{-1} s^{-2} ; 1 bar = 10^5 Pa]

    (A) 14501 bar   (B) 29001 bar   (C) 58001 bar   (D) 1450 bar

20. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below.
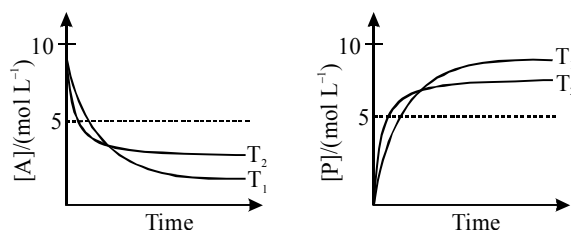
    If $T_2 > T_1$, the correct statement(s) is (are)   **[JEE 2018]**

    (Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than $\dfrac{T_2}{T_1}$. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

    (A) $\Delta H^\theta < 0, \Delta S^\theta < 0$ (B) $\Delta G^\theta < 0, \Delta H^\theta > 0$ (C) $\Delta G^\theta < 0, \Delta S^\theta < 0$ (D) $\Delta G^\theta < 0, \Delta S^\theta > 0$

21. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below

    $2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$
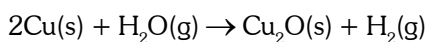
    p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is ___.

    (Given : total pressure = 1 bar, R (universal gas constant) = 8 JK^{-1}mol^{-1}, ln(10) = 2.3. Cu(s) and Cu$_2$O(s) are mutually immiscible.

    At 1250 K : $2Cu(s) + 1/2 O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\theta = -78{,}000$ J mol^{-1}

    $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g)$; $\Delta G^\theta = -1{,}78{,}000$ J mol^{-1}; G is the Gibbs energy)   **[JEE 2018]**

22. Consider the following reversible reaction,   **[JEE 2018]**

        $A(g) + B(g) \rightleftharpoons AB(g).$
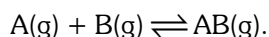
    The activition energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^θ (in J mol^{-1}) for the reaction at 300 K is___.   ***(Given ; ln (2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)***

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	B	D	A	D	B	B	A	A	D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	C	A	A	B	B	C	A	A	A
Que.	21	22	23	24						
Ans.	D	C	B	A						

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	AC	CD	AC	BCD	ACD	ACD	ABD	ABCD	ABD	BCD

- **Match the Column**

  11*. (A) - (s), (B) - (p), (C) - (r), (D) - (r)   **12*.** (A) - (q), (B) - (ps), (C) - (p), (D) - (r)

EXERCISE-3

1. (i) + w, (ii) – w, (iii) + w, (iv) + w, (v) – w

2. q = –65J, w = 20 J, ΔE = –45 J

3. (a) 0.47 g , (b) 0.47 kg

4. ΔE = 75.11 kJ

5. ΔE = 0.993 kcal, ΔH = 1 kcal

6. –741.5 kJ

7. $\Delta H \cong \Delta E$ = 1440 calories

8. –10 J

9*. ΔE = –39.03 kJ mol^{-1}, q = –36.5 kJ, w = –2.53 J

10*. w_{irr} = –9356.25 J, w_{rev} = –17291.6 J, $\Delta U = \Delta H = 0$

11. T_2 = 100 k, w = –5.016 kJ

12*. $C_{v,m}$ = 31.6 Jk^{-1} mol^{-1}

13. w = –3.988 kJ

14*.

Table-1			
State	P	V	T
1	1	22.4L	273
2	2atm	22.4	546K
3	1atm	44.8	546K

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	3/2 R(273)	0	3/2 R(273)	5/2 R (273)
B	Isothermal	546 R ln 2	–546 R ln 2	0	0
C	Isobaric	–5/2 R (273)	R (273)	–3/2 R(273)	–5/2 R(273)
overall	cyclic	546Rln2–273R	273R–546Rln2	0	0

15*. ΔH^o_{373} (H$_2$O, (ℓ)) = –284.11 kJ

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	B	A	B	D	A	C	C	D	D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	A	A	A	D	D	B	A	B	D	B
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	A	D	C	A	A	C	C	D	A
Que.	31	32	33	34	35					
Ans.	C	A	B	C	C					

EXERCISE-5

1. (D)   **2.** (A)   **3.** –557 kJ/mol   **4.** (A)

5. (A)   **6.** (D)   **7.** (AD or ACD)   **8*.** (2)

9*. (A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t)   **10*.** (AD)

11. (AC)   **12.** (B)   **13*.** (C)   **14.** (B)

15*. (ABC)   **16*.** (A) → (R), (T), (B) → (P), (Q), (S), (C) → (P), (Q), (S), (D) → (P), (Q), (S), (T)

17*. (C)   **18*.** (ABD)   **19*.** (A)   **20.** (AC)

21. –14.6   **22.** 8500

THERMOCHEMISTRY

Recap of Early Classes

In Thermodynamics we discuss about the laws of thermodynamics and feasibility. Now this chapter Thermochemistry deals with the measurement and study of heat change that occur when a chemical reaction takes place. Heat is generally evolved or absorbed whenever a chemical reaction takes place, a solution is formed or other changes in the state of matter (vaporisation, fusion, phase transition etc) occurs. The heat chane accompanying chemical reactions or physical changes are measured experimentally with the help of calorimeter.

THERMOCHEMISTRY

1.0 ENDOTHERMIC/EXOTHERMIC REACTIONS

SL AL

All chemical processes are associated with energy changes in chemical reactions. A thermochemical equation, represents both the material change and the energy. While writing a thermochemical equation, the heat evolved in case of exothermic reaction, or the heat absorbed in case of endothermic reaction, is indicated on the product side of the balanced chemical equation. For example,

(i) $\quad H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = -285.91 \text{ kJ}$

(ii) $\quad C(\text{graphite}) + 2S(\text{rhombic}) \rightarrow CS_2 \qquad \Delta H = +91.96 \text{ kJ}$
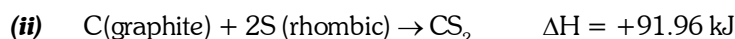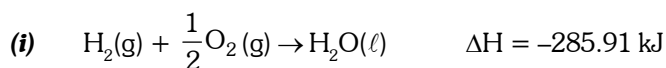
The most stable physical state of the reacting species and the products is also indicated in brackets. Thus, a thermochemical equation gives complete information about the material change and the associated heat change. It is clear that the first reaction is exothermic and the second one endothermic.

- **Examples of exothermic reactions**

  Coal is burnt simply for the large amount of energy available during its combustion : When water is added to quick lime (CaO) for preparing whitewash, a considerable amount of heat is produced during the reaction. The heat produced warms up the water. When we add dilute hydrochloric acid to a test tube containing granulated zinc, hydrogen gas is evolved. The reaction is accompanied by evolution of heat.

- **Examples of endothermic reactions**

  When a small quantity of ammonium chloride (NH_4Cl) is dissolved in water in a test tube, the tube becomes colder than before. During this chemical reaction heat is absorbed from the surroundings (test tube).

  When the crystals of sodium thiosulphate ($Na_2S_2O_3.5 H_2O$) commonly called hypo, are dissolved in water, a cooling effect takes place.

  One mole of nitrogen reacts with one mole of oxygen to form two moles of nitric oxide. 180.5kJ of heat is absorbed at constant temperature and the reaction may be expressed as:

  or $N_2(g) + O_2(g) \rightarrow 2NO(g)$
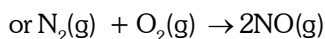
2.0 STANDARD ENTHALPY OF REACTION

SL AL

Enthalpy of reaction is defined as the quantity of heat evolved or absorbed. When molar quantities of substances react in amounts represented by chemical equation at constant pressure and temperature, the substances being in their standard states.

For example :

$\qquad H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad \Delta H = -183.92 \text{ kJ}$
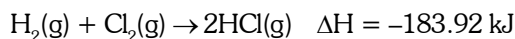
Thus, when one mole of gaseous hydrogen reacts with one mole of gaseous chlorine, 183.92 kJ of heat is evolved. This is the heat of the reaction for the above chemical reaction.

$\qquad \Delta H_r = \Sigma H_{products} - \Sigma H_{reactants}$

Factors Affecting Heat or Enthalpy Change : The enthalpy change of reaction (ΔH) depends upon the following factors :

Physical state of the reactants and the products : The ΔH of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the heat of reaction is different than when they combine to form gaseous water.
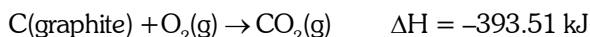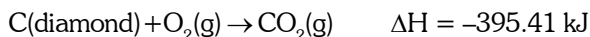
$\qquad H_2(g) \quad + \quad O_2(g) \qquad \rightarrow \qquad H_2O(\ell) \quad \Delta H = -285.83 \text{ kJ}$

$\qquad H_2(g) \quad + \quad O_2(g) \qquad \rightarrow \qquad H_2O(g) \quad \Delta H = -241.82 \text{ kJ}$
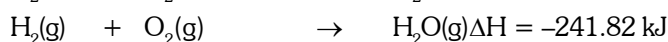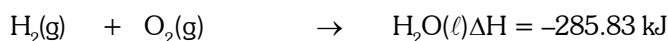
- **Quantities of reactants**

    The amount of heat evolved or absorbed depends upon the amount of reactants. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.

- **Allotropic modification**

    The amount of heat evolved or absorbed for different forms of the same substance are different. For example,

    $$C(diamond) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -395.41 \text{ kJ}$$
    $$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.51 \text{ kJ}$$

    Although ΔH changes with temperature, it can be considered constant within a small range of temerpature.

    As the heat of a reaction varies with temperature it is desirable to fix up a standard or a reference state. A substance is said to be in standard state when it is present in its most stable state at 298 K under a pressure of one atmosphere. The heat change that occurs when a process is carried out at 298K and one atmospheric pressure is called standard heat change. It is represented as $\Delta H°$ where the superscript (°) indicates the standard state. If the reactants and products are in their standard states, then the enthalpy of a reaction is termed as the standard enthalpy of reaction

    Note : *The thermodynamic standard state can be established at any temperature, but most book tabulate standard enthalpy at 298.15K.The superscript (°) indicate rather pressure of 1 bar. Thus there can be one standard state at each temperature.*

3.0 HESS'S LAW OF CONSTANT HEAT OF SUMMATION

SL AL

This law put forth by Hess states that "the resultant enthalpy change in a reaction is the same whether it occurs in one or several steps".

We illustrate this law by considering a example :

(i) The formation of urea from carbon, oxygen and ammonia may take place directly in one step or in two steps as shown below :
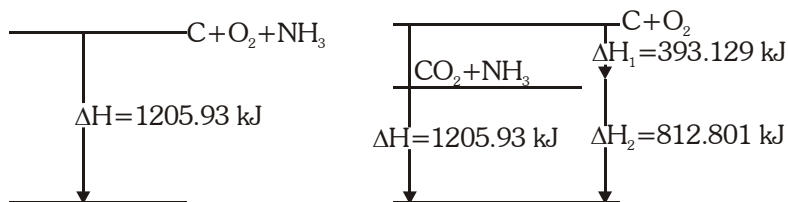
(i) One step reaction   **(ii)** Two step reaction

The enthalpy change when the reaction takes place in two steps is given by

$$\Delta H_1 + \Delta H_2 = -393.129 - 812.801 = -1205.93 \text{ kJ}$$

This is seen to be equal to ΔH, the change involved in one step reaction.

———— Illustrations ————

Illustration 1*. Calculate the standard heat of formation of carbon disulphide (ℓ). Given that the standard heats of combustion of carbon (s) sulphur (s) and carbon disulphide (ℓ) are 393.3, –293.72 and –1108.76kJ mol^1 respectively.

Solution. The given data can be written in thermochemical equation form as :

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -393.5 \text{ kJ} \qquad ...(i)$$
$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad\qquad \Delta H = -293.72 \text{ kJ} \qquad ...(ii)$$
$$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g) \qquad \Delta H = -1108.76 \text{ kJ} ...(iii)$$

The required equation is:

$$C(s) + 2S(g) \longrightarrow CS_2(\ell) \qquad\qquad \Delta H = ?$$

Multiplying equation (ii) by 2 and adding to equation (i) we get,

$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g)$ $\Delta H = -587.44$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g)$ $\Delta H = -980.74$ kJ
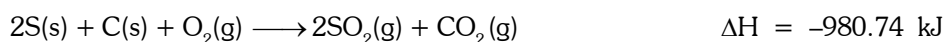
Subtracting equation (iii) from the above equation we have,

$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g)$ $\Delta H = -980.74$ kJ

$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g)$ $\Delta H = -1108.76$ kJ

$C(s) + 2S(g) \longrightarrow CS_2(\ell)$ $\Delta H = -128.02$ kJ
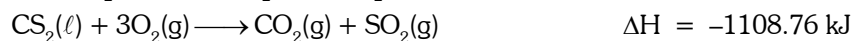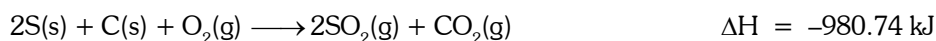
4.0 STANDARD ENTHALPY OF FORMATION

SL AL

The heat of formation ΔH_f depends upon the condition of temperature, pressure and physical state (gas, liquid or solid) of the reactants and the products. Therefore the heat change accompanying the formation of one mole of a compound from its elements when all the substances are in their standard states (1 atm pressure and 298 K), is called the standard heat of formation. It is expressed as ΔH_f°.

Since no heat changes are involved in the formation of elements form themselves in their standard states, the standard enthalpy of formation of all elements is zero.

For example, the standard enthalpy of formation (ΔH_f°) for $H_2O_{(\ell)}$ is - 286 kJ mol^{-1} i.e., when one mole of liquid water is formed from its elements $H_{2(g)}$ and $O_{2(g)}$ at 298 K and 1 atm pressure. The negative value of ΔH_f° indicates the formation of a stable compound.

5.0 STANDARD HEAT OF REACTION FROM STANDARD HEATS OF FORMATION

SL AL

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions. The standard heat of any reaction (ΔH°) is equal to the difference between the sum of ΔH_f° of all the reactants and that of ΔH_f of all the products properly multiplied by their stiochiometric coefficients.

ΔH° = Sum of the standard heats of formation of products - Sum of the standard heats of formation of reactants.

i.e., $\Delta H^\circ = \Sigma\Delta H_{f\ (products)}^\circ - \Sigma\Delta H_{f\ (reactants)}^\circ$ For a reaction,
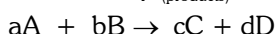
     $aA + bB \rightarrow cC + dD$

     $\Delta H^\circ = \Sigma\Delta H_{f\ (products)}^\circ - \Sigma\Delta H_{f\ (reactants)}^\circ$

     $= [c\Delta H_f^\circ (C) + d\Delta H_f^\circ (D)] - [a\Delta H_f^\circ (A) + b\Delta H_f^\circ (B)]$

Consider the combustion of CH_4, the enthalpy change of the reaction is equal to the entahlpy of combustion of CH_4.

$$\Delta H_r^\circ = [\Delta H_f^\circ(CO_{2(g)}) + 2.\Delta H_f^\circ(H_2O_{(\ell)})] - [2\Delta H_f^\circ(O_{2(g)}) + \Delta H_f^\circ(CH_4)]$$
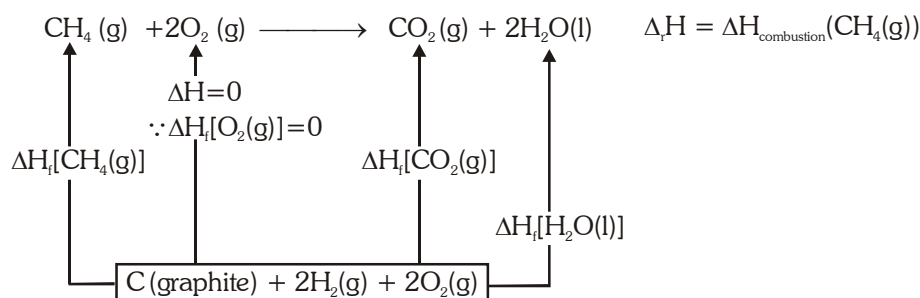
6.0 ENTHALPY OF COMBUSTION
SL AL

Enthalpy of combustion of a given compound is defined as follows :

It is the enthalpy change when one mole of this compound combines with the requisite amount of oxygen to given products in their stable forms.

For example, the standard enthalpy of combustion of methane at 298.15 K is –890.36 kJ mol^{-1}. This implies the following reaction :

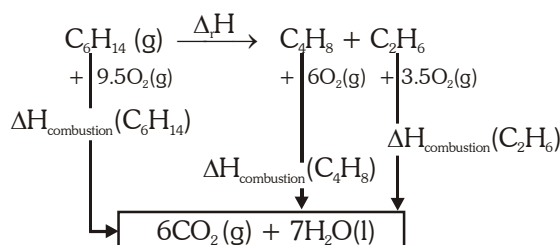$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \quad \Delta H° = -890.36 \text{ kJ mol}^{-1}$$
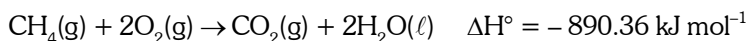
The standard enthalpy of combustion of methane at 298.15 K may be written as

$$\Delta_c H°(CH_4, g, 298.15 \text{ K}) = -890.36 \text{ kJ mol}^{-1}$$

6.1 Application of Enthalpy of Combustion
SL AL

Consider a reaction of disproportination of C_6H_{14} into C_4H_8 and C_2H_6. The following diagram shows how enthalpy of combustions can be used to estimate entlalpy of reaction.

$$C_6H_{14} (g) \xrightarrow{\Delta_r H} C_4H_8 + C_2H_6$$

$$+ \Big| 9.5O_2(g) \qquad + \Big| 6O_2(g) \ + \Big| 3.5O_2(g)$$

$$\Delta H_{combustion}(C_6H_{14}) \qquad\qquad\qquad \Delta H_{combustion}(C_2H_6)$$

$$\Delta H_{combustion}(C_4H_8)$$

$$\boxed{6CO_2 (g) + 7H_2O(l)}$$

From the inspection of the above diagram, it is clear that

$$\Delta H_{reaction} = \Delta H_{combustion}(C_6H_{14}) - \Delta H_{combustion}(C_4H_8) - \Delta H_{combustion}(C_2H_6)$$

Hence $\quad \Delta H_{reaction} = \Delta H_{combustion}(\text{Reactant's}) - \Delta H_{combustion}(\text{Products})$

6.2 Experimental Determination of Enthalpy of Combustion
SL AL

- **Constant volume bomb calorImeter**

  The heat changes in chemical reactions are measured with the help of calorimeters. Depending upon the requirements of experiments different types of calorimeters are used. In general, reactions taking place at constant volume and involving gases are carried out in a closed container with rigid walls that can withstand high pressures such as a bomb calorimeter. The body of the bomb calorimeter is made of heavy steel. The steel vessel is coated inside with gold or platinum to avoid oxidation of steel during the chemical reactions. The vessel is fitted with a tight screw cap.

Constant volume bomb calorimeter

There are two electrodes R_1 and R_2, which are connected to each other through a platinum wire S, which remains dipped in a platinum cup just below it. The substance under investigation is taken in platinum cup (few grams). The vessel is then filled with excess of oxygen at a pressure of about 15200 to 19000 mm of Hg and sealed. It is now dipped in an insulated water bath provided with a mechanical stirrer and a thermometer, sensitive enough to read upto 0.01°C (Beckmann's thermometer). The initial temperature of water is noted and the chemical reaction (combustion) is initiated by passing electric current through the platinum wire. The heat evolved during the chemical reactions raises the temperature of water, which is recorded from the thermometer. By knowing the heat capacity of the calorimeter and also the rise in temperature, the heat of chemical reaction or heat of combustion at constant volume can be calculated by using the expression.

$$\Delta U = -C \times \Delta T \times (M/w)$$

where, C = Heat capacity of calorimeter system, ΔT = Rise in temperature, M = Molecular mass of substance and w = Mass of substance taken.
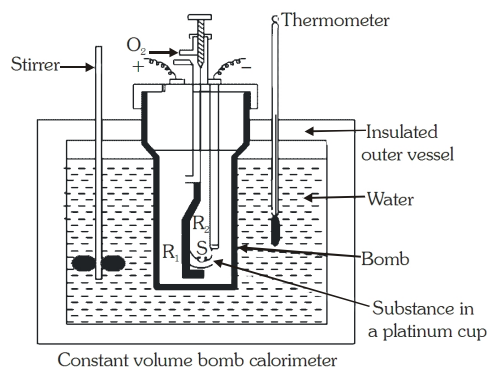
Illustrations

Illustration 2*. 0.138 gm sample of solid magnesium (molar mass = 24.3 g mol^{-1}) is burned in a constant volume bomb calorimeter that has a heat capacity of 1.77 kJ/°C. The calorimeter contains 300 mL of water (density = 1g/mL) and its temperature is raised by 1.126°C. Calculate enthalpy of combustion of magnesium at 289 K.

Solution. We have, $q_{water} = m_{water} \, C_{water} \, \Delta T$

or
$q_{water} = 300 \times 1 \times 4.184 \times 1.126 = 1413 \text{ J} = 1.413 \text{ kJ}$

$q_{bomb} = (m_{bomb} \cdot C_{bomb}) \Delta T$
$= 1.77 \times 1.126 = 1.992 \text{ kJ}$

$q_{comb} = -(q_{water} + q_{bomb})$
$= -(1.413 + 1.992) = -3.405 \text{ kJ}$

$$\Delta U = \frac{q_{comb}}{m_{subs}/M_{subs}} = \frac{-3.405 \text{ kJ}}{\dfrac{0.138}{24.3}} = -599.6 \text{ kJ mol}^{-1}$$

The combustion reaction is

$Mg(s) + 1/2 O_2 (g) \rightarrow MgO(s)$ $\Delta n_g = -1/2$

$\Delta H = \Delta U + (\Delta n_g) RT$
$= -599.6 + (-1/2)(8.314 \times 10^{-3})(298)$
$= -599.6 - 1.24 = -600.84 \text{ kJ mol}^{-1}$
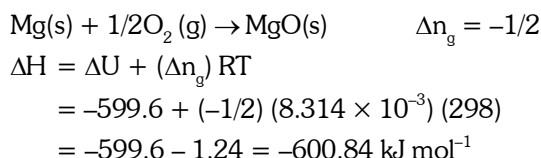
- **Constant Pressure Bomb Calorimeter**

The only difference with the constant volume calorimeter is that the bomb is fitted with a piston which is maintained at constant pressure.

Thus the heat liberated during the chemical reaction q_p directly gives enthalpy of reaction by the expression

$\Delta H = - C \times \Delta T \times (M/w)$

where, C = Heat capacity of calorimeter system, ΔT = Rise in temperature, M = Molecular mass of substance w = Mass of substance taken.

7.0 CALORIFIC VALUE OF A FUEL

SL AL

Nutritional value of foods, and the usefulness of fuels is determined by the heat (energy) they produce on heating. The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energy per gram. It is known as calorific value. It is defined as the amount of heat produced in calories (or joules) when one gram of a substance (food or fuel) is completely burnt. The calorific value is usually expressed in kcal per gram or kilojoules per gram (1 kcal = 4.184 kJ).

For example when Methane burns

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 891 \text{ kJ energy}$
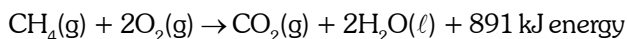
therefore calorific value of meathan is $891/16 = 55.6 \text{kJ/gm}$

The fuel are graded according to their calorific value. Greater the calorfic value of a fuel, greater is the prize. Hydrogen has greatest calorific value.

8.0 BOND ENTHALPY

SL AL

In chemical reactions the formation of a chemical bond is accompanied by the release of energy. Conversely energy has to be supplied for the breaking of a bond. Bond strengths are commonly described by their bond dissociation energies which is the energy required to break one mole of a bond of particular type. This is a definite quantity and is expressed in kJ mol^{-1}. For diatomic molecules the **bond dissociation energy** is same as **bond energy**, whereas in polyatomic molecules the **bond energy** is taken as the mean average of the various **bond dissociation energies** of the bonds of a given type.

Thus bond energy is avarage energy needed to break one mole of a particular bond in a gaseous molecule to convert it into gaseous atoms.

The thermochemical data is useful in determining the bond energies of different bonds. For example, the **bond energy** of C-H bond in methane can be calculated form its heat of formation. The heat for formation of methane from carbon and hydrogen gaseous atoms has been found to be -1663 kJmol^{-1}.

$$C(g) + H(g) \rightarrow CH_4(g) \qquad \Delta H = -1663 \text{ kJmol}^{-1}$$
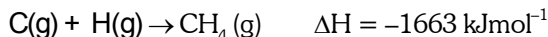
Methane has four C-H bonds and the energy required to break all the four C-H bonds is 1663 kJ. Therefore the average C-H bond energy is

$$1663/4 = 413.25 \text{ kJmol}^{-1}$$

- **Application of Bond Enthalpy in Estimating Enthalpy of Reactions**

    Bond energies can be utilized to quickly estimate enthalpy of reactions. The enthalpy obtained from bond energy data often match very well with actual enthalpy obtained from other methods like enthalpy of combustion, or formation enthalpy data.

    $$\Delta H = B.E(\text{reactant's}) - B.E.(\text{product's})$$

    Example : 1 - consider the reaction

    $$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \qquad \textbf{\textit{...(i)}}$$
    $$C_2H_4(g) \rightarrow 2C(g) + 4H(g) \qquad \textbf{\textit{...(ii)}}$$
    $$H_2 \rightarrow 2H(g) \qquad \textbf{\textit{...(iii)}}$$
    $$C_2H_6(g) \rightarrow 2C(g) + 6H(g) \qquad \textbf{\textit{...(iv)}}$$
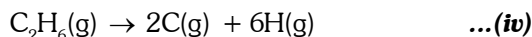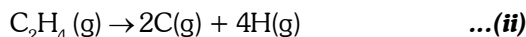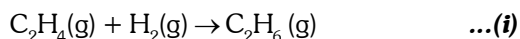
    Now (i) = (i) + (iii) − (iv)

    clearly from the equations the given formula is justified

    Example : 2 - Figure in the following the enthalpies are indicated for .

    $$\Delta_r H_{\text{Theortical}} = \varepsilon_{c=c} + 4\varepsilon_{c-c} - 6\varepsilon_{c-c} - \varepsilon_{c-c}$$
    $$\Delta_r H_{\text{Theortical}} = B.E.(\text{reactant's}) - B.E.(\text{product's})$$
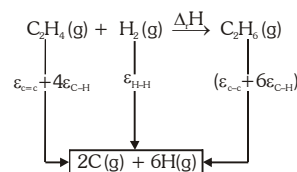
9.0 RESONANCE ENERGY, CONCEPT AND CALCULATION USING BOND ENENGY

SL AL

When the structure of molecule can be explained by two or more valid Lewis structures the molecule is said to be resoance stabilised. Due to resonance, the molecule gain stability. The actual structure of molecule is avarage of many possible canonical structures possible for molecule. Resonance energy is difference in energy of most stable canonical sturcture and energy of actual molecule. When ever there is possibility of resonance in molecule, the molecule become more stable. Resonance energy = Eenrgy of the resonance hybrid -Energy of the most stable resonating structure. Resonance energy can be calculated using the formula

ΔH (Actual) - ΔH(theoretical) = Resonance energy of products - Resonance energy of reactants

The proof of above formula is given by following diagram. Consider a reaction $A(g) + B^*(g) \rightarrow C(g) + D^*(g)$ where (*) showing that molecules exhibit phenomena of resonance. Remember where ever resonance take place, bond breaking become difficult. Actual energy required to break a bond is equal to $\in_{\text{actual}} = \in_{\text{theoretical}}$ - resonance energy
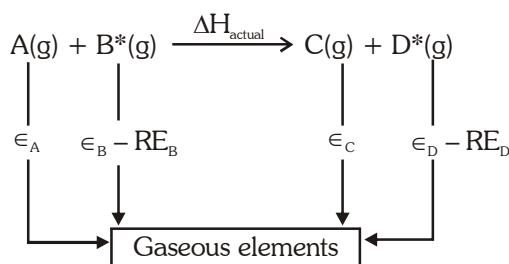
$$\Delta H_{actual} = \in_A + \in_B - R.E_B - \{\in_C + \in_D - R.E_D\}$$

$$\Delta H_{actual} = (\in_A + \in_B - \in_C - \in_D) + R.E_D - R.E_B$$

$$\Rightarrow \quad \Delta H_{actual} - \Delta H_{Theoretical} = R.E_D - R.E_B$$

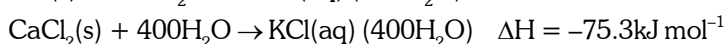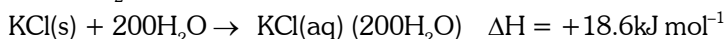$$[\Delta H_{actual} - \Delta H_{Theoretical} = R.E_{Products} - R.E_{reactants}]$$

keep it in mind that resonance energy are expressed as -ive number because due to resonance, the molecule gain stability. Due to resonance in a molecule, bond breaking become difficult hence actual energy required to break a bond = theoretical bond energy - resonance energy.

10.0 ENTHALPY OF SOLUTION

SL AL

When a solute is dissolved in a solvent a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. Such heat changes under constant pressure conditions are known as the enthalpy of solution. 'The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution'.To avoid the amount of solvent, heat of solution is usually defined for an infinite dilute solution. Thus, heat of solution at infinite dilution is the heat change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change.

Here 'aq' represents aqueous meaning a large excess of water. For substances, which dissolve with the absorption of heat (endothermic), the enthalpy of solution is positive while for the substances which dissolve by liberating heat (exothermic), the enthalpy of solution is negative. For example, when KCl is dissolved in water, heat is absorbed. Thus, the enthalpy of solution of KCl is positive. For a 200 times dilution (water : KCl = 200 : 1), the enthalpy change during the process, So, the enthalpy of solution of KCl at a dilution of 200 is 18.6 kJ mol^{-1}. The dissolution of $CaCl_2$(s) in water is an exothermic process. So, the enthalpy of solution of calcium chloride ($CaCl_2$) is negative. At a dilution of 400, the enthalpy change for the reaction, So, the enthalpy of solution of $CaCl_2$(s) at a dilution of 400 is –75.3 kJ mol^{-1}.

$$KCl(s) + 200H_2O \rightarrow KCl(aq) \ (200H_2O) \quad \Delta H = +18.6 kJ \ mol^{-1}$$

$$CaCl_2(s) + 400H_2O \rightarrow KCl(aq) \ (400H_2O) \quad \Delta H = -75.3 kJ \ mol^{-1}$$

- **Important points to remember about enthalpy of solution**

  It is generally negative for anhydrous salts

  It is generally positive for salts which do not have water of hydration like NaCl

  It is generally positive for hydrated salts like $CuSO_4.5H_2O$

  If lattice energy|U|is more than |Hydration energy|of gaseous ions, enthalpy of solution is positive.

  If lattice energy|U|is less than |Hydration energy|of gaseous ions, enthalpy of solution is negative.

  Note that even when $\Delta H_{solution}$ is positive, salts are freely soluble in water due to favourable entropy change.

11.0 ENTHALPY OF HYDRATION

SL AL

This is defined as the heat change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) ; \quad \Delta H_{Hydration} = -78.21 \ kJ \ mol^{-1}$$
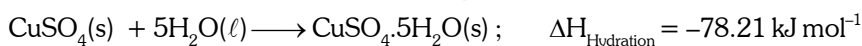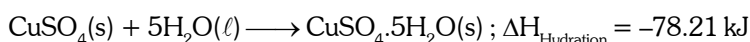
Hydration is generally exothermic change.

If integral heat of solution of the hydrated and anhydrous salt is known, then heat of hydration can be calculated.

For example :

(a) $CuSO_4$(anhydrous) $+ 800 \ H_2O(\ell) \longrightarrow CuSO_4 \ (800 \ H_2O) ; \Delta H = -66.50 \ kJ$

(b) $CuSO_4.5H_2O$(s) $+ 795H_2O \ (\ell) \longrightarrow CuSO_4 \ (800 \ H_2O) ; \Delta H = 11.71 \ kJ$

Thus, (a – b) gives

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) ; \Delta H_{Hydration} = -78.21 \ kJ$$
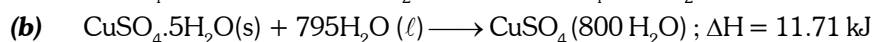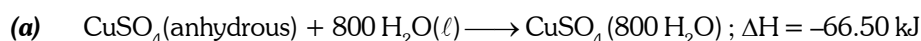
12.0 ENTHALPY OF NEUTRALISATION

SL AL

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The heat change when one gram equivalent of an acid is completely neutralised by a base or vice versa in dilute solution, is called heat of neutralization. Examples of heat of neutralization are :

Neutralization of HCl with NaOH

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell) \qquad \Delta H = -57.1 \text{ kJ}$$
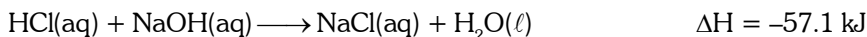
Neutralization of CH_3COOH with NaOH

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa + H_2O(\ell) \qquad \Delta H = -55.9 \text{ kJ}$$

It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of H^+ ions and 1 mole of OH^- ions to form 1mole of water and 57.1 kJ of heat is liberated.

$$H^+(aq) + OH^- \longrightarrow H_2O(\ell) \qquad \Delta H = -57.1 \text{kJ}$$

Now, one gram equivalent of various acids on complete dissociation liberates one mole of H^+ ions. But one mole of the acid may produce more than one mole of H^+ ions in solution depending upon its basicity; for example 1mol of H_2SO_4 gives 2 mol of H^+ ions and 1mol of H_3PO_4 gives 3 mol of H^+ ions on complete dissociation. But 1gram equivalent of both (H_2SO_4 or H_3PO_4) produces only 1 mol of H^+ ions.Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of neutralization of any strong acid by a strong base is found to be –57.7. This is because strong acids and strong bases are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contains the same number of H^+ ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contains same number of OH^-. The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of H^+ ions (from an acid) and OH^- ions (from a base) to form unionized water molecules. For example, the reaction between hydrochloric acid and sodium hydroxide. The neutralization can be represented as :

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) \, Cl^-(aq) + H_2O(\ell) \qquad \Delta H = -57.1 \text{ kJ}$$
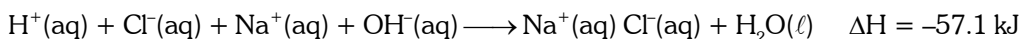
Cancelling common ions :

$$H^+(aq) + OH^- \longrightarrow H_2O(\ell) \qquad \Delta H = -57.1 \text{ kJ}$$
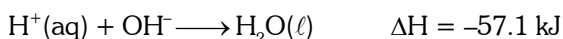
12.1 Experimental Determination of Enthalpy of Neutralization

SL AL

In this experiment, an aqueous hydrochloric acid solution will be added to an aqueous sodium hydroxide solution. The neutralization reaction will occur until either H^+ or OH^- is entirely consumed. The reactant which is consumed completely is called the limiting reactant.

The molar enthalpy of neutralization is defined as

$$\Delta H_{neut} = q_{neut}/n$$

Where q_{neut} is the heat of neutralization, measured calorimetrically, and n is the moles of the limiting reactant.

Approach ∵ Add a known volume of 3.00 M aqueous HCl to a known volume of 1.00 M aqueous NaOH.

- Observe the temperature of the system before and after the neutralization reaction occurs.
- Calculate the change in temperature (ΔT) for the system.
- Use the temperature change and heat capacities (C) for the calorimeter and aqueous solution to calculate the heat of neutralization.
- Divide the heat of neutralization by the moles of the limiting reactant to determine the molar enthalpy of neutralization.

$$\Delta H_{neut} = -\frac{C\Delta T}{n}$$

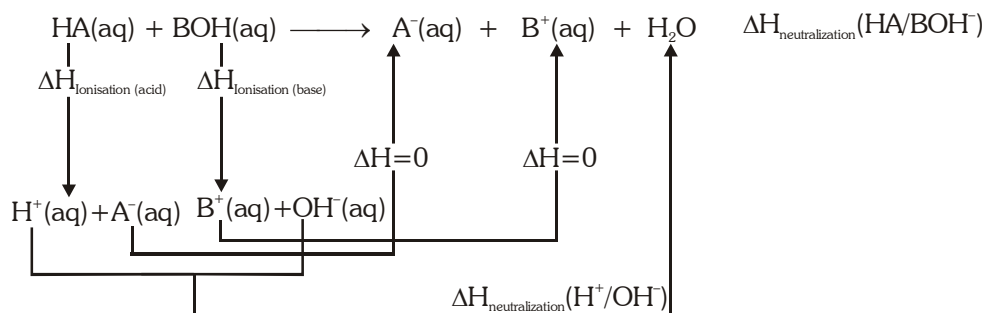## 12.2 The enthalpy of Neutralization of Weak Acid and Weak base

SL AL

Consider the neutralisation of weak acid HA with weak base BOH.

Where, $\Delta H_{ionisation}$ (HA) = Enthalpy of ionization of acid HA

$\Delta H_{ionisation}$ (BOH) = Enthalpy of ionization of base BOH

$\Delta H_{neutralisation}$ (H^+/OH) = Enthalpy change for the reaction of H^+ and OH^- to form water.

$$HA(aq) + BOH(aq) \longrightarrow A^-(aq) + B^+(aq) + H_2O \qquad \Delta H_{neutralization}(HA/BOH^-)$$

Thus for weak acid :

$$\Delta H_{neut}(BOH/HA) = \Delta H_{ion.}(HA) + \Delta H_{ion}(BOH) + \Delta H_{neut}(H^+OH^-)O$$

13.0 BORN - HABER CYCLE FOR NaCl

SL AL

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the ionic compound (lattice) is formed from its isolated ions in the gaseous state under standard condition.

BORN-HABER CYCLE FOR NaCl

$$nA^{m+}(g) + mB^{n-}(g) \longrightarrow A_nB_m(s)$$
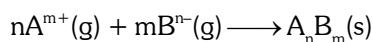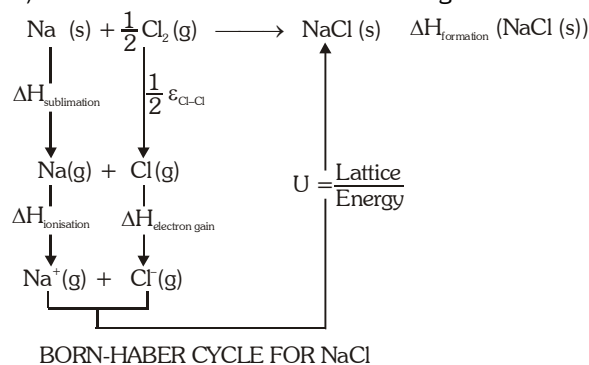
$\Delta H = -U$ (lattice energy)

Formation of NaCl(s) lattice involves thus,

$$S + I + \frac{\varepsilon_{Cl-Cl}}{2} - E - U = q$$

hence, U can be calculated.

here, S = enthalpy of sublimation of Na(s) = $\Delta H_{sublimation}$

I = ionisation of energy of Na(g) = $\Delta H_{ionization}$

ε = bond energy of Cl_2

U = lattice energy

q = enthalpy of formation of NaCl(s) = $\Delta H_{formation}$

If lattice is MgX_2 (s) then

$$S + (I_1 + I_2) + \varepsilon - 2E - U = q$$

where, $(I_1 + I_2)$ = total ionisation energy to form Mg^{2+}(g).

──────── Illustrations ────────

Illustration 3.   Calculate lattice energy for the change,

$$Li^+(g) + Cl^-(g) \longrightarrow LiCl(s)$$
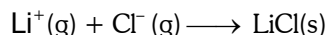
Given that

$\Delta H_{subl.}$ of Li = 160.67 kJ mol^{-1},

$\Delta H_{Dissociation}$ of Cl_2 = 244.34 kJ mol^{-1},

$\Delta H_{ionisation}$ of Li(g) = 520.07 kJ mol^{-1},

$\Delta H_{E.A}$ of Cl(g) = – 365.26 kJ mol^{-1},

ΔH_f of LiCl(s) = – 401.66 kJ mol^{-1}.

Solution.   Considering the different changes that occur in the formation of solid lithium chloride based on the data given the lattice energy of the above can be constituted as:
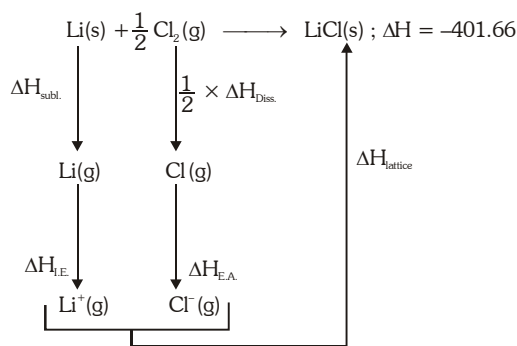
$$\Delta H°_f = \Delta H_{subl.} + \Delta H_{I.E.} + \frac{1}{2}\Delta H_{Diss.} + \Delta H_{E.A} + \Delta H_{lattice}$$

or $\quad \Delta H_{lattice} = \Delta H°_f - \Delta H_{subl.} - \Delta H_{I.E.} - \frac{1}{2}\Delta H_{Diss.} - \Delta H_{E.A} = -839.31$ kJ mol^{-1}

14.0 ENTHALPY OF ATOMISATION

SL **AL**

Enthalpy change to covert 1 mole of molecule into gaseous atoms is called enthalpy of atomisation :

Example :

$CH_4(g) \longrightarrow C(g) + 4H(g)$; $\Delta H_{atomisation}$ ($CH_4(g)$)

$C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$; $\Delta H_{atomisation}$ ($C_2H_6(g)$)

$H_2(g) \longrightarrow 2H(g)$; $\Delta H_{atomisation}$ ($H_2(g)$)
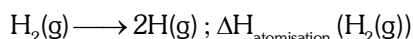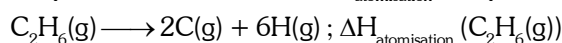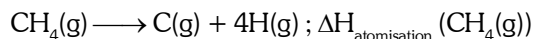
──────── Illustrations ────────

Illustration 4*.   The bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are + 435.95 kJmol^{-1} and + 941.8 kJ mol^{-1} and enthalpy of formation of $NH_3(g)$ is –46.024 kJ mol^{-1}.

(a) What is the enthalpy of atomization of $NH_3(g)$?

(b) What is the bond enthalpy of N – H bond ?

Solution.   (a) The desired equation is

$$NH_3(g) \rightarrow N(g) + 3H(g)$$
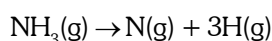
we can consider the reaction as

$$NH_{3(g)} \xrightarrow{\Delta H_1} N(g) + 3H(g) \xrightarrow{\Delta H_2} \frac{1}{2} N_{2}(g) + \frac{3}{2} H_{2}(g)$$
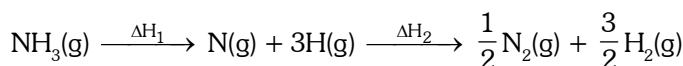
$\therefore \quad \Delta H_1 + \Delta H_2 = +46.024 \text{ kJ mol}^{-1}$

Now $\Delta H_2 = -\frac{3}{2} (435.95) - \frac{1}{2} (941.80)$

$\therefore \quad \Delta H_1 = 46.024 + \frac{3}{2} (435.925) + \frac{1}{2} (941.8)$

or $\quad \Delta H_1 = 46.024 + 653.925 + 470.9$

or $\quad \Delta H_1 = 1170.849 \text{ kJ mol}^{-1}$

or $\quad \Delta H_1 = 1.170849 \text{ MJ mol}^{-1}$

(b) The average bond enthalpy of N – H bond

$$= \frac{1170.849}{3} = 390.283 \text{ kJ mol}^{-1}$$

15.0 ENTHALPY OF ELECTRON GAIN

SL AL

Enthalpy change when 1 mole electrons are added to gaseous species is called electron gain enthalpy.

Example :

$Cl(g) + e \longrightarrow Cl^- (g)$; $\Delta H_{electron\ gain}$
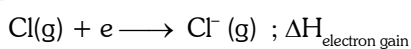
$\Delta H_{electron\ gain}$ is usually negatigve for non metals.

However electron gain enthalpy of negatively charged gaseous species is positive.

$O^- + e \longrightarrow O^{2-}$; $\Delta H_{electron\ gain} = +ive$
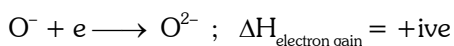
16.0 IONISATION ENTHALPY

SL AL

Enthalpy change when one mole of gaseous atom is converted into gaseous ion be removing one mole electron from ground state is called ionisation enthalpy.

Example :

$Na(g) \longrightarrow Na^+ (g) + e$; $\Delta H_{Ionization} (Na(g))$

$H(g) \longrightarrow H^+ (g) + e$; $\Delta H_{Ionization} (H(g))$
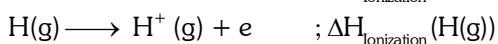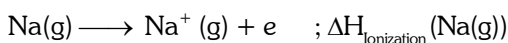
BEGINNER'S BOX–1

Thermochemistry

1. The enthalpy of the reaction,

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}$ is ΔH_1 and that of $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$ is ΔH_2 then–

(A) $\Delta H_1 < \Delta H_2$ (B) $\Delta H_1 + \Delta H_2 = 0$ (C) $\Delta H_1 < \Delta H_2$ (D) $\Delta H_1 = \Delta H_2$

2*. If the bond energies of H—H, Br—Br and H—Br are 433, 192 and 364 kJ mol^{-1} respectively, $\Delta H°$ for the reaction $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$ is

(A) –261 kJ   (B) +103 kJ   (C) +261 kJ   (D) –103 kJ

3. Enthalpy of neutralization of HCl by NaOH is –55.84 kJ/mol and by NH_4OH is –51.34 kJ/mol. The enthalpy of ionization of NH_4OH is

(A) –107.18 kJ   (B) 107.18 kJ   (C) 4.5 kJ   (D) –4.5 kJ

4. For the reaction $OF_{2(g)} \longrightarrow O_{(g)} + 2F_{(g)}$, $\Delta_{rxn}H$ is 368 kJ. What is the average O—F bond energy ?

(A) 184 kJ   (B) 368 kJ   (C) 536 kJ   (D) 736 kJ

5*. The enthalpy change for which of the following processes represents the enthalpy of formation of AgCl?

(A) $Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$ (B) $Ag_{(s)} + \frac{1}{2}Cl_{(g)} \longrightarrow AgCl_{(s)}$

(C) $AgCl_{(s)} \longrightarrow \frac{1}{2}Cl_{(g)}$ (D) $Ag_{(s)} + AuCl_{(s)} \longrightarrow Au_{(s)} + AgCl_{(s)}$

6*. On the basis of following thermochemical data

$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq.)}$; $\Delta H = 57.32$ kJ $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$: $\Delta H = -286.2$ kJ

The value of enthalpy of formation of OH^- ion at 25°C is–

(A) +288.88 kJ   (B) –343.52 kJ   (C) –22.88 kJ   (D) –228.88 kJ

7. Heat of hydrogenation of ethene is x_1 and that of Benzene is x_2 Hence resonance energy is

(A) $x_1 - x_2$ (B) $x_1 + x_2$ (C) $3x_1 + x_2$ (D) $x_1 - 3x_2$

8*. The lattice energy of NaCl is –780 kJ mol^{-1}. The enthalpies of hydration of $Na^+_{(g)}$ and $Cl^-_{(g)}$ ions are –406 kJ mol^{-1} and –364 kJ mol^{-1}. The enthalpy of solution of $NaCl_{(s)}$ is–

(A) 738 kJ mol^{-1} (B) 10 kJ mol^{-1} (C) –10 kJ mol^{-1} (D) –822 kJ mol^{-1}

9*. The heat of combustion of ethanol in a bomb calorimeter is –670.48 Kcal mol^{-1} at 25⁰C. What is ΔE at 25⁰C for the reaction ?

(A) – 269.24 Kcal   (B) – 469.28 Kcal   (C) – 670.48 Kcal   (D) +770.48 Kcal

10. $4S(s) + 6O_2 \longrightarrow 4SO_3(g)$.; ΔH for this reaction is – 1583.2 KJ. The enthalpy of formation of sulphur trioxide is -

(A) – 395.8 KJ   (B) 395.8 KJ   (C) 495.5 KJ   (D) 595.5 KJ

11. The heat change for the reaction

$C(s) + 2S(s) \longrightarrow CS_2(\ell)$ is called the heat of

(A) Reaction   (B) Fusion   (C) Formation   (D) Combustion

12*. Based on the following thermochemical equation

$H_2O(g) + C(s) = CO(g) + H_2(g)$; $\Delta H = 131$ KJ, $CO(g) + \frac{1}{2} O_2(g) = CO_2(g)$; $\Delta H = -282$ KJ

$H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$; $\Delta H = -242$ KJ $C(s) + O_2(g) = CO_2(g)$; $\Delta H = -x$KJ

The value of x will be

(A) 393 KJ   (B) – 393 KJ   (C) 655 KJ   (D) – 655 KJ

13. In a reversible reaction of the type $A + B \rightleftharpoons AB$, in general -

(A) The combination reaction will be exothermic and the dissociation reaction will be endothermic

(B) The combination reaction will be endothermic and the dissociation reaction will be exothermic

(C) Both the reaction will be exothermic

(D) Neither of the reactions will be endothermic

14*. If enthalpies of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(\ell)$ at 25^0C and 1 atm, pressure are 52, –394 and –286 KJ/mol respectively, then enthalpy of combustion of $C_2H_4(g)$ will be

(A) – 141.2KJ/mol   (B) –1412 KJ/mol   (C) 14.2 KJ/mol   (D) +14.12 KJ/mol

15*. Given that $C + O_2 \longrightarrow CO_2$, $\Delta H^0 = -x$ KJ ,

$2CO + O_2 \longrightarrow 2CO_2$; $\Delta H^0 = -y$ KJ

The enthalpy of formation of carbon monoxide will be

(A) $y - 2x$ (B) $\dfrac{2x - y}{2}$ (C) $\dfrac{y - 2x}{2}$ (D) $2x - y$

16. Change in enthalpy for reaction

$2H_2O_2(\ell) \rightarrow 2H_2O(\ell) + O_2(g)$ If heat of formation of $H_2O_2(\ell)$ and $H_2O(\ell)$ are –188 & – 286 KJ/mol respectively:–

(A) – 196 KJ/mol   (B) + 196 KJ/mol   (C) + 948 KJ/mol   (D) – 948 KJ/mol

17. For which one of the following equations is $\Delta H^\circ_{reaction}$ equal to ΔH°_f for the product :-

(A) $N_2(g) + O_3(g) \rightarrow N_2O_3(g)$ (B) $CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(l) + 2HCl(g)$

(C) $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$ (D) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

18. Molar heat of vapourisation of a liquid is 6 kJ mol^{-1}. If the entropy change is 16 J mol^{-1} K^{-1}, the boiling point of the liquid is :-

(A) 375°C   (B) 375 K   (C) 273 K   (D) 102°C

19*. Heat of formation of $CO_2(g)$, $H_2O(\ell)$ and $CH_4(g)$ are –94, –68.4 and –17.9 kcal mol^{-1} respectively. the heat of combustion of $CH_4(g)$ is :-

(A) –212.9 kcal mol^{-1} (B) –136.8 kcal mol^{-1} (C) –304.3 kcal mol^{-1} (D) –105.2 kcal mol^{-1}

20*. Heat of combustion ΔH° for C(s), $H_2(g)$ and $CH_4(g)$ are – 94, – 68 and – 213 Kcal/mol. then ΔH° for $C(s) + 2H_2(g) \rightarrow CH_4(g)$ is :-

(A) – 17 Kcal   (B) – 111 Kcal   (C) – 170 Kcal   (D) – 85 Kcal

GOLDEN KEY POINTS

● ***Different types of standard enthalpy changes (Based on IUPAC recommendations)***.

	Transition Enthalpy	Example	Definition	Symbol
1.	Enthalpy of formation	$K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s)$	One mole of the compound formed from its elements	$\Delta_f H°$ or $\Delta H°_f$
2.	Enthalpy of combustion	$C_2H_6(g) + O_2(g) \longrightarrow$ $CO_2(g) + 3H_2O(\ell)$	One mole of the compound(fuel) is burnt completely in oxygen	$\Delta_c H$ or $\Delta H°_c$
3.	Enthalpy of fusion	$H_2O(s) \longrightarrow H_2O(\ell)$	One mole of the liquid is formed from the solid without a change in temperature	$\Delta_{fus} H°$ or $\Delta H°_{fus}$
4.	Enthalpy of vaporisation	$H_2O(\ell) \longrightarrow H_2O(g)$	One mole of the vapour formed from the liquid without a change in temperature	$\Delta_{vap} H°$ or $\Delta H°_{vap}$
5.	Enthalpy of sublimation	$I_2(s) \longrightarrow I_2(g)$	One mole of the vapour formed the solid	$\Delta_{sub} H°$ or $\Delta H°_{sub}$
6.	Enthalpy of atomisation	$H_2(g) \longrightarrow 2H(g)$	One mole of the substance broken into isolated atoms in the gas phase	$\Delta_{at} H°$ or $\Delta H°_{at}$
7.	Enthalpy of reaction	$A \longrightarrow B$	Enthalpy change taking place in a reaction	$\Delta_r H°$ or $\Delta H°_r$
8.	Enthalpy of neutralisation	$HCl(aq) + NaOH(aq) \longrightarrow$ $H_2O + NaCl(aq)$	One mole of water formed by the neutralisation of an acid by a base	$\Delta_n H°$ or $\Delta H°_n$
9.	Enthalpy of ionisation	$Na(g) \longrightarrow Na^+(g) + e^-$	One mole atoms ionised - all species in gaseous phase	$\Delta_{ion} H°$ or $\Delta H°_{ion}$
10.	Electron-gain enthalpy	$X(g) + e^- \longrightarrow X^-(g)$	One mole of anions being formed all species in the gaseous phase	$\Delta_{eg} H°$ or $\Delta H°_{eg}$
11.	Lattice enthalpy	$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$	One mole of a crystal completely separated into isolated particles in the gaseous phase	$\Delta_L H°$ or $\Delta H°_L$ or U
12.	Bond dissociation enthalpy (bond A – B)	$HCl(g) \longrightarrow H(g) + Cl(g)$	One mole of bonds broken - all species in the gaseous phase	$\Delta H°_{A-B} = \varepsilon_{A-B}$

13.	Enthalpy of solution	$NaCl(s) + H_2O(excess) \longrightarrow$ $NaCl(aq)$	One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change	$\Delta_{sol}H°$ or $\Delta H°_{sol}$
14.	Enthalpy of hydration	$X^{\pm}(g) \longrightarrow X^{\pm}(aq)$	One mole of the ion in gaseous phase is hydrated	$\Delta_{hyd}H°$ or $\Delta H°_{hyd}$
15.	Enthalpy of mixing	pure substances $\rightarrow$ mixture	One mole each of the two or more substances is mixed	$\Delta_{mix}H°$ or $\Delta H°_{mix}$

- Heat change expressed at constant pressure $= \Delta H$
  Heat change expressed at constant volume $= \Delta E$
  $$\Delta H = \Delta E + P\Delta V$$
  $$\Delta H = \Delta E + \Delta nRT$$
  Δ = No. of moles of product – No. of moles of reactants ; as represented by stoichiometry of change.
  (count only gaseous phase molecule for Δn)

- **Kirchoff's Equation :** Variation of ΔH and ΔE with temperature
  $$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$
  $$\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$$
  $$\Delta C_p = \Sigma C_{p\ Products} - \Sigma C_{p\ Reactants}$$
  $$\Delta C_v = \Sigma C_{v\ Products} - \Sigma C_{v\ Reactants}$$
  ΔC_p and ΔC_v are changes in molar heat capacities at constant and volume respectively during the change.

- **Standard Heat Enthalpy (H°)**
  $$H°_{(Compound)} = \Delta H°_{(Formation\ of\ compound)}$$

- **Heat of solution for electrolytes (ΔH_s)**
  $$\Delta H_s = \Delta H_i + \Delta H_h$$
  ΔH_i and ΔH_h are heat of ionisation and heat of hydration respectively

- **Heat of neutralization**
  $$H^+ + OH^- \rightleftharpoons H_2O \; ; \; \Delta H \text{ (neutralization)} = -13.7 \text{ kcal} = -57.27 \text{ kJ}.$$

SOME WORKED OUT EXAMPLES

Illustration 1*.

From the following data at 25°C

Reaction	$\Delta_r H^o/KJ\, mol^{-1}$
$1/2\, H_2(g) + 1/2 O_2(g) \rightarrow OH(g)$	42.09
$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g)$	–241.84
$H_2(g) \rightarrow 2H(g)$	435.88
$O_2(g) \rightarrow 2O(g)$	495.04

Calculate $\Delta_r H°$ for the following reactions

(a) $OH(g) \rightarrow H(g) + O(g)$

(b) $H_2O(g) \rightarrow 2H(g) + O(g)$

(c) $H_2O(g) \rightarrow H(g) + OH(g)$

Solution.

(a) The desired equation is

$$OH(g) \rightarrow H(g) + O(g)$$
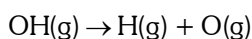
We are to develop the desired equation by using the four given equations

(i) $\dfrac{1}{2} H_2(g) \rightarrow H(g)$ $\qquad\qquad \Delta_r H° = \dfrac{435.88}{2}$

(ii) $OH(g) \rightarrow \dfrac{1}{2} H_2(g) + \dfrac{1}{2} O_2(g)$ $\qquad \Delta_r H° = -42.09$

(iii) $\dfrac{1}{2} O_2(g) \rightarrow O(g)$ $\qquad\qquad \Delta_r H° = \dfrac{495.04}{2}$

By adding equation (i), (ii) & (iii),

we get

$$OH(g) \rightarrow H(g) + O(g)$$
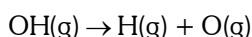
$$\Delta_r H° \rightarrow \frac{435.88}{2} - 42.09 + \frac{495.04}{2}$$

or $\qquad \Delta_r H° = 423.37$ kJ/mol. $\hfill$ **Ans.**

(b) The desired equation is
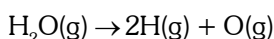
$$H_2O(g) \rightarrow 2H(g) + O(g)$$

(i) $\dfrac{1}{2} O_2(g) \rightarrow O(g)$ $\qquad\qquad \Delta_r H° = \dfrac{495.04}{2}$

(ii) $H_2(g) \rightarrow 2H(g)$ $\qquad\qquad \Delta_r H° = 435.88$

(iii) $H_2O(g) \rightarrow H_2(g) + \dfrac{1}{2} O_2(g)$ $\qquad \Delta_r H° = 241.88$

The net equation is,
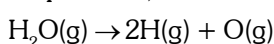
$\qquad H_2O(g) \rightarrow 2H(g) + O(g)$ $\qquad \Delta_r H° = 925.28$ kJ/mol $\qquad$ **Ans.**

(c) The desired equation is

$\qquad H_2O(g) \rightarrow H(g) + OH(g)$
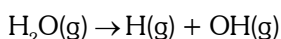
(i) $H_2O(g) \rightarrow 2H(g) + O(g)$ $\qquad \Delta_r H° = 925.28$ kJ/mol

(ii) $H(g) + O(g) \rightarrow OH(g)$ $\qquad \Delta_r H° = 423.37$ kJ/mol

By adding eq^n (i) and (ii)
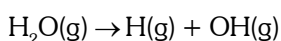
$\qquad H_2O(g) \rightarrow H(g) + OH(g)$ $\qquad \Delta_r H° = 1348.65$ kJ/mol $\qquad$ **Ans.**

Illustration 2.

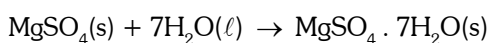From the given data prove that graphite is more stable allotrope of carbon than diamond from the given data

$$C_{dia} + O_2 \rightarrow CO_2 \qquad \Delta H_1° = -94500 \text{ cal}$$
$$C_{gra} + O_2 \rightarrow CO_2 \qquad \Delta H_2° = -94050 \text{ cal}$$

Solution.

$$C_{dia} + O_2(g) \rightarrow CO_2 \qquad \Delta H_1° = -94500 \text{ cal}$$
$$C_{gra} + O_2(g) \rightarrow CO_2 \qquad \Delta H_2° = -94050 \text{ cal}$$

on substraction

$$C_{dia} \rightarrow C_{gra} \qquad \Delta_r H° = -450 \text{ cal}$$
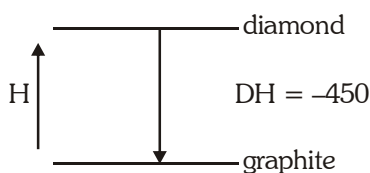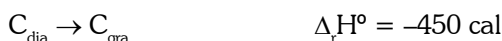
since heat content of diamond > graphite

Therefore diamond is less stable than graphite.

Illustration 3.

At 25° C, 1 mole $MgSO_4$ was dissolved in water. The heat evolved was found to be 91.211 kJ. One mole of $MgSO_4 \cdot 7H_2O$ on dissolution gives a solution of the same composition accompained by an absorption of 13.807 kJ. Find the enthalpy of hydration, i.e., ΔH for the reaciton

$$MgSO_4(s) + 7H_2O(\ell) \rightarrow MgSO_4 \cdot 7H_2O(s)$$

Given that

(i) $MgSO_4(s) + aq \rightarrow MgSO_4(aq)$ $\qquad\qquad \Delta_r H_1 = -91.211 \text{ kJ mol}^{-1}$

(ii) $MgSO_4 \cdot 7H_2O(s) + aq \rightarrow MgSO_4(aq)$ $\qquad \Delta_r H_2 = +13.807 \text{ kJ mol}^{-1}$

Solution.

$$MgSO_4 \cdot 7H_2O(s) + aq \rightarrow MgSO_4(aq) \qquad \Delta_r H_2 = +13.807 \text{ kJ mol}^{-1} \qquad ...(ii)$$
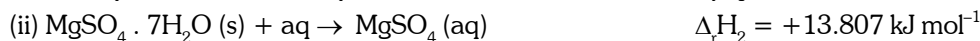
Equation (i) can be written as follows :

$$MgSO_4(s) + 7H_2O(\ell) + aq \rightarrow MgSO_4(aq) \qquad \Delta_r H = -91.211 \text{ kJ mol}^{-1} \qquad ...(iii)$$

eqn (iii) – (ii) will give
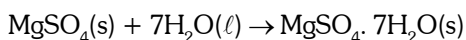
$$MgSO_4(s) + 7H_2O(\ell) \rightarrow MgSO_4 \cdot 7H_2O(s)$$
$$\Delta_r H = -91.211 - 13.807 = -105.018 \text{ kJ mol}^{-1}.$$

Illustration 4*.

Enthalpy of neutralization of HCl by NaOH is –57.32 kJ mol^{-1} and by NH_4OH is –51.34 kJ mol^{-1}. Calculate the enthalpy of dissociation of NH_4OH.
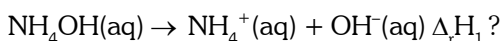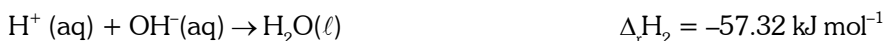
Solution.

Given that

$$H^+(aq) + NH_4OH(aq) \rightarrow NH_4^+(aq) + H_2O(\ell) \qquad \Delta_r H = -51.34 \text{ kJ mol}^{-1}$$
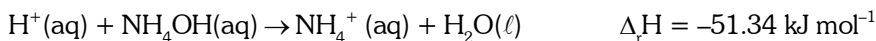
we may consider neutralization in two steps :

(i) ionization

$$NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq) \quad \Delta_r H_1 ?$$

(ii) neutralization

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) \qquad \Delta_r H_2 = -57.32 \text{ kJ mol}^{-1}$$
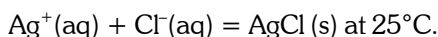
Thus, $\Delta_r H = \Delta_r H_1 + \Delta_r H_2$

Therefore,

$$\Delta_r H_1 = \Delta_r H - \Delta_r H_2$$
$$= -51.34 + 57.32 = 5.98 \text{ kJ/mol}^{-1}$$

Illustration 5.

Calculate $\Delta_r H°$ for the reaction

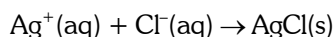$Ag^+(aq) + Cl^-(aq) = AgCl(s)$ at 25°C.

Given :

$$\Delta_f H° (Ag^+, aq) = 105.58 \text{ kJ mol}^{-1},$$
$$\Delta_f H° (Cl^-, aq) = -167.16 \text{ kJ mol}^{-1} \text{ and } \Delta_f H°$$
$$(AgCl, s) = -127.07 \text{ kJ mol}^{-1}$$

Solution.

For the reaction

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

We have

$$\Delta_r H° = (AgCl, s) - \Delta_f H° (Ag^+, aq) - \Delta_f H° (Cl^-, aq)$$
$$= [-127.07 - 105.58 - (-167.16)]$$
$$= -65.49 \text{ kJ mol}^{-1}$$

Illustration 6*.

The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5536 kJ mol⁻¹ respectively. Calculate the resonance energy of benzene, compared with Kekule structure. The bond enthalpy of C – H bond is given as equal to 410.87 kJ mol⁻¹.

Solution.

Bond enthalpy of C – C bond

= Enthalpy required to break C_2H_6 into gaseous atoms –6 × bond enthalpy of C – H bond

= 2839.2 kJ mol⁻¹ – 6 × 410.87 kJ mol⁻¹

= 373.98 kJ mol⁻¹

Bond enthalpy of C = C bond = Enthalpy requried to break C_2H_4 into gaseous atoms –4 × bond enthalpy of C – H bond

= 2275.2 kJ mol⁻¹ – 4 × 410.87 kJ mol⁻¹

= 631.72 kJ mol⁻¹

For the formation of benzene having Kekule structure, we have to form 3 C – C bonds, 3 C = C bonds and 6 C – H bonds for which enthalpy released is

[3 (–373.98) + 3(–631.72) + 6(–410.87)]

= –5482.32 kJ mol⁻¹

But the given value of $\Delta_f H$ is

$\Delta_f H$ (actual) = –5536 kJ mol⁻¹

Hence resonance energy compared to Kekule structure

= $\Delta_f H$ (actual) – $\Delta_f H$ (Kekule structure)

= (–5536 + 5482.32)

= –53.68 kJ mol⁻¹

Illustration 7.

Using bond enthalpy data given below, estimate enthalpy of formation of acetic acid.

Bond	Bond enthalpies
C – H	413.38 kJ mol^{-1}
C – C	347.69 kJ mol^{-1}
C = O	728.02 kJ mol^{-1}
C – O	351.46 kJ mol^{-1}
O – H	462.75 kJ mol^{-1}

Enthalpy of atomization

C	718.39 kJ atom^{-1}
H	217.94 kJ atom^{-1}
O	247.52 kJ atom^{-1}

The observed $\Delta_f H°$ for acetic acid is –438.15 kJ mol^{-1}. Compute the resonance energy of acetic acid.

Solution.

The desired reaction for the formation of CH_3COOH is

$2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(\ell)$
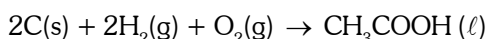
$\Delta_r H° = -3 \times 413.38 - 1 \times 347.69 - 728.02 - 351.46 - 462.75 + 2 \times 718.39 + 4 \times 217.94 + 2 \times 247.52$

$= -326.48$ kJ mol^{-1}

Resonance energy $= \Delta H°_{obs} - \Delta H°$

$= -438.15 + 326.48$

$= -111.67$ kJ mol^{-1}

Illustration 8.

The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C ?

Solution.

Given

$I_{2(s)} \longrightarrow I_{2(v)}$; $\Delta H = 24$ cal/g at 200°C

$\Delta C_{P(cal/g)} = C_P$ of product – C_P of reatant

$= 0.031 - 0.055 = -0.024$ cal/g
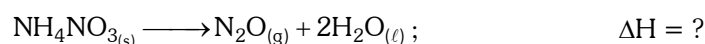
Now $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$

$\Delta H_2 - 24 = -0.024 \times (523 - 473)$

$\therefore$ $\Delta H_2 = 24 - 1.2 = 22.8$ cal/g.

Illustration 9.

The molar heat of formation of $NH_4NO_{3(s)}$ is –367.54 kJ and those of $N_2O_{(g)}$, $H_2O_{(l)}$ are 81.46 and –285.8 kJ respectively at 25°C and 1 atmosphere pressure. Calculate ΔH and ΔE of the reaction .

$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(\ell)}$

Solution.

We have to find ΔH for

$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(\ell)}$; $\Delta H = ?$
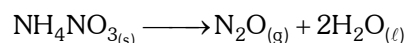
$\Delta H_{reaction} = \Delta H_{Products} - \Delta H_{Reactants}$

$= \Delta H_{N_2O} + \Delta H_{H_2O} \times 2 - \Delta H_{NH_4NO_3}$

Given, $\Delta H_{N_2O} = +81.46$ kJ , $\Delta H_{H_2O} = -285.8$ kJ , $\Delta H_{NH_4NO_3} = -367.54$ kJ

$\therefore$ $\Delta H_{reaction} = +81.46 + 2(-285.8) - (-367.54)$
        $\Delta H = -122.6$ kJ

Further $\Delta H = \Delta E + \Delta nRT$ ($\Delta n = 1 - 0 = 1$, R = 8.314 J, = 298 K)

$\therefore$ $-122.6 \times 10^3 = \Delta E + 1 \times 8.314 \times 298$
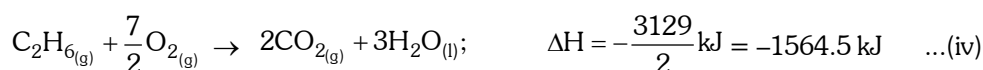
$\therefore$ $\Delta E = -125077$ joule = 125.077 kJ

Illustration 10.*

When 2 mole of $C_2H_{6(g)}$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of

$C_2H_{6(g)}.\Delta H_f$ for $CO_{2(g)}$ and $H_2O_{(l)}$ are –395 and –286 kJ mol^{-1} respectively.

Solution.

We have to find

$$2C(s) + 3H_{2(g)} \rightarrow C_2H_{6(g)} ; \qquad\qquad \Delta H = ? \qquad\qquad ...(i)$$

Given, $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} ; \qquad\qquad \Delta H = -395$ kJ $\qquad\qquad ...(ii)$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; \qquad\qquad \Delta H = -286 \text{ kJ} \qquad\qquad ...(iii)$$

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}; \qquad \Delta H = -\frac{3129}{2}\text{kJ} = -1564.5 \text{ kJ} \qquad ...(iv)$$

Multiplying Eq. (ii) by 2 and Eq. (iii) by 3, then adding

$$2C_{(s)} + 3H_{2(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}; \qquad \Delta H = -1648 \text{ kJ} \qquad\qquad ...(v)$$
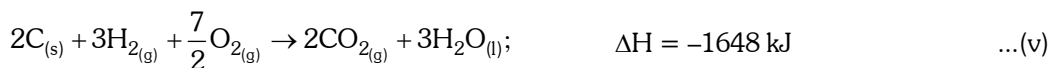
Subtracting Eq. (iv) from Eq. (v)

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}; \qquad\qquad \Delta H = -1564.5 \text{ kJ}$$

$$-\qquad\quad -\qquad\quad -\qquad\qquad -\qquad\qquad\qquad\qquad +$$

$$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}; \qquad\qquad \Delta H = -83.5 \text{ kJ}$$
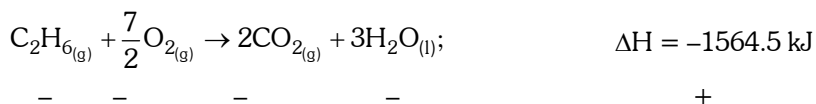
$\therefore$ ΔH_f of $C_2H_6 = -83.5$ kJ

Illustration 11.*

The heats of combustion of $C_2H_{4(g)}$, $C_2H_{6(g)}$ and $H_{2(g)}$ are –1409.5, –1558.3 and –285.6 kJ respectively.
Calculate heat of hydrogenation of ethylene.

Solution.

We have to find
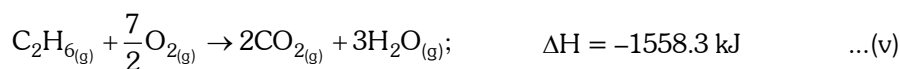
$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)} ; \qquad\qquad \Delta H = ?$$

Given, $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 3CO_{2(g)} + 2H_2O_{(g)}; \qquad\qquad \Delta H = -1409.5$ kJ $\qquad\qquad ...(i)$

$$C_2H_6 + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; \qquad\qquad \Delta H = -1558.3 \text{ kJ} \qquad\qquad ...(ii)$$

$$H_2 + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}; \qquad\qquad \Delta H = -285.6 \text{ kJ} \qquad\qquad ...(iii)$$

Adding Eqs. (i) and (iii)

$$C_2H_{4(g)} + \frac{7}{2}O_{2(g)} + H_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; \; \Delta H = -1695.1 \text{ kJ} \quad \quad ...(iv)$$
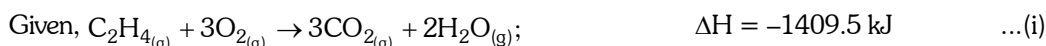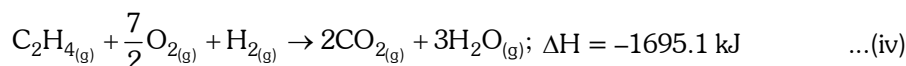
Subtracting Eq. (ii) from (iv)

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; \quad \quad \Delta H = -1558.3 \text{ kJ} \quad \quad ...(v)$$

$$\quad - \quad\quad - \quad\quad - \quad\quad - \quad\quad\quad + $$

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}; \quad\quad\quad\quad\quad \Delta H = -136.8 \text{ kJ}$$

∴   Heat of hydrogenation of C_2H_4 = 136.8 kJ

Illustration 12.

ΔH for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is better gas welder and why ?

Solution.

A better gas welder is one which posses high calorific value, i.e., heat produced by 1 g of fuel.

$\Delta H_{combustion}$ for C_2H_6 = –341.1 kcal

∴   Calorific value = $\dfrac{-341.1}{30}$ kcal/g = –11.37 kcal/g

$\Delta H_{combustion}$ for C_2H_2 = –310.0 kcal

∴   Calorific value = $\dfrac{-310.0}{26}$ kcal/g = –11.92 kcal/g

∴ C_2H_2 is better gas welder.

Illustration 13.

The heat of formation of methane is –17.9 kcal. If the heats of atomisation of carbon and hydrogen are 170.9 and 52.1 kcal per mole, calculate the C–H bond energy in methane.

Solution.

Given that

$$C(s) + 2H_2(g) \rightarrow CH_4(g); \quad\quad \Delta H = -17.9 \text{ kcal}$$
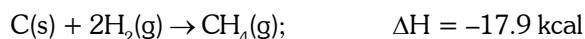
Energy change in reactants :

Heat of atomisation of 1 mole of C = 170.9 kcal

Heat of atomisation of 4 moles of H = 4 × 52.1 kcal

Energy change in product :

Heat of formation of 4 moles of C–H bonds = 4 × x kcal.

(where x is the energy of formation of C–H bonds in kcal/mole).

Since the algebraic sum of all the heat changes is equal to the heat of formation of the above given equation, we have

170.9 + 4 × 52.1 + 4x = –17.9; x = –99.3 kcal

Thus the bond energy = +99.3 kcal/mole.

Illustration 14*.

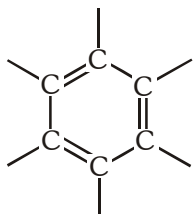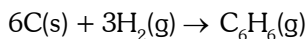Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

C–C = 83 kcal,   C=C = 140 kcal,   C–H = 99 kcal

Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

Solution.

We have to calculate ΔH for the reaction

$6C(s) + 3H_2(g) \rightarrow C_6H_6(g)$

DH = ?

For reactants :

Heat of atomisation of 6 moles of C = 6 × 170.9 kcal

Heat of atomisation of 6 moles of H = 6 × 52.1 kcal

For products :

Heat of formation of 6 moles of C – H bonds = –6 × 99

Heat of formation of 3 moles of C – C bonds = –3 × 83

Heat of formation of 3 moles of C = C bonds = –3 × 140

On adding, we get heat of formation of C_6H_6, i.e.,

$\Delta H = 6 \times 170.9 + 6 \times 52.1 – 6 \times 99 – 3 \times 83 – 3 \times 140 = 75.0$ kcal.

*****

ANSWERS

BEGINNER'S BOX-1

1.	(A)	**2*.**	(D)	**3.**	(C)	**4.**	(A)	**5*.**	(B)
6*.	(D)	**7.**	(C)	**8*.**	(B)	**9*.**	(C)	**10.**	(A)
11.	(C)	**12*.**	(A)	**13.**	(A)	**14*.**	(B)	**15*.**	(C)
16.	(A)	**17.**	(C)	**18.**	(B)	**19*.**	(A)	**20*.**	(A)

EXERCISE – 1   **MCQ (SINGLE CHOICE CORRECT)**

1. Which of the following equations represents a reaction that provides the heat of formation of ethane (CH_3CH_3)?

(A) $2\,C(s) + 6\,H(g) \rightarrow CH_3CH_3(g)$ (B) $2\,C(s) + 3\,H_2(g) \rightarrow CH_3CH_3(g)$

(C) $CH_2 = CH_2(g) + 2\,H_2(g) \rightarrow CH_3CH_3(g)$ (D) $CH^-CH(g) + 2\,H_2O(g) \rightarrow CH_3CH_3(g) + O_2(g)$

2. Which of the following equations represents a reaction that provides the heat of formation of CH_3Cl?

(A) $C(s) + HCl(g) + H_2(g) \rightarrow CH_3Cl(g)$ (B) $C(s) + 3/2\,H_2(g) + 1/2\,Cl_2(g) \rightarrow CH_3Cl(g)$

(C) $C(s) + 3\,H(g) + Cl(g) \rightarrow CH_3Cl(g)$ (D) $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

3*. Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction:

$$TiCl_4(g) + 2\,H_2O(g) \rightarrow TiO_2(g) + 4\,HCl(g)$$

$\Delta H^\circ_f\,TiCl_4(g) = -763.2\ kJ/mole$ $\Delta H^\circ_f\,TiO_2(g) = -944.7\ kJ/mole$

$\Delta H^\circ_f\,H_2O(g) = -241.8\ kJ/mole$ $\Delta H^\circ_f\,HCl(g) = -92.3\ kJ/mole$

(A) – 278.1   (B) + 369.2   (C) + 67.1   (D) – 67.1

4. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively. Using the data for the following combustion reaction, calculate the heat of formation of $C_3H_8(g)$.

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H^\circ = -2221.6\ kJ$$

(A) 212.2   (B) – 143.3   (C) 185.4   (D) – 103.6

5*. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively. Using the data for the following combustion reaction, calculate the heat of formation of $C_2H_2(g)$.

$$2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -2601\ kJ$$

(A) – 238.6   (B) 253.2   (C) 238.7   (D) 226.7

6. Using the following information calculate the heat of formation of NaOH.

$$2\,Na(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(s) + H_2(g) \qquad \Delta H^\circ = -281.9\ kJ, \ \Delta H^\circ_f\,H_2O(l) = -285.8\ kJ/mole$$

(A) – 141.6   (B) – 712.6   (C) – 426.8   (D) – 650.4

7*. Using the following information calculate the heat of formation of CH_4.

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -890.4\ kJ$$

$\Delta H^\circ_f\,CO_2(g) = -393.5\ kJ/mole$

$\Delta H^\circ_f\,H_2O(l) = -285.9\ kJ/mole$

(A) – 98.6   (B) – 65.5   (C) – 74.9   (D) – 43.5

8. The heat of formation of $CO_2(g)$ is –394 kJ/mole and that of $H_2O(l)$ is –286 kJ/mole. The heat of combustion of C_2H_4 is –1412 kJ/mole. What is the heat of formation of C_2H_4?

$$C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l)$$

(A) +1360   (B) – 108   (C) + 52   (D) +108

9*. What amount of heat energy (kJ) is released in the combustion of 12.0 g of C_3H_4?

(Atomic weights: C = 12.01, H = 1.008, O = 16.00).

$$C_3H_4(g) + 4\,O_2(g) \rightarrow 3\,CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -1939.1\ kJ$$

(A) 725   (B) 504   (C) 783   (D) 581

10. The standard heat of combustion of solid boron is equal to :-

(A) $\Delta H°_f(B_2O_3)$ (B) $\frac{1}{2} \Delta H°_f(B_2O_3)$ (C) $2\Delta H°_f(B_2O_3)$ (D) $\frac{1}{2} \Delta H°_f(B_2O_3)$

11. The average, S – F bond energy in SF_6 if the $\Delta H°_f$ value are –1100, +275 and +80 kJ/mol respectively for $SF_6(g)$, $S(g)$ and $F(g)$ is :-

(A) 390.1 kJ/mol   (B) 103.9 kJ/mol   (C) 903.1 kJ/mol   (D) 309.1 kJ/mol

12*. The average O–H bond energy in H_2O with the help of following data :-

(1) $H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$; $\Delta H = + 40.6$ kJ mol^{-1} (2) $2H_{(g)} \longrightarrow H_{2(g)}$; $\Delta H = - 435.0$ kJ mol^{-1}

(3) $O_{2(g)} \longrightarrow 2O_{(g)}$; $\Delta H = + 489.6$ kJ mol^{-1}

(4) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O(\ell)$; $\Delta H = - 571.6$ kJ mol^{-1}

(A) 584. 9 kJ mol^{-1} (B) 279.8 kJ mol^{-1} (C) 462.5 kJ mol^{-1} (D) 925 kJ mol^{-1}

13. The enthalpy change for the following reaction is 514 kJ. Calculate the average Cl – F bond energy.
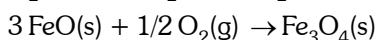
$ClF_3(g) \rightarrow Cl(g) + 3 F(g)$
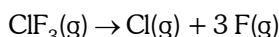
(A) 1542   (B) 88   (C) 171   (D) 514
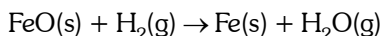
14. Given the following equations and $\Delta H°$ values, determine the heat of reaction (kJ) at 298 K for the reaction:

$4 H_2O(g) + 3 Fe(s) \rightarrow Fe_3O_4(s) + 4 H_2(g)$

$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g)$ $\Delta H°/kJ = -285.8$

$3 FeO(s) + 1/2 O_2(g) \rightarrow Fe_3O_4(s)$ $\Delta H°/kJ = -302.4$
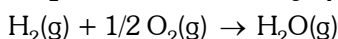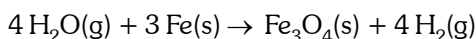
$FeO(s) + H_2(g) \rightarrow Fe(s) + H_2O(g)$ $\Delta H°/kJ = -13.8$

(A) +391.7   (B) – 24.8   (C) – 602.0   (D) +24.8

15. If heat of dissociation of $CHCl_2COOH$ is 0.7 kcal/mole then ΔH for the reaction :-

$CHCl_2COOH + KOH \rightarrow CHCl_2COOK + H_2O$
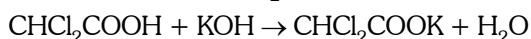
(A) –13 kcal   (B) + 13 kcal   (C) –14.4 kcal   (D) –13.7 kcal

16*. A solution is 500 mL of 2 M KOH is added to 500 mL of 2 M HCl and the mixture is well shaken. The rise in temperature T_1 is noted. The experiment is then repeated using 250 mL of each solution and rise in temperature T_2 is again noted. Assume all heat is taken by the solution :-

(A) $T_1 = T_2$ (B) T_1 is 2 times as large as T_2

(C) T_2 is twice of T_1 (D) T_1 is 4 times as large as T_2

17. Anhydrous $AlCl_3$ is a covalent compound. From the data given below, predict whether it would remain covalent or become ionic in an aqueous solution .

(Ionisation energy of Al = 5137 kJ mol^{-1}),

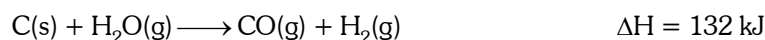ΔH hydration for Al^{3+} = –4665 kJ mol^{-1}. ΔH hydration for Cl^- = –381 kJ mol^{-1}

(A) Ionic   (B) Covalent   (C) Partially ionic   (D) Partially covalent

18*. Given, $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$, $\Delta H°_1$ and standard enthalpy of condensation of bromine is $\Delta H°_2$, standard enthalpy of formation of HBr at 25°C is :-

(A) $\frac{\Delta H°_1}{2}$ (B) $\frac{\Delta H°_1}{2 + \Delta H°_2}$ (C) $\frac{\Delta H°_1}{2 - \Delta H°_2}$ (D) $\frac{(\Delta H°_1 - \Delta H°_2)}{2}$

19. From the following data of ΔH, of the following reaction,

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \qquad \Delta H = -110 \text{ kJ}$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) \qquad \Delta H = 132 \text{ kJ}$$

What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273K, keeping temperature constant :-

(A) 0.5 : 1   (B) 0.6 : 1   (C) 0.8 : 1   (D) 1 : 1

20*. The standard enthalpy of formation of propene, C_3H_6, is +20.6 kJ/mole. Calculate the heat of combustion of one mole of C_3H_6. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –394 kJ/mole and –285.8 kJ/mole respectively.

(A) 1721.2   (B) –1939.1   (C) 2060.0   (D) 2221.6

21. Using the enthalpies of formation, calculate the energy (kJ) released when 3.00 g of $NH_{3(g)}$ reacts according to the following equation.
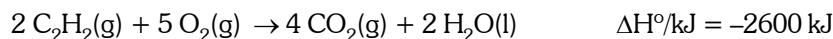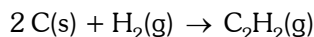
(Atomic weights: B = 10.81, O = 16.00, H = 1.008).

$$4 NH_3(g) + 5 O_2(g) \rightarrow 4 NO(g) + 6 H_2O(g)$$
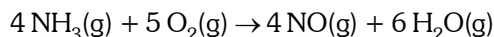
$\Delta H° NH_3(g) = -46.1 \text{ kJ/mole}$

$\Delta H° NO(g) = +90.2 \text{ kJ/mole}$

$\Delta H° H_2O(g) = -241.8 \text{ kJ/mole}$

(A) 34.3   (B) 30.8   (C) 39.9   (D) 42.6

22*. Calculate the value of ΔH°/kJ for the following reaction using the listed thermochemical equations:

$$2 C(s) + H_2(g) \rightarrow C_2H_2(g)$$

$2 C_2H_2(g) + 5 O_2(g) \rightarrow 4 CO_2(g) + 2 H_2O(l) \qquad \Delta H°/kJ = -2600 \text{ kJ}$

$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H°/kJ = -390 \text{ kJ}$

$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l) \qquad \Delta H°/kJ = -572 \text{ kJ}$

(A) +184   (B) +214   (C) +202   (D) +234

23*. Determine ΔH°/kJ for the following reaction using the listed enthalpies of reaction:

$$4 CO(g) + 8 H_2(g) \rightarrow 3 CH_4(g) + CO_2(g) + 2 H_2O(l)$$

$C(graphite) + 1/2 O_2(g) \rightarrow CO(g) \qquad \Delta H°/kJ = -110.5 \text{ kJ}$

$CO(g) + 1/2 O_2(g) \rightarrow CO_2(g) \qquad \Delta H°/kJ = -282.9 \text{ kJ}$

$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l) \qquad \Delta H°/kJ = -285.8 \text{ kJ}$

$C(graphite) + 2 H_2(g) \rightarrow CH_4(g) \qquad \Delta H°/kJ = -74.8 \text{ kJ}$

(A) – 622.4   (B) – 686.2   (C) – 747.5   (D) – 653.5

EXERCISE – 2   **MCQ (ONE OR MORE CHOICE CORRECT)**

1. For which of the following change $\Delta H = \Delta E$?
(A) H_2 (g) + I_2 (g) $\longrightarrow$ 2HI (g)   (B) HCI (aq) + NaOH (aq) $\longrightarrow$ NaCl(aq) + H_2O (l)
(C) C(s) + O_2 (g) $\longrightarrow$ CO_2 (g)   (D) N_2 (g) + $3H_2$(g) $\longrightarrow$ 2 NH_3 (g)

2. ΔH_r of which of the following reactions is not zero ?
(A) H_2 (g) $\longrightarrow$ $2H^+$ (g) + $2e^-$ (B) 2H (g) + aq $\longrightarrow$ $2H^+$ (aq) + $2e^-$
(C) 2H (g) $\longrightarrow$ $2H^+$ (g) + $2e^-$ (D) H_2 (g) + aq $\longrightarrow$ $2H^+$ (aq) + $2e^-$

3*. Which of the following statements is (are) correct ?
(A) the reaction between the strong acid and strong base takes place with the evolution of heat
(B) $\Delta H_{neut.}$ of weak acid/strong base is less than the $\Delta H_{neut.}$ of strong acid/strong base
(C) $\Delta H_{neut.}$ of strong acid/strong base is equal to the ΔH of formation of H_2O(l) from its ions in the aqueous medium
(D) $\Delta H_{neut.(weak acid/strong base)} - \Delta H_{neut.(strong acid/strong base)} = \Delta H_{ioni(weak acid)}$

4*. Which of the following statement is (are) correct ?

(A) for an exothermic reactions, $\sum \Delta H_f^\circ$ (products) $<$ $\sum \Delta H_f^\circ$ (reactants)

(B) $\sum \Delta H_f^\circ$ of CO_2(g) is same as the $\Delta H^\circ_{comb.}$ of carbon graphite

(C) all exothermic reactions have a free energy change negative

(D) for a reaction $N_{2(g)}$ + $O_{2(g)}$ $\longrightarrow$ $2NO_{(g)}$, the heat at constant pressure and the heat at constant volume at a given temperature are same

5*. Which of the following is true?

(A) For the reaction $CaCO_3$(calcite) $\longrightarrow$ $CaCO_3$ (aragonite) given : $\Delta_f G^o_{298}$ (calcite) = –1128.8 kJ/mol,

$\Delta_f G^o_{298}$ (aragonite) = – 1127.75 kJ/mol, then calcite form is thermodynamically more stable at standard conditions.
(B) For the reaction,
(a) C(diamond) + $2H_2$ (g) $\longrightarrow$ CH_4(g) ΔH_1
(b) C(g) + 4H(g) $\longrightarrow$ CH_4(g) ΔH_2
then more heat is evolved in reaction (b).
(C) $\Delta_f H^\circ$ (I_2, g) = $\Delta_{sub}H$ [I_2, s] at 25°C.
(D) For the exothermic reaction 2Ag(s) + 1/2 O_2(g) $\longrightarrow$ $2Ag_2O$(s) at 298 K. $\Delta H < \Delta U$

6. Which of the following do(es) not represent ΔH formation of the product.

(A) $\dfrac{1}{2} H_2$(g) + (aq) $\longrightarrow$ H^+(aq)   (B) $\dfrac{2}{3} O_3$(g) $\longrightarrow$ O_2(g) + e^-

(C) NH_4^+ (g) + Cl^-(g) $\longrightarrow$ NH_4Cl(s)   (D) P_4(black) + $5O_2$ (g) $\longrightarrow$ P_4O_{10}(s)
(E) Reaction representing $\Delta H_{combustion}$ of C (graphite).

7. Which of the reactions can not define molar ΔH_f°?

(A) CaO(s) + CO_2(g) $\longrightarrow$ $CaCO_3$ (s)   (B) $\dfrac{1}{2} Br_2$ (g) + $\dfrac{1}{2} H_2$ (g) $\longrightarrow$ HBr(g)

(C) N_2 (g) + $2H_2$ (g) + $\dfrac{3}{2} O_2$ (g) $\longrightarrow$ NH_4NO_3 (s)   (D) I_2 (s) + H_2 (g) $\longrightarrow$ 2HI (g)

8. For the reaction, C(graphite) + $\dfrac{1}{2} O_2$ (g) $\rightarrow$ CO(g) at 298 K and 1 atm ΔH = – 26.4 k cal. Which of the following statements are true (Molar vol. of graphite is = 0.0053L) :
(A) ΔH = – 26.7 k cal   (B) ΔHg = 0.5   (C) ΔE = – 26.7 k cal   (D) ΔE = 0

9. For which of the following ΔH_f^0 is zero :

(A) Br_2 (g)   (B) I_2 (g)   (C) Cl_2 (g)   (D) F_2(g)

10*. Which of the following represent(s) $\Delta H_{atomization}^{\circ}, H_2O(s)$?

(A) $\Delta H_{sublimation,H_2O(s)}^{\circ} + 2\Delta H_{BE,O-H}^{\circ}$ (B) $\Delta H_{fusion,H_2O(s)}^{\circ} + 2\Delta H_{vapourisation,H_2O(\ell)}^{\circ}$

(C) $-\Delta H_{formation,H_2O(s)}^{\circ} + \Delta H_{BE,H-H}^{\circ} + \dfrac{\Delta H_{BE,O=O}^{\circ}}{2}$ (D) $-\Delta H_{fusion,H_2O(s)}^{\circ} + \Delta H_{atomization,H_2O(\ell)}^{\circ}$

11*. Select the correct statement for the neutralisation of strong acid & strong base in a solution :

(A) $\Delta S = -ve$ (B) $\Delta H = -ve$ (C) $\Delta G = -ve$ (D) $\Delta U = -ve$

12*. Which of the following mixture of strong acid & strong base will give same temperature change for solution (Assume density & specific heat same for all solutions)-

(A) 50 ml 0.1 M HCl + 50 ml 0.1 M NaOH   (B) 30 ml 0.1 M HCl + 30 ml 0.1 M NaOH

(C) 25 ml 0.1 M H_2SO_4 + 50 ml 0.1 M KOH   (D) 50 ml 0.1 M H_2SO_4 + 50 ml 0.1 M NaOH

Match the Column

13*. Match the reaction (In Column I) with relation between ΔH and ΔE (in Column II) :

	Column-I		**Column-II**
(A)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	(p)	$\Delta H = \Delta E + RT$
(B)	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	(q)	$\Delta H = \Delta E$
(C)	$NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$	(r)	$\Delta H = \Delta E - 2RT$
(D)	$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2$	(s)	$\Delta H = \Delta E + 2RT$
(E)	$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	(t)	$\Delta H = \Delta E - RT$

14.

	Column-I		**Column-II**
(A)	$S(g) + O_2(g) \longrightarrow SO_2(g)$; ΔH	(p)	Heat of solution
(B)	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; ΔH	(q)	Heat of neutralisation
(C)	$NaOH(s) + aq \longrightarrow NaOH (aq)$; ΔH	(r)	Heat of formation
(D)	$NaOH(aq) + HCl(aq) \longrightarrow NaCl (aq) + H_2O(l)$; ΔH	(s)	Heat of combustion

Comprehension Based Questions

Using the data (all values are in kJ/mol at 25° C) given below :

$\Delta H^{\circ}_{combustion}$ (ethane) $= -1559.8$; $\Delta H^{\circ}_{combustion}$ (ethene) $= -1410.9$

$\Delta H^{\circ}_{combustion}$ (acetylene) $= -1299.7$; $\Delta H^{\circ}_{combustion}$ (acetaldehyde) $= -1192.3$

ΔH°_f $CO_2(g) = -393.5$; ΔH°_f of $H_2O(l) = -285.8$

ΔH° for $C_{(s)}$ (graphite) $\rightarrow C_{(g)} = +716.68$;   Bond enthalpy of $H-H = 435.94$

Bond enthalpy of $O = O = 498.94$

Calculate the following bond energies :

15*. $C-C$

(A) 97.81 kJ   (B) 195.62 kJ   (C) 48.9 kJ   (D) 434.3 kJ

16*. $C-H$

(A) 227.32 kJ   (B) 454.64 kJ   (C) 151.54 kJ   (D) 909.28 kJ

17*. $C = O$

(A) 402.13 kJ   (B) 201.06 kJ   (C) 804.26 kJ   (D) 1608.52 kJ

18*. $C = C$

(A) 97.81 kJ   (B) 195.62 kJ   (C) 217.15 kJ   (D) 434.3 kJ

19*. $C \equiv C$

(A) 733.48 kJ   (B) 366.74 kJ   (C) 1466.96 kJ   (D) None of these

EXERCISE – 3   SUBJECTIVE

1. When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated. Calculate the heat of formation, $\Delta H°_f$ for C_2H_6. Give $\Delta H°_f$ for $CO_2(g)$ & $H_2O(l)$ are –395 & –286 kJ respectively.

2*. The standard heats of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(l)$ are –76.2, –398.8, –241.6 kJ mol^{-1}. Calculate amount of heat evolved by burning $1m^3$ of methane measured under normal (STP) conditions.

3. Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed $\Delta H°_f$ for $Ca^{2+}(aq)$, CO_3^{2-} (aq) and $CaCO_3(s)$ are –129.80, –161.65, –288.5 kcal mol^{-1} respectively.

4*. The enthalpies of neutralization of NaOH & NH_4OH by HCl are –13680 calories and –12270 cal respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl is solution ? Assume that NH_4OH and NaCl are quantitatively obtained.

5*. The heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

6. The heat of reaction $\dfrac{1}{2} H_2(g) + \dfrac{1}{2} Cl_2(g) \longrightarrow HCl(g)$ at 27°C is –22.1 kcal. Calculate the heat of reaction at 77°C. The molar heat capacities at constant pressure at 27°C for hydrogen, chlorine & HCl are 6.82, 7.70 & 6.80 cal mol^{-1} respectively.

7. Calculate standard heats of formation of carbon-di-sulphide (*l*). Given the standard heat of combustion of carbon (s), sulphur (s) & carbon-di-sulphide (*l*) are : –393.3, –293.72 and –1108.76 kJ mol^{-1} respectively.

8. The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is –2480 cal. geq^{-1} and –13.68 kcal, geq^{-1} respectively. Find the enthalpy of dissociation of HCN at the same temperature.

9. At 300K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ & $H_2O(l)$ are; –408, –393 & –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at :
   (i) constant pressure   *(ii)* constant volume.

10*. The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ. This heat has been measured at constant volume & at 27°C. Calculate the heat of combustion of benzene at constant pressure.

11*. If the enthalpy of formation of HCl (g) and Cl$^-$ (aq) are –92.3 kJ/mole and –167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

12. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at
   (i) constant volume   *(ii)* constant pressure.
   The thermal capacity of calorimeter system is 17.7 kJ K^{-1}. (R = 8.313 mol^{-1}K^{-1})

13. When 1.0 g of fructose $C_6H_{12}O_6(s)$ is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56°C. If the heat capacity of the calorimeter and its contents is 10.0 kJ/°C. Calculate the enthalpy of combustion of fructose at 298 K.

14*. The enthalpy of dissociation of PH_3 is 954 kJ/mol and that of P_2H_4 is 1.485 M J mol^{-1}. What is the bond enthlapy of the P–P bond ?

15*. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction,

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$
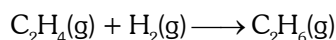
Data :

Bond	C – C	C = C	C – H	H – H
Bond Enthalpy	336.81 kJ/mol	606.68 kJ/mol	410.87 kJ/mol	431.79 kJ/mol

16*. The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows:

$CH_4(g) \longrightarrow C(g) + 4H(g)$ $\qquad \Delta_r H = 396$ kcal/mole

$C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ $\qquad \Delta_r H = 676$ kcal/mole
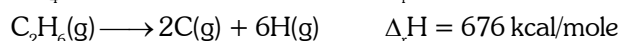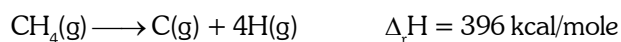
Calculate C–C bond energy in C_2H_6 & heat of formation of $C_2H_6(g)$

Given : $\qquad \Delta_{sub} C(s) = 171.8$ kcal/mole

$\qquad\qquad$ B.E. (H–H) = 104.1 kcal/mole

17. Find the enthalpy of S–S bond from the following data.

(i) $\quad C_2H_5–S–C_2H_5(g) \qquad \Delta H°_f = –147.2$ kJ/mol

(ii) $\quad C_2H_5–S–S–C_2H_5(g) \quad \Delta H°_f = –201.9$ kJ/mol

(iii) $\quad S(g) \qquad\qquad\qquad\quad \Delta H°_f = –222.8$ kJ/mol
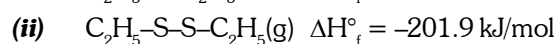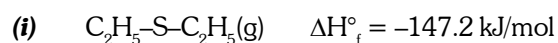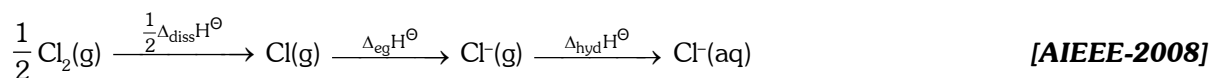
18*. Calculate the electron affinity of fluorine atom using the following data. Make Born–Haber's cycle. All the values are in kJ mol^{-1} at 25°C, $\Delta H_{diss}(F_2) = 160$, $\Delta H_f°$ (NaF(s)) = –571. I.E. [Na(g)] = 494, ΔH_{vap} [Na(s)] = 101. Lattice energy of NaF(s) = –894.

EXERCISE – 4   **RECAP OF AIEEE/JEE (MAIN)**

1. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction :   **[AIEEE-2003]**

$H_2C=CH_2(g) + H_2(g) \longrightarrow H_3C–CH_3(g)$ at 298 K will be :-

(A) +125 kJ   (B) –125 kJ   (C) +250 kJ   (D) –250 kJ

2*. The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole :-   **[AIEEE-2004]**

(A) 110.5 kJ   (B) 676.5 kJ   (C) –676.5 kJ   (D) –110.5 kJ

3. Consider the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$ carried out at constant temperature and pressure, if ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true?

[AIEEE-2005]

(A) $\Delta H = \Delta U$ (B) $\Delta H = 0$ (C) $\Delta H > \Delta U$ (D) $\Delta H < \Delta U$

4*. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be :-   **[AIEEE-2005]**

(A) 200 kJ mol^{-1} (B) 100 kJ mol^{-1} (C) 800 kJ mol^{-1} (D) 300 kJ mol^{-1}

5*. The standard enthlapy of formation ($\Delta_f H°$) at 298K for methane, $CH_4(g)$, is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C–H bond formation would be:-

(A) Latent heat of vapourization of methane   **[AIEEE-2006]**

(B) The first four ionization energies of carbon and electron gain enthalpy of hydrogen

(C) The dissociation energy of hydrogen molecule H_2

(D) The dissociation energy of H_2 and enthalpy of sublimation of carbon

6*. The enthalpy changes for the following processes are listed below :   **[AIEEE-2006]**

$Cl_2(g) = 2Cl(g)$,   242.3 kJ mol^{-1}

$I_2(g) = 2I(g)$,   151.0 kJ mol^{-1}

$ICl(g) = I(g) + Cl(g)$,   211.3 kJ mol^{-1}

$I_2(s) = I_2(g)$,   62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for $ICl(g)$ is :-

(A) –16.8 kJ mol^{-1} (B) +16.8 kJ mol^{-1} (C) +244.8 kJ mol^{-1} (D) –14.6 kJ mol^{-1}

7. $(\Delta H – \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is

$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$ **[AIEEE-2006]**

(A) 1238.78 J mol^{-1} (B) –2477.57 J mol^{-1} (C) 2477.57 J mol^{-1} (D) –1238.78 J mol^{-1}

8. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1} will be) :-   **[AIEEE-2007]**

(A) 4.100 kJ mol^{-1} (B) 3.7904 kJ mol^{-1} (C) 37.904 kJ mol^{-1} (D) 41.00 kJ mol^{-1}

9. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:
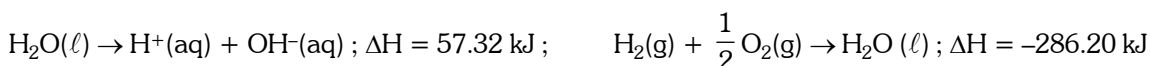
$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus}} Cl(g) \xrightarrow{\Delta_{eg}H^{\ominus}} Cl^-(g) \xrightarrow{\Delta_{hyd}H^{\ominus}} Cl^-(aq)$$ **[AIEEE-2008]**

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$

(using the data $\Delta_{diss}H_{Cl_2}^{\ominus} = 240$ kJ mol^{-1}, $\Delta_{eg}H_{Cl}^{\ominus} = -349$ kJ mol^{-1}, $\Delta_{hyd}H_{Cl^-}^{\ominus} = -381$ kJ mol^{-1}) will be:-

(A) -610 kJ mol^{-1} (B) -850 kJ mol^{-1} (C) $+120$ kJ mol^{-1} (D) $+152$ kJ mol^{-1}

10*. On the basis of the following thermochemical data : $\left(\Delta G_f^0 H_{(aq)}^+ = 0\right)$

$H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$; $\Delta H = 57.32$ kJ ; $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -286.20$ kJ

The value of enthalpy of formation of OH$^-$ ion at 25°C is :-   **[AIEEE-2009]**

(A) $+228.88$ kJ   (B) -343.52 kJ   (C) -22.88 kJ   (D) -228.88 kJ

11*. The standard enthalphy of formation of NH$_3$ is -46.0 kJ mol^{-1}. If the enthalpy of formation of H$_2$ from its atoms is -436 kJ mol^{-1} and that of N$_2$ is -712 kJ mol^{-1}, the average bond enthalpy of N–H bond in NH$_3$ is:-

[AIEEE-2010]

(A) -1102 kJ mol^{-1} (B) -964 kJ mol^{-1} (C) $+352$ kJ mol^{-1} (D) $+1056$ kJ mol^{-1}

12*. The value of enthalpy change (ΔH) for the reaction $C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$ at 27°C is -1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be :-

[AIEEE-2011]

(A) -1371.5 kJ   (B) -1369.0 kJ   (C) -1364.0 kJ   (D) -1361.5 kJ

13. Consider the reaction :

$4NO_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$, $\Delta_r H = -111$kJ.
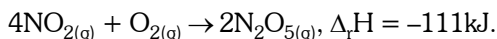
If $N_2O_{5(s)}$ is formed instead of $N_2O_{5(g)}$ in the above reaction, the $\Delta_r H$ value will be :-

(given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1})   **[AIEEE-2011]**

(A) -165 kJ   (B) $+54$ kJ   (C) $+219$ kJ   (D) -219 kJ

14. The enthalpy of neutralisation of NH$_4$OH with HCl is -51.46 kJ mol^{-1} and the enthalpy of neutralisation of NaOH with HCl is -55.90 kJ mol^{-1}. The enthalpy of ionisation of NH$_4$OH is :-   **[AIEEE-2012]**

(A) $+107.36$ kJ mol^{-1} (B) -4.44 kJ mol^{-1} (C) -107.36 kJ mol^{-1} (D) $+4.44$ kJ mol^{-1}

15. The difference between the reaction enthalpy change ($\Delta_r H$) and reaction internal energy change ($\Delta_r U$) for the reaction : $2C_6H_6(\ell) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(\ell)$ at 300K is (R = 8.314 J mol^{-1} K^{-1}) **[AIEEE-2012]**

(A) 0 J mol^{-1} (B) 2490 J mol^{-1} (C) -2490 J mol^{-1} (D) -7482 J mol^{-1}

16*. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208J heat. The values of q and w for the proces will be :

(R = 8.314 J/mol K) (In 7.5 = 2.01)   **[JEE Main-2013]**

(A) q = $+$ 208 J, w = $-$ 208 J   (B) q = $-$ 208 J, w = $-$ 208 J

(C) q = $-$ 208 J, w = $+$ 208 J   (D) q = $+$ 208 J, w = $+$ 208 J

17*. For complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomd calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion,

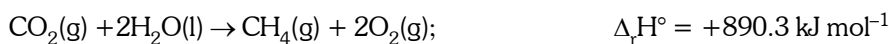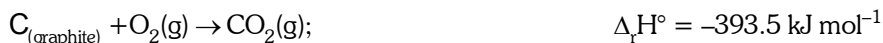$\Delta_c H$, for the reaction will be: (R = 8.314 kJ mol^{-1})   **[JEE main-2014]**

(A) $-$ 1366.95 kJ mol^{-1} (B) $-$ 1361.95 kJ mol^{-1} (C) $-$ 1460.50 kJ mol^{-1} (D) $-$ 1350.50 kJ mol^{-1}

18*. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is   *[JEE Main-2016]*

(A) 110.5   (B) 676.5   (C) –676.5   (D) –110.5

19*. Given :

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g); \qquad\qquad \Delta_r H° = -393.5 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \qquad\qquad \Delta_r H° = -285.8 \text{ kJ mol}^{-1}$$

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g); \qquad \Delta_r H° = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$ will be;   *[JEE Main-2017]*

(A) –144.0 kJ mol^{-1} (B) +74.8 kJ mol^{-1} (C) +144.0 kJ mol^{-1} (D) –74.8 kJ mol^{-1}

20. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is :   *[JEE Mains-2017]*

(Given $\Delta_{fus}H = 6$ kJ mol^{-1} at 0°C, $C_P(H_2O, l) = 75.3$ J mol^{-1} K^{-1}, $C_P(H_2O, s) = 36.8$ J mol^{-1} K^{-1})

(A) 6.56 kJ mol^{-1} (B) 5.81 kJ mol^{-1} (C) 6.00 kJ mol^{-1} (D) 5.44 kJ mol^{-1}

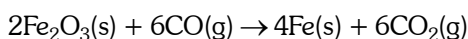**21.** The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be (R = 8.314 JK^{-1} mol^{-1})   *[JEE Mains-2018]*

(A) –452.46   (B) 3260   (C) –3267.6   (D) 4152.6

22. Given   *[JEE Mains-2018]*

(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$; $\Delta_r G° = +1487.0$ kJ mol^{-1}

(ii) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$; $\Delta_r G° = -514.4$ kJ mol^{-1}
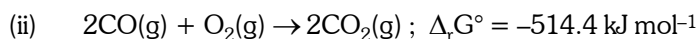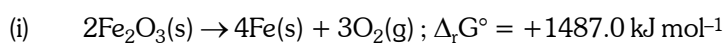
Free energy change, $\Delta_r G°$ for the reaction

$2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$

will be :-

(A) –112.4 kJ mol^{-1} (B) –56.2 kJ mol^{-1} (C) 168.2 kJ mol^{-1} (D) 208.0 kJ mol^{-1}

23. The reaction, $MgO(s) + C(s) \rightarrow Mg(S) + CO(g)$, for which $\Delta_r H° = +491.1$ kJ mol^{-1} and $\Delta_r S° = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is :   *[JEE Mains-2019]*

(A) 1890.0 K   (B) 2480.3 K   (C) 2040.5 K   (D) 2380.5 K

24. For the equilibrium, $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of $\Delta G°$ at 298 K is approximately : *[Mains-2019]*

(A) –80 kJ mol^{-1} (B) –100 kJ mol^{-1} (C) 100 kJ mol^{-1} (D) 80 kJ mol^{-1}

25. Given :

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g); \qquad\qquad \Delta_r H° = x$ kJ mo^{-1}

(ii) $C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \qquad\qquad \Delta_r H° = y$ kJ mo^{-1}

(iii) $CO(graphite) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \qquad\qquad \Delta_r H° = z$ kJ mo^{-1}
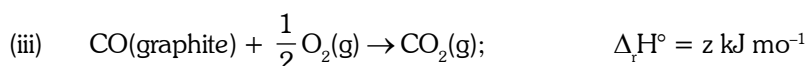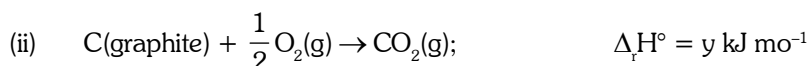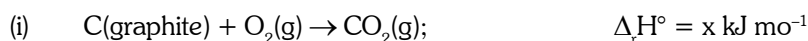
Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?   *[JEE Mains-2019]*

(A) z = x + y   (B) x = y – z   (C) x = y + z   (D) y = 2z – x

26. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal g^{-1}K^{-1} respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is :

(A) 2.85   (B) 11.4   (C) 5.7   (D) 22.8

EXERCISE – 5	RECAP OF IIT-JEE/JEE (ADVANCED)

1. Which of the following reaction defines ΔH°_f ? **[IIT-JEE-2003]**

(A) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$

(B) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g)$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(D) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$

2*. Estimate the average S–F bond energy in SF_6. The ΔH°_f values of $SF_6(g)$, S(g) and F(g) are –1100, 275 and 80 kJ/mol respectively. **[IIT-JEE-2005]**

3. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The **enthalpy** of formation of $CO_2(g)$, $H_2O(l)$ and propene (g) are –393.5, –285.8 & 20.42 kJ/mol respectively. The enthalpy of isomerisation of cyclopropane to propene is –33.0 kJ/mol. **[IIT-JEE-2005]**

4*. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is **[IIT-JEE-2009]**

5*. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C \equiv C$ bond in C_2H_2. That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1}.) **[IIT-JEE-2012]**

$$2\,C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H = 225 \text{ kJ mol}^{-1}$$
$$2\,C(s) \longrightarrow 2C(g) \qquad \Delta H = 1410 \text{ kJ mol}^{-1}$$
$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 330 \text{ kJ mol}^{-1}$$

(A) 1165 (B) 837 (C) 865 (D) 815

6*. The standard enthalpies of formation of $CO_2(g)$, $H_2O(\ell)$ and glucose (s) at 25°C are 400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is : **[IIT-JEE-2013]**

(A) + 2900 kJ (B) – 2900 kJ (C) – 16.11 kJ (D) + 16.11 kJ

Comprehension (Q.7 & Q.8)

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt.2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt.1) where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions are 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

7. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is **[JEE 2015]**

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4

8. The pH of the solution after Expt. 2 is **[JEE 2015]**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0

9. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation.

(1) $\frac{3}{2} O_2(g) \rightarrow O_3(g)$

(2) $\frac{1}{8} S_8(s) + O_2(g) \rightarrow SO_2(g)$

(3) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(4) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	B	D	D	D	C	C	C	D	B	D	C	C	D	A

Que.	16	17	18	19	20	21	22	23
Ans.	A	A	D	B	C	C	D	C

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	ABC	ABC	ABCD	ABD	ABCD	ABCD	ABD	BC	CD	ACD

Que.	11	12
Ans.	BCD	ABD

- **Match the Column**
  13*. (A) - (q), (B) - (r), (C) - (s), (D) - (p), (E) - (t)
  14. (A) - (r), (B) - (s), (C) - (p), (D) - (q)

- **Comprehension Based Questions**
  15*. (A)   **16*.** (B)   **17*.** (C)   **18*.** (D)   **19*.** (A)

EXERCISE-3
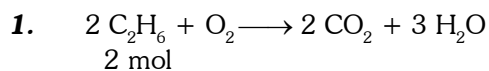
1. $2\ C_2H_6 + O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$
     2 mol
$(\Delta H)/$ mole $= -01560$ kJ
$= 2\ (-345) + 3(286) - (\Delta H^\circ_f)_{C_2H_6}$
$\Delta H^\circ_f = -790 - 858 + 15 - 98$ kJ
$= -88$ kJ/mol
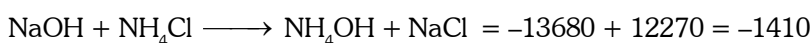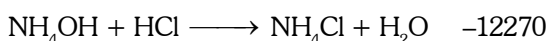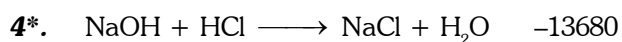
2*. $CH_2 + 2O_2 \longrightarrow CO_2 + 2H_2O$
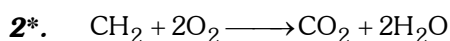
$\Rightarrow \quad -398.8 - 291.6 - 291.6 + 76.2 = -805.8$

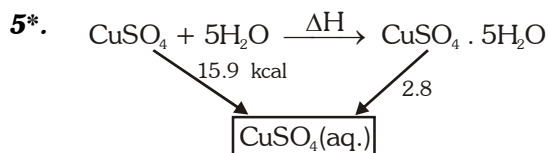$\dfrac{PV}{RT} = n \Rightarrow \dfrac{1.01325 \times 1000}{0.0521 \times 293} \Rightarrow 36.42$ MJ

3. $CaCl \longrightarrow Ca^{+2} + 2Cl^-$

$Na_2CO_3 \longrightarrow$

$CaCl_2 + Na_2CO_3 \longrightarrow 2Na^+ + 2Cl^- + CaCO_3$
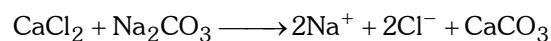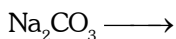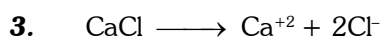
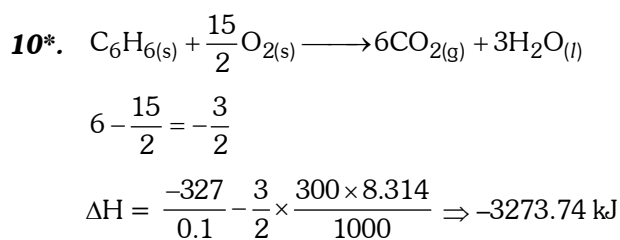$\Rightarrow \Delta H = -288.5 + (129.8 + 161.65)$
     $= 2.95$ Kcal

4*. $NaOH + HCl \longrightarrow NaCl + H_2O \quad -13680$

$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O \quad -12270$

$NaOH + NH_4Cl \longrightarrow NH_4OH + NaCl = -13680 + 12270 = -1410$

5*. $CuSO_4 + 5H_2O \xrightarrow{\Delta H} CuSO_4 . 5H_2O$

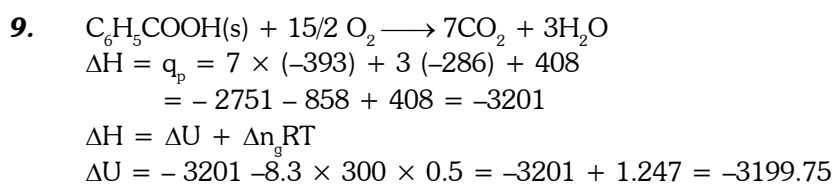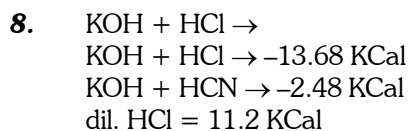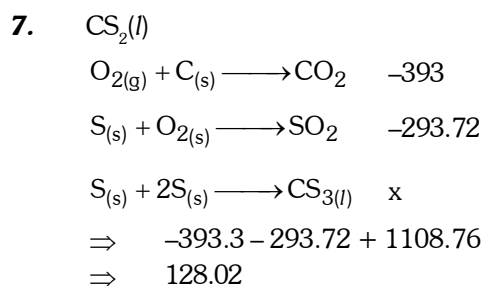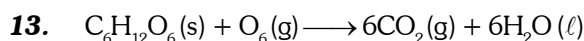15.9 kcal $\qquad\qquad$ 2.8

$\boxed{CuSO_4(aq.)}$

Applying Hess's law $\Delta H + 2.8 = -15.9$

$\Delta H = -15.9 - 2.8$ $\quad \Delta H = 18.7$

6. $\Delta H_2 - (-22.1) \times 1000 = \left(6.80 - \dfrac{(7.70 + 6.82)}{2}\right)50$

$\Delta H_2 = -22.123$ KCal

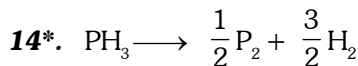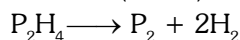**7.** $CS_2(l)$

$O_{2(g)} + C_{(s)} \longrightarrow CO_2 \qquad -393$

$S_{(s)} + O_{2(s)} \longrightarrow SO_2 \qquad -293.72$

$S_{(s)} + 2S_{(s)} \longrightarrow CS_{3(l)} \qquad x$

$\Rightarrow \qquad -393.3 - 293.72 + 1108.76$

$\Rightarrow \qquad 128.02$

8. $KOH + HCl \rightarrow$
$KOH + HCl \rightarrow -13.68$ KCal
$KOH + HCN \rightarrow -2.48$ KCal
dil. $HCl = 11.2$ KCal

9. $C_6H_5COOH(s) + 15/2\ O_2 \longrightarrow 7CO_2 + 3H_2O$
$\Delta H = q_p = 7 \times (-393) + 3(-286) + 408$
$\qquad = -2751 - 858 + 408 = -3201$
$\Delta H = \Delta U + \Delta n_g RT$
$\Delta U = -3201 - 8.3 \times 300 \times 0.5 = -3201 + 1.247 = -3199.75$

10*. $C_6H_{6(s)} + \dfrac{15}{2}O_{2(s)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$

$6 - \dfrac{15}{2} = -\dfrac{3}{2}$

$\Delta H = \dfrac{-327}{0.1} - \dfrac{3}{2} \times \dfrac{300 \times 8.314}{1000} \Rightarrow -3273.74$ kJ

11*. $\frac{1}{2}H_2 \quad \frac{1}{2}Cl_2 \xrightarrow{92.3} HCl\ (g)$

$\uparrow \qquad \uparrow^{-167.44} \qquad \searrow^{x}$

$H^+(eq.) \quad Cl^-_{(aq.)} \swarrow$

$-92.30 + x = -167.44$

$x = -75.14$ kJ/mol

12. $\Delta G = \dfrac{17.7 \times 0.5 \times 1}{0.01}$

$\Delta G = 885$ kJ

$\Delta G = -885 - \dfrac{2 \times 8.314 \times 300}{1000}$

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O$

$\Delta G = -889.98$ kJ

13. $C_6H_{12}O_6(s) + O_6(g) \longrightarrow 6CO_2(g) + 6H_2O(\ell)$
    1.0 g

$\Delta U = m\ Cv\ dt$

$\Delta U = -10\ kJ \times\ 1.56 = 15.6\ kJ$

for 1 mole $= 15.6 \times 180 = -2808\ kJ$

14*. $PH_3 \longrightarrow \dfrac{1}{2}P_2 + \dfrac{3}{2}H_2$

954 = 3 (P – H)

$P_2H_4 \longrightarrow P_2 + 2H_2$

1485 = 4 (P–H) + (P–P)

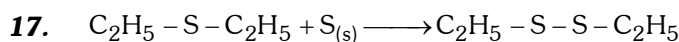$1485 = 4 \times \dfrac{954}{3} + (P–P)$

(P–P) = – 1272 +1485 = 213 kJ/mol

15*.
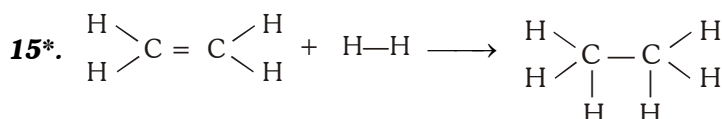
6.6.68 + 4(910.87) + 431.79 – 336.81 –6(910.87) = –120.08

16*.
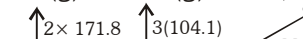
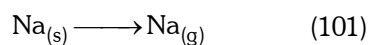$\Delta_r H = -676+343.6+312.3 = -676 + 655.9 = 20.1$

4 (C – H) = 396   (C–C) + 6(99) = 676

  C – H = 99 K   (C–C) = 676 –594 = 84

17. $C_2H_5 - S - C_2H_5 + S_{(s)} \longrightarrow C_2H_5 - S - S - C_2H_5$

$\Delta H_{Rxn} = B.E._{S_{(s)} \to S_{(g)}} + 10.B.E._{C-H} + 2B.E._{C-S} - 108E_{C-H} - 2B.E._{C-S} - 1 \times B.E._{S-S}$

18*. $\dfrac{1}{2}F_2 \longrightarrow F$ (80)

$Na_{(s)} + \dfrac{1}{2}F_{2(g)} \longrightarrow NaF$ (–571)

$Na_{(s)} \longrightarrow Na_{(g)}$ (101)

$Na_{(g)} \longrightarrow Na^+_{(g)} + C^-$ (794)

$Na^+_{(g)} + F^-_{(g)} \longrightarrow NaF$ (–894)

$F_{(g)} + e^- \longrightarrow F^-_{(g)}$ (x)
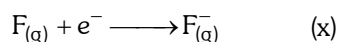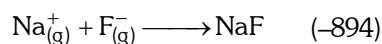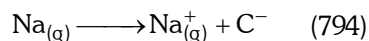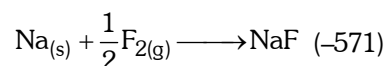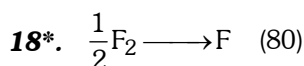
–571 = – 219 + x

x = –352

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	D	D	C	D	B	A	C	A	D	C	C	D	D	D

Que.	16	17	18	19	20	21	22	23	24	25	26
Ans.	A	A	D	D	A	C	B	B	D	C	D

EXERCISE-5

    1. (B)   **2*.** 309.16 kJ/ mol   **3.** –2091.32 kJ mol⁻¹   **4*.** (9)

    5*. (D)   **6*.** (C)   **7.** (A)   **8.** (B)   **9.** (1, 2)

Important Notes

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