Chemistry Question Bank

Career Endeavor - Chem Academy - Saraswati Dham

CSIR-UGC NET-JRF Chemistry

IIT-JAM Chemistry

🏆 Chemistry - A Free Initiative for Study Material 🏆

🥭 **1. Chemistry People**
https://kutumb.app/chemistry-group?ref=ODB82

🥭 **2. CSIR NET-JRF CHEMISTRY**
https://kutumb.app/c-s-i-r-j-r-f-c?ref=TRYN4

🥭 **3. CSIR NET-GATE JAM Chemistry**
https://kutumb.app/c-n-g-j-c?ref=TRYN4

🥭 **4. Gate Chemistry**
https://kutumb.app/gate-chemistry?ref=TRYN4

🥭 **5. IIT-JAM Chemistry**
https://kutumbapp.page.link/5xEADxvTyi2CgEPY9

🥭 **6. Target NEET/IIT-JEE (NTA) Chemistry**
https://kutumbapp.page.link/fgsPekDYfKHvvSgG7

🥭 **7. Target UPSC - Free Study Material**
https://kutumb.app/target-upsc-fsm?ref=TRYN4

🥭 **8. Global Teacher Association**
https://kutumb.app/Global-Teachers-Association?ref=ODB82

🥭 **9. College Students Association**
https://kutumb.app/csa?ref=ODB82

🥭 **10. Indian Research Scholar Association**
https://kutumb.app/i-r-s-a?ref=ODB82

🥭 **11. Government Job Alerts**
https://kutumb.app/government-job-alerts?ref=ODB82

IIT JAM ✓

B113 J60

~~69hy|88~~

S.P. Sharma

PHYSICAL CHEMISTRY

VOLUME - 2

IIT-JAM

INDEX

CHAPTER

6

CHEMICAL EQUILIBRIUM

If the two opposing processes in a reversible change are chemical changes and the state in this change when the two opposing reactions occur at the same rate, so that concentration of the reactant and product do not change with time is termed as chemical equilibrium.

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

$$K_x = K_n(n_T)^{-\Delta n_g}$$

$$K_C = K_n(V)^{-\Delta n_g}$$

$$K_P = K_n\left(\frac{P_T}{n_T}\right)\Delta n_g$$

Relation of Vapour Density and α (Degree of Dissociation)

Vapour Density = M.M/2.

$$\text{Effective Molar Mass} = \frac{\Sigma w}{\Sigma_1 n}$$

A	$\rightleftharpoons$	nB	n_T	w_T
a		–	a	$a \times M_A$
$a - a\alpha$		$na\alpha$	$a[1+(n-1)\alpha]$	$a \times M_A$

$$\text{Effective Molar Mass} = \frac{a \times M_A}{a[1+(n-1)\alpha]}$$

$$M_A = 2 \times (V.D.)_A \to \Delta$$

Effective Molar Mass = $2 \times (V.D.)_{mix} \to d$.

Relation of Density and V.D.

$$PV = nRT$$

$$P = \frac{w}{M} \times \frac{nRT}{V}$$

$PM = dRT \qquad \Rightarrow dRT = PM$

$$d = \frac{P}{RT}(2 \times V.D.)$$

Thermodynamics of Equilibrium :

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

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

where $\Delta G =$ Gibb's Free energy change

$\Delta G^0 =$ Standard Gibb's Free energy change

$Q =$ reaction quotient

Since, at equlibrium, $Q = K$

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$$K = \frac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n} \quad ; \qquad \text{Here } a_X \text{ denotes the activity of X.}$$

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.

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

EXERCISE I

Single Answer Type

Equilibrium Constant and Their Relations

1. For the reaction $3A(g) + B(g) \rightleftharpoons 2C(g)$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 moles each of A, B and C exists in equilibrium?

   ✓(a) 6L (b) 9L (c) 36 L (d) None of these

2. What is the expression of equilibrium constant for the reaction;

   $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$:

   (a) $K_c = \dfrac{1}{[O_2]^5}$ (b) $K_c = \dfrac{[P_4O_{10}]}{5[P_4][O_2]^5}$ (c) $K_c = [O_2]^5$ (d) $K_c = \dfrac{[P_4O_{10}]}{[P_4][O_2]^5}$

3. For the following three reactions 1, 2 and 3, equilibrium constants are given :

   (1) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1

   (2) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2

   (3) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

   Which of the following relations is correct ?

   (a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$ (c) $K_3 = K_1K_2$ (d) $K_3 \cdot K_2^3K_1^2$

4. For the reaction : $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$, K_p/K_c is :

   (a) RT (b) $(RT)^{-1}$ (c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

5. For the reaction; $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

   $K_c = 1.8 \times 10^{-6}$ at 184° C and $R = 0.083\ JK^{-1}\ mol^{-1}$. When K_p and K_c are compared at 184°C, it is found that :

   (a) $K_p > K_c$ (b) $K_p < K_c$

   (c) $K_p = K_c$ (d) $K_p \geq K_c$ depends upon pressure of gases

6. $\log\dfrac{K_p}{K_c} + \log RT = 0$ is a relationship for the reaction :

   (a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

   (c) $H_2 + I_2 \rightleftharpoons 2HI$ (d) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Application of Equilibrium Constant

Imp

7. 1 mole N_2 and 3 moles H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The equilibrium constant K_p for dissociation of NH_3 is:

   (a) $\dfrac{1}{0.5} \times (1.5)^3\ atm^{-2}$ (b) $0.5 \times (1.5)^3\ atm^2$ (c) $\dfrac{0.5 \times (1.5)^3}{3 \times 3}\ atm^2$ (d) $\dfrac{3 \times 3}{0.5 \times (1.5)^3}\ atm^{-2}$

check what he is asking clearly always..

8. 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} mol/L and 1.2×10^{-2} mol/L respectively. The value of K_c for the reaction is :

(a) 3×10^{-3} M (b) 3×10^{3} M (c) 3.3×10^{2} M (d) 3×10^{-1} M

9. The equilibrium constant for the given reaction :

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g) ; K_c = 4.9 \times 10^{-2}$$

The value of K_c for the reaction :

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

(a) 416.5 (b) 2.40×10^{-3} (c) 9.8×10^{-2} (d) 4.9×10^{-2}

10. A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

(a) 0.78 M (b) 0.039 M (c) 0.033 M (d) 0.021 M

11. The reaction quotient Q for : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when:

(a) $Q = K_c$ (b) $Q < K_c$ (c) $Q > K_c$ (d) $Q = 0$

12. $X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$ reaction was studied at a certain temperature. In the beginning 1 mole of X_2 was taken in a one litre flask and 2 moles of Y_2 was taken in another 2 litre flask and both these containers are connected so that equilibrium can be established. What is the equilibrium concentration of X_2 and Y_2? Given Equilibrium concentration of [XY] = 0.6 moles/litre.

(a) $\left(\frac{1}{3} - 0.3\right), \left(\frac{2}{3} - 0.3\right)$ (b) $\left(\frac{1}{3} - 0.6\right), \left(\frac{2}{3} - 0.6\right)$

(c) $(1 - 0.3), (2 - 0.3)$ (d) $(1 - 0.6), (2 - 0.6)$

Degree of Dissociation and Vapour Density

13. For the reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation (α) of HI(g) is related to equilibrium constant K_P by the expression

(a) $\frac{1 + 2\sqrt{K_p}}{2}$ (b) $\sqrt{\frac{1 + 2K_p}{2}}$ (c) $\sqrt{\frac{2K_p}{1 + 2K_p}}$ (d) $\frac{2\sqrt{K_p}}{1 + 2\sqrt{K_p}}$

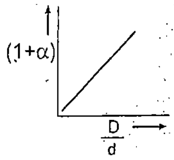
14. Consider the following equilibrium in a closed container

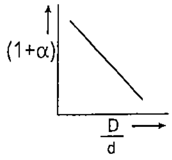
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

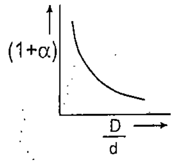
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_P) and degree of of dissociation (α)?

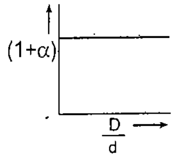
(a) Neither K_p not α changes
(b) Both K_p and α change
(c) K_p changes but α does not change
(d) K_p does not change but α changes

15. In the dissociation of N_2O_4 into NO_2, $(1 + \alpha)$ values with the vapour densities ratio $\left(\frac{D}{d}\right)$ is as given by :
[α-degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]

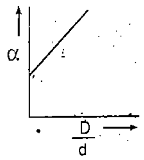
(a)


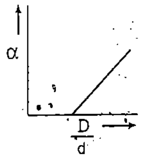
(b)


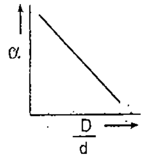
(c)


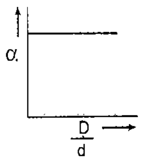
(d)


16. In the above question, α varies with $\frac{D}{d}$ according to :

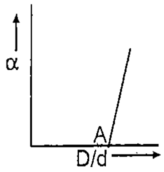
(a)


(b)


(c)


(d)


17. Before equilibrium is set-up for the chemical reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, vapour density d of the gaseous mixture was measured. If D is the theoretical value of vapour density, variation of α with D/d is given by the graph. What is value D/d at point A?



(a) 0
(b) 0.5
(c) 1
(d) 1.5

18. The degree of dissociation is 0.4 at 400 K & 1.0 atm for reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. The density of equilibrium mixture at 1 atm & 400 K is
(a) 3.5 g/L
(b) 4.5 g/L
(c) 4.0 g/L
(d) 2.0 g/L

19. At 523 K, 1L of partially dissociated PCl_5 at 1 atm weighs 2.695 g. The percentage dissociation of PCl_5 at 523 K will be
(a) 0.6
(b) 0.8
(c) 60
(d) 80

Lechatlier Principle

20. The volume of a closed reaction vessel is halved in which the equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ exist, Now}$$

(a) the rates of forward and backward reactions will remains the same.
(b) the equilibrium will not shift.
(c) the equilibrium will shift to the right.
(d) the equilibrium will shift to left

21. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equliibrium :

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ (b) $C(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g)$

(c) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$ (d) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

22. The conditions favourable for the formation of SO_3 are:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H° = -198$ kJ

(a) low temperature, high pressure (b) any value of T and P

(c) low temperature and low pressure (d) high temperature and high pressure

23. 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 at constant pressure. Which of the following statements is/are correct.

consult once about volume change

(a) concentrations of SO_2, Cl_2 and SO_2Cl_2 do not change

(b) more chlorine is formed

(c) concentration of SO_2 is reduced

(d) more SO_2Cl_2 is formed

24. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium, The true statement is

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

(a) K_p does not change with pressure

(b) α does not change with pressure

(c) concentration of NH_3 does not change with pressure

(d) concentration of hydrogen is less than that of nitrogen

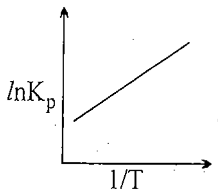
25. An equilibrium mixture in a vessel of capacity 100 litre contain 1 mol N_2, 2 mol O_2 and 3 mol NO. Number of moles of O_2 to be added so that at new equilibrium the conc. of NO is found to be 0.04 mol/lit.:

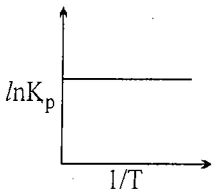
(a) (101/18) (b) (101/9) (c) (202/9) (d) None of these

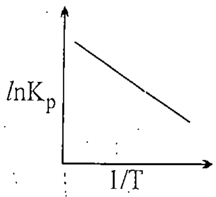
left

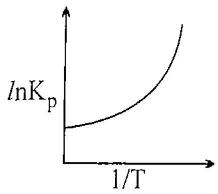
Equilibrium Constant & Thermodynamic Parameter

26. An exothermic reaction is represented by the graph :

(a)


(b)


(c)


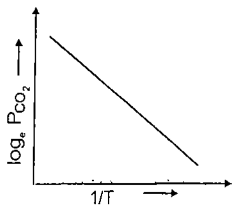
(d)


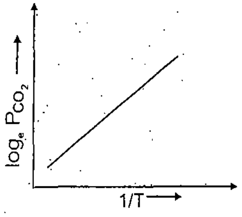
27. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is

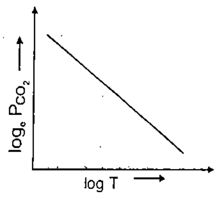
(a) $-\Delta G° = RT\,ln\,K$ (b) $\Delta G = RT\,ln\,K$ (c) $-\Delta G = RT\,ln\,K$ (d) $\Delta G° = RT\,ln\,K$

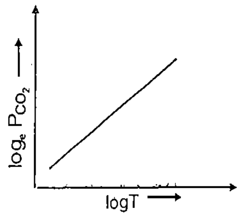
28. For the chemical equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

ΔH_f° can be determined from which one of the following plots ?

(a)


(b)


(c)


(d)


Simultaneous Equilibrium

4000

~~29.~~ The equilibrium constants K_{P_1} and K_{P_2} for the reactions

$X \rightleftharpoons 2Y$ 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 pressures at these equilibria is :

(a) 1 : 36 (b) 1 : 1 (c) 1 : 3 (d) 1 : 9

✓

30. When N_2O_5 is heated at temp. T, it dissociates as $N_2O_5 \rightleftharpoons N_2O_3 + O_2$, $K_c = 2.5$. At the same time N_2O_3 also decomposes as : $N_2O_3 \rightleftharpoons N_2O + O_2$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was found to be 2.5 M. Equilibrium concentration of N_2O is

✓ (a) 1.0 (b) 1.5 (c) 2.166 (d) 0.334

31. If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly only the initial concentration of reactants are given.

In a study of equilibrium

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

1 mol of H_2 and 3 moles of I_2 gave rise at equilibrium to x moles of HI.

Addition of a further 2 moles of H_2 gave an additional x moles of HI. What is x?

(a) 0.5 (b) 1 (c) 1.5 (d) None of these

EXERCISE II

One or More Than One Correct Type

1. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) introducing PCl_5 at constant volume.

2. 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 concentration 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

3. The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction		Equilibrium constant
$A(g) \rightleftharpoons B(g)$	:	$K_1 = ?$
$B(g) \rightleftharpoons C(g)$	:	$K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$	:	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

(a) [A] + [B] + [C] = 1 M at any time of the reactions
(b) Concentration of C is 4.1 M at the attainment of equilibrium in all the reactions
(c) The value of K_1 is $\dfrac{1}{0.24}$
(d) Isomer [A] is least stable as per thermodynamics.

4. For the gas phase exothermic reaction, $A_2 + B_2 \rightleftharpoons C_2$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by

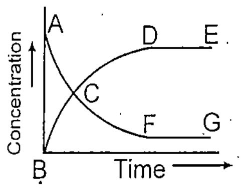
(a) increasing the temperature
(b) decreasing the pressure
(c) adding inert gas at constant pressure
(d) removing some C_2

5. For a reversible reaction $aA + bB \rightleftharpoons cC + dD$; the variation of K with temperature is given by

$$\log \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ then,}$$

(a) $K_2 > K_1$ if $T_2 > T_1$ for an endothermic change
(b) $K_2 < K_1$ if $T_2 > T_1$ for an endothermic change
(c) $K_2 > K_1$ if $T_2 > T_1$ for an exothermic change
(d) $K_2 < K_1$ if $T_2 > T_1$ for an exothermic change

6. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_c = 4$. This reversible reaction is studied graphically as shown in figure. Select the correct statement(s)



I : Reaction quotient has maximum value at point A

II : Reaction proceeds left to right at a point when

$$[N_2O_4] = [NO_2] = 0.1 \text{ M}$$

III : $K_c = Q$ when point D or F is reached :

(a) I
(b) II
(c) III
(d) None

7. (i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g);$ K_1

(ii) $\left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightleftharpoons NO(g);$ K_2

(iii) $2NO(g) \rightleftharpoons N_2(g) + O_2(g);$ K_3

(iv) $NO(g) \rightleftharpoons \left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g);$ K_4

Correct relation between K_1, K_2 and K_4 is/are :

(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

EXERCISE III

Numerical Answer Type

Imp deal with

1. At 46°C, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.667 atm. Compute the percentage dissociation of N_2O_4 at 46° C at a total pressure of 380 Torr.

Imp

2. 20.0 grams of $CaCO_3(s)$ were placed in a closed vessel, heated & maintained at 727° C under equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ 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.

Imp

3. 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 concentrations of NO, N_2, and O_2 when the reaction mixture reaches equilibrium?

✓ Imp weak

4. 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 equlibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Imp

5. At 90°C, the following equilibrium is established :

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$ $K_p = 6.8 \times 10^{-2}$

If 0.2 mol of hydrogen and 1.0 mol of sulphur are heated to 90°C in a 1.0 litre vessel, what will be the partial pressure of H_2S at equilibrium?

Imp

6. The equilibrium constant for the reaction is 9.40 at 900°C $S_2(g) + C(s) \rightleftharpoons CS_2(g)$. Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of C(s) come to equilibrium.

✓ PCl_5 dissociates according to the reaction $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$. At 523 K, K_p = 1.78 atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

Imp

8. A reaction system in equilibrium according to the equation $2SO_2 + O_2 \rightleftharpoons 2SO_3$ in 1 litre reaction vessel at a given temperature was found to contain 0.11 mol of SO_2, 0.12 mol of SO_3 and 0.05 mol of O_2. Another 1 litre reaction vessel contains 64 g of SO_2 at the same temperature. What mass of O_2 must be added to this vessel in order that at equilibrium half of SO_2 is oxidised to SO_3? → means Kc remain same

Imp

9. In a closed container nitrogen and hydrogen mixture initially in a mole ratio of 1:4 reached equilibrium. It is found that the half hydrogen is converted to ammonia. If the original pressure was 180 atm, what will be the partial pressure of ammonia at equilibrium. (There is no change in temperature)

When the reaction is carried out at a certain temperature, the equilibrium concentration of P and Q are 3M and 4M respectively. When the volume of the vessel is doubled and the equilibrium is allowed to be reestablished, the concentration of Q is found to be 3M. Find (A) K_c (B) concentration of R at two equilibrium stages.

EXERCISE IV

Previous Year Questions

IIT-JAM Previous Year Questions

1. For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium constant, K_p is expressed as

(a) $3^3K_p = \frac{p_{NH_3}}{p^2_{N_2}}$ (b) $3^3K_p = \frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}}$ (c) $3^3K_p = \frac{p^2_{NH_3}}{p^4_{N_2}}$ (d) $3^{3/2}K_p^{1/2} = \frac{p^2_{NH_3}}{p^4_{N_2}}$

2. The temperature (T) dependence of the equilibrium constant (K) of a chemical reaction is correctly described by the following statement:

(a) For an endothermic reaction, the slope of ln K vs 1/T plot is positive

(b) For an exothermic reaction, K is proportional to T

(c) For an exothermic reaction, K at a higher temperature is lower than K at a lower temperature

(d) If ΔH is independent of temperature, the change in K with T is smaller at lower temperatures.

3. The relationship between the equilibrium constant K_1 for the reaction:

$CO(g) + 1/2O_2(g) \rightleftharpoons CO_2(g)$

and the equilibrium constant K_2 for the reaction:

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ is

(a) $2K_1 = K_2$ (b) $K_1 = K_2^2$ (c) $K_1 = K_2$ (d) $K_1^2 = K_2$

4. A 10 L flask containing 10.8 g of N_2O_5 is heated to 373 K, which leads to its decomposition according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If the final pressure in the flask is 0.5 atm, then the partial pressure of $O_2(g)$ in atm is

[Given: R = 0.0821 L atm K^{-1} mol^{-1}]

5. For the following equilibrium at 300°C,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

[illegible] p dissociatho 0. ~~0~~791

Calculate K_p when N_2O_4 is 30% dissociated and the total pressure is 2 bar.

6. Equilibrium constant for a reaction doubles as the temperature is increased from 300 K to 600 K. Calculate the standard reaction enthalpy (in kJ mol^{-1}) assuming it to be constant in this temperature range. (given: R = 8.3 JK^{-1} mol^{-1}, *l*n 2 = 0.7).

IIT-JEE Previous Year Questions

7. 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 the container (d) increasing the amount of CO(g).

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

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 $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ 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.

9. When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction:

(a) is zero
(b) decrease with time
(c) independent of time
(d) increases with time

10. For the reversible reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C. The value of K_p is 1.44×10^{-5}, when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mol L^{-1} is :

(a) $1.44 \times 10^{-5}/(0.082 \times 500)^2$
(b) $1.44 \times 10^{-5}/(8.314 \times 773)^2$
(c) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
(d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

11. At constant temperature, the equilibrium constant (K_P) for the decomposition reaction. $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_P = 4x^2P/(1-x^2)$ where P is pressure, x is extent of decomposition. Which of the following statement is true ?

(a) K_P increases with increase of P
(b) K_P increases with increase of x
(c) K_P increases with decrease of x
(d) K_P remains constant with change in P or x

12. 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 holds true regarding the equilibrium constant (K_P) and degree of dissociation (α) :

Imp

(a) Neither K_P nor α changes
(b) ~~Both K_P~~ and α change
(c) K_P changes, but α does not change
(d) K_P ~~does not~~ change, but α changes

13. A sample of air consisting of N_2 and O_2 was heated to 2500K until the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO$ was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mol% of NO was 1.8. Estimate the initial composition of air in mol fraction of N_2 and O_2.

✓ 14. For the reaction, $N_2O_5(g) \rightleftharpoons 2NO_2(g) + 0.5\ O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at any time is 960 mm Hg. Assume ideal gas behaviour .

$PV = nRT$ deal with (n)

$P \propto n$

15. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

Given: $\Delta G^o_{N_2O_4} = 100 \text{ kJ mol}^{-1}$; $\Delta G^o_{NO_2} = 50 \text{ kJ mol}^{-1}$

Find ΔG for reaction at 298 K under given condition.

16. When 3.06g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_C & K_P for the reaction at 27°C.

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

ANSWER KEY

EXERCISE - I

1. a 2. a 3. c 4. c 5. a 6. b 7. b
8. a 9. a 10. b 11. c 12. a 13. d 14. d
15. a 16. b 17. c 18. b 19. d 20. c 21. d
22. a 23. b 24. a 25. a 26. a 27. a 28. a
29. a 30. d 31. c

EXERCISE - II

1. c,d 2. a,b,c,d 3. a,c,d 4. a,b,c 5. a,d 6. b,c 7. a,b,c

EXERCISE - III

1. 50%
2. 0.821 atm
3. [NO] = 0.056 M, $[N_2] = [O_2] = 1.37$ M
4. $K_P = 1.3 \times 10^{-3}$ atm^{-2} 2.3×10^{-8}
5. 0.379 atm
6. $P_{CS_2} = 1.284$ atm, $P_{S2} = 0.1365$ atm
7. 2.7 g / lit
8. 9.34 g
9. 48 atm
10. $K_C = 1/12$, [R] = 4 (initial eqm.) & 1.5 (final eqm.)

EXERCISE - IV

1. c 2. c 3. d
4. 0.064
5. 42.22 0.78
6. 3.486
7. d 8. b 9. d 10. d 11. d 12. d
13. $X_{N2} = 0.79$, $X_{O2} = 0.21$
14. Fraction decomposed = 0.4
15. (i) $5.705 \times 10^3 \text{ J mol}^{-1}$
16. (i) $K_c = 8.1 \times 10^{-5}$; $K_p = 4.91 \times 10^{-2}$

(ii) No effect

CHAPTER

7

IONIC EQUILIBRIUM

According to strength ionic conductors are of 2 types:

1. **Strong electrolyte:** Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

   Ex. Na^+Cl^-, K^+Cl^-, etc.

   For strong elecrolyte the value of degree of dissociation is 100%.

   i.e. $\alpha = 1$

   Ex. (a) Strong acid → H_2SO_4, HCl, HNO_3 $HClO_4$, H_2SO_5, HBr, HI

   (b) Strong base → KOH, NaOH, $Ba(OH)_2$ CsOH, RbOH

   (c) All Salts → NaCl, KCl, $CuSO_4$.....

2. **Weak electrolytes:** Those electrolytes whicha re partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

   Ex. (a) Weak acid → HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$, → H_3BO_3 (boric acid)

   (b) Weak base → NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$

pH of mixture of two strong acids: $[H^+] = N = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

pH of mixture of two strong bases: $[OH^-] = N = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$ $\quad [H^+] = \dfrac{10^{-14}}{[OH^-]}$

pH of mixture of a strong acid and a strong base:

Number of H^+ ions from I-solution = N_1V_1

Number of OH^- ions from II-solution = N_2V_2

$\downarrow$

If $N_1V_1 > N_2V_2$

$$[H^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

Solution will be acidic in nature

$\downarrow$

If $N_2V_2 > N_1V_1$

$$[OH^-] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

Solution will be basic in nature

$$[H^+] = \frac{10^{-14}}{[OH^-]}$$

pH of a weak acid (monoprotic) Solution:

$$pH = \frac{1}{2}\ (pK_a - \log C)$$

pH of a mixture of weak acid (monoprotic) and a strong acid solution:

Total H^+ ion concentration = $C_1 + C_2a$

pH of a mixture of two weak acid (both monoprotic) solution

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

pH of a acidic buffer solution (Handerson equation):

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

pH of basic buffer solution:

$$pOH = pK_b + \log\frac{[salt]}{[Base]} \Rightarrow pH = 14 - pOH$$

(1) **Hydrolysis of strong acid - weak base [SA – WB] type sale -**

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

(1) $k_h = \dfrac{K_w}{K_b}$

(2) $h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{K_w}{K_b \times C}}$

(3) $[H^+] = Ch = \sqrt{\dfrac{K_w \times C}{K_b}}$

(4) $pH = -\log\,[H^+]$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

(2) **Hydrolysis of [WA – SB] type salt**

Ex. KCN, NaCN, K_2CO_3, $BaCO_3$, K_3PO_4

(1) $k_h = \dfrac{K_w}{K_a}$

(2) $h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{K_w}{K_a \times C}}$

(3) $[OH^-] = Ch = \sqrt{\dfrac{K_w \times C}{K_a}}$

(4) $[H^+] = \sqrt{\dfrac{K_w \times K_a}{C}}$ (5) $pH = -\log[H^+]$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

(3) **Hydrolysis of (WA - WB) type salt**

Ex. NH_4CN, $CaCO_3$, $(NH_4)_2CO_3$, $ZnHPO_3$

(1) $K_h = \dfrac{K_w}{K_a \times K_b}$ (2) $h = \sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a \times K_b}}$

(3) $[H^+] = \sqrt{\dfrac{K_w \times K_a}{K_b}} = K_a h$ (4) $pH = -\log[H^+]$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

SOLUBILITY (s) AND SOLUBILITY PRODUCT (K_{sp})

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution

1. Simple solution in H_2O
2. Effect of common ions on solubility
3. Simultaneous solubility
4. Condition for precipitation
5. Solubility in a buffer solution
6. Solubility due to complex formation

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 situation on solubility of a salt.

Simple solubility

Solubility is the maximum conc. of the salt that exist in the form of ions.

Let the salt is $A_x B_y$, in solution in water, let the solubility in H_2O = 's' M, then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{-x}$$

$$- \qquad xs \qquad ys \qquad \therefore \qquad K_{xp} = (xs)^x\,(ys)^y = x^x,\, y^y.\,(s)^{x+y}$$

EXERCISE - I

Single Answer Type

pH Calculations of Weak Electrolytes and Strong Electrolytes

1. The pH of 10^{-7} M of NaOH solution

(a) 7.0 (b) 7.21 (c) 6.79 (d) None

2. The pH of mixture of (400 mL, $\frac{1}{200}$M H_2SO_4) + (400 mL, $\frac{1}{100}$M HCl) + (200 mL of water) will be

(a) 2.7 (b) 2.1 (c) 3.1 (d) 1.8

3. 1 c.c. of 0.1 N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be

(a) 7 (b) 3 (c) 4 (d) 1

4. 10 ml of $\frac{M}{200}$ H_2SO_4 is mixed with 40 ml of $\frac{M}{200}$ H_2SO_4. The pH of the resulting solution is

(a) 1 (b) 2 (c) 2.3 (d) none of these

5. Which of the following expression 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 .

6. A 50 ml solution of strong acid of pH = 1 is mixed with a 50 ml solution of strong acid of pH = 2. The pH of the mixture will be nearly (log 5.5 = 0.74)

(a) 0.74 (b) 1.26 (c) 1.76 (d) 1.5

7. 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^{-5} M NaOH solution at 25°C

8. The $[OH^-]$ in 100.0 ml of 0.016 M-HCl (aq) is :

(a) 5×10^{12} M (b) 3×10^{-10} M (c) 6.25×10^{-13} M (d) 2.0×10^{-9} M.

9. The pH of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is :

(a) 13 (b) 12 (c) 1.0 (d) 2.0

10. 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.

11. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5}. The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is equal to

(a) 0.41 (b) 0.13 (c) 1.69×10^{-3} (d) 0.013.

✓ Nice

12. 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) $\sqrt{30} \times 10^{-8}$

13. A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of

(a) 10 (b) 4 (c) 4000 (d) 10000

14. Which of the following has the highest degree of ionisation ?

(a) 1 M NH_3 (b) 0.001 M NH_3 (c) 0.1 M NH_3 (d) 0.0001 M NH_3.

15. K_w of H_2O at 373 K is 1×10^{-12}. Identify which of the following is incorrect.

(a) pK_w of H_2O is 12 (b) pH of H_2O is 6 (c) H_2O is neutral (d) H_2O is acidic

16. At 25°C in H_2O, $[H^+] = 10^{-7}$ and pH = 7

When temperature is raised to 90°C, $[H^+] = 10^{-6}$ and pH = 6

So solution becomes

(a) acidic (b) Basic (c) Highly acidic (d) Neutral

Buffer Solution

17. If 50 ml of 0.2 M KOH is added to 40 ml of 0.5 M HCOOH. the pH of the resulting solution is: ($K_a = 1.8 \times 10^{-4}$, log 18 = 1.26)

✓ good (a) 3.74 (b) 5.64 (c) 7.57 (d) 3.42

18. Aniline behaves as a weak base. When 0.1 M, 50 ml solution of aniline was mixed with 0.1 M, 25 ml solution of HCl the pH of resulting solution was 8. Then the pH of 0.01 M solution of anilinium chloride will be ($K_w = 10^{-14}$) Check it

(a) 6 (b) 6.5 (c) 5 (d) 5.5

Good

19. 1 M benzoic acid ($pK_a = 4.20$) and 1M C_6H_5 COONa solutions are given separately. What is the volume of benzoic acid required to prepare a 300 ml buffer solution of pH = 4.5 ? [log 2 = 0.3]

(a) 200 ml (b) 150 ml (c) 100 ml (d) 50 ml

Good ✓

20. To prepare a buffer of pH 8.26 amount of $(NH_4)_2SO_4$ to be added to 500 mL of 0.01 M NH_4OH solution [$pK_a(NH_4^+) = 9.26$] is → Use $K_w = K_a \times K_b$ (valid only for conjugate acid/base pair)

(a) 0.05 mole (b) 0.025 mole (c) 0.10 mole (d) 0.005 mole

Good ✓ ✓ good

21. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt Na^+A^- to make the pH of solution 5.5. Given pK_a (HA) = 5. (Use antilog (0.5) = 3.16)

(a) 2.08×10^{-1} (b) 3.05×10^{-3} (c) 2.01×10^{-2} (d) None of these

calculated in ionic copy about at end of copy

✓

22. 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is

(a) not a buffer solution and with pH < 7 (b) not a buffer solution with pH > 7

(c) a buffer solution with pH < 7 (d) a buffer solution with pH > 7

23. Buffer capacity of a buffer solution is x, the volume of 1 M NaOH added to 100 mL of this solution if change in the pH by 1 is

(a) 0.1 x mL (b) 10 x mL (c) 100 x mL (d) x mL

√24. K_a for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 ml of 2M HCN solution is (log 2 = 0.3)

(a) 4 ml (b) 8 ml (c) 2 ml (d) 10 ml

Salt Hydrolysis

25. The pH of 0.4 M aqueous NaCN solution will be (Given pK_b of $CN^- = 4.70$)

(a) 2.548 (b) 3.513 (c) 10.123 (d) 11.450

√26. The pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH) will be Given that K_a : 1.8×10^{-5}, and $K_b = 1.8 \times 10^{-5}$

(a) 6 (b) 7 (c) 8 (d) 9

27. Which of the following salts undergoes anionic hydrolysis?

(a) $CuSO_4$ (b) NH_4Cl (c) $AlCl_3$ (d) K_2CO_3.

28. The sodium salt of a certain weak monobasic organic acid is hydrolysed to an extent of 3% in its 0.1M solution at 25°C. Given that the ionic product of water is 10^{-14} at this temperature, what is the dissociation constant of the acid?

(a) $\approx 1 \times 10^{-10}$ ~~(b) $\approx 1 \times 10^{-9}$~~ (c) 3.33×10^{-9} (d) 3.33×10^{-10}

29. 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) 10%

30. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$

(a) 2.48 (b) 5.26 (c) 8.2 (d) 9.6

√31. If equilibrium constant of

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ is 1.8×10^{-5}, equilibrium constant for [illegible] Ka1 & Ka2

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ is

(a) 1.8×10^{-9} (b) 1.8×10^{9} (c) 5.55×10^{-9} (d) 5.55×10^{10}

32. 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

Solubility (S) and Solubility Product (K_{sp})

√33. The solubility product of SrF_2 in water is 8×10^{-10}. Its solubility in 0.1 M NaF aqueous solution will be

(a) 8×10^{-8} (b) 8×10^{-3} (c) 2.8×10^{-5} (d) None

34. Which of the following is most soluble in water?

(a) MnS ($K_{sp} = 8 \times 10^{-37}$) (b) ZnS ($K_{sp} = 7 \times 10^{-16}$)

(c) Bi_2S_3 ($K_{sp} = 1 \times 10^{-72}$) (d) $Ag_3(PO_4)$ ($K_{sp} = 1.8 \times 10^{-18}$)

35. The precipitate of CaF_2(K_{sp} = 1.7×10^{-10}) is obtained when equal volumes of the following are mixed

(a) 10^{-4} M Ca^{2+} + 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^-

36. The solubility of AgCl in water, 0.01 M $CaCl_2$, 0.02 M NaCl and 0.05 M $AgNO_3$ are denoted by S_1, S_2, S_3 and S_4 respectively. Which of the following relationship is correct?

(a) $S_1 > S_2 > S_3 > S_4$ (b) $S_1 = S_2 = S_3 = S_4$ (c) $S_1 > S_3 > S_2 > S_1$ (d) $S_1 > S_2 = S_3 > S_4$

37. The solubility product $Mg(OH)_2$ in water at 25°C is $2.56 \times 10^{-13}(mol/lt)^3$ while that of $Al(OH)_3$ is $4.32 \times 10^{-34}(mol/lt)^4$. If s_1 and s_2 are the solubilities of $Mg(OH)_2$ and $Al(OH)_3$ in water in mol/lt at 25°C, what is the ratio, s_1/s_2 ?

(a) 2×10^5 (b) 2×10^4 (c) 3×10^6 (d) 3×10^3

38. The solubility of CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$) in 0.1 M solution of NaF would be

(a) 3.4×10^{-12} M (b) 3.4×10^{-10} M (c) 3.4×10^{-9} M (d) 3.4×10^{-13} M.

39. The solubility of Ag_2CO_3 in water at 25°C is 1×10^{-4} mole/litre. What is its solubility in 0.01 M Na_2CO_3 solution? Assume no hydrolysis of CO_3^{2-} ion occurs.

(a) 6×10^{-6} mole/litre (b) 4×10^{-5} mole/litre (c) 10^{-5} mole /litre (d) 2×10^{-5} mole/litre

40. What is the solubility of $Al(OH)_3$, ($K_{sp} = 1 \times 10^{-33}$) in a buffer solution pH = 4 ?

(a) 10^{-3} M (b) 10^{-6} M (c) 10^{-4} M (d) 10^{-10} M.

41. The solubility of $Fe(OH)_3$ would be maximum in

(a) 0.1 M NaOH (b) 0.1 M HCl (c) 0.1 M KOH (d) 0.1 M H_2SO_4.

42. At 25°C, the solubility product values of AgCl and AgCNS are 1.8×10^{-10} and 1.6×10^{-11} respectively. When a solution is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution.

(a) 1.125, 4×10^{-6}M (b) 11.25, 1.4×10^{-5}M

(c) 11.25, 4×10^{-5}M (d) 1.25, 4×10^{-6}M

43. What is the minimum pH when $Fe(OH)_3$ starts precipitating from a solution containing 0.1M $FeCl_3$? K_{sp} of $Fe(OH)_3$ = 8×10^{-13} M^3

(a) 3.7 (b) 5.7 (c) 10.3 (d) 8.3

44. Which of the following statements is correct for a solution saturated with AgCl and AgBr if their solubilities in moles per litre in separate solutions are x and y respectively ?

(a) $[Ag^+] = x + y$ (b) $[Ag^+] = [Br^-] + [Cl^-]$

(c) $[Br^-] = y$ (d) $[Cl^-] > x$.

(a) 1.2×10^{-10} g (b) 1.2×10^{-9} g (c) 6.2×10^{-5} g (d) 5.0×10^{-8} g

pH of amphiprotic salts and pH of anions

45. pH of 0.1M Na_2HPO_4 and 0.2M NaH_2PO_4 are respectively : pK_a for H_3PO_4 are 2.2, 7.2 and 12.0.

(a) 4.7, 9.6 (b) 9.6, 4.7 (c) 4.7, 5.6 (d) 5.6, 4.7

46. 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}

47. For ortho phosphoric acid,

$$H_3PO_4\,(aq) + H_2O\,(aq) \rightleftharpoons H_3O^+\,(aq) + H_2PO_4^-\,(aq)\,;K_{a1}$$
$$H_2PO_4\,(aq) + H_2O\,(aq) \rightleftharpoons H_3O^+\,(aq) + HPO_4^{2-}\,(aq)\,;K_{a2}$$
$$HPO_4^{2-}\,(aq) + H_2O\,(aq) \rightleftharpoons H_3O^+\,(aq) + PO_4^{3-}\,(aq)\,;\;K_{a3}$$

The correct order of K_a values is :

(a) $K_{a_1} > K_{a_2} < K_{a_3}$ (b) $K_{a_1} < K_{a_2} < K_{a_3}$ (c) $K_{a_1} > K_{a_2} > K_{a_3}$ (d) $K_{a_1} < K_{a_2} > K_{a_3}$

48. Pure water is added into the following solutions causing a 10% increase in volume of each. The greatest % change in pH would be observed in which case (a), (b), (c) or (d) ?

(a) 0.1 M $NaHCO_3$ (b) 0.2 M NaOH

(c) 0.3 M NH_3 – 0.2 M NH_4^+ system (d) 0.4 M CH_3COONH_4

49. Three reactions involving $H_2PO_4^-$ are given below :

(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$ (ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ?

(a) (ii) only (b) (i) and (ii) (c) (iii) only (d) (i) only

EXERCISE - II

One or More Than One Correct Answer Type

1. Out of the following, amphiprotic species is are

(I) HPO_3^{2-} (II) OH^- (III) $H_2PO_4^-$ (IV) HCO_3^-

(a) I (b) II (c) III (d) IV

2. Degree of hydrolysis for a salt of strong acid and weak base is

(a) independent of dilution (b) increases with dilution

(c) increases with decrease in K_b of the bases

(d) decreases with decrease in temperature.

3. A solution containing a mixture of 0.05 M NaCl and 0.05 M NaI is taken (K_{sp} of AgCl = 10^{-10} and K_{sp} of AgI =4×10^{-16}). When $AgNO_3$ is added to such a solution.

(a) the concentration of Ag^+ required to precipitate Cl^- = 2×10^{-9} mol/L.

(b) the concentration of Ag^+ required to precipitate I^- = 8×10^{-15} mol/L.

(c) AgCl and AgI will be precipitated together.

(d) first AgI will be precipitated.

4. Choose the correct statement

(a) pH of acidic buffer solution decrease if more salt is added.

(b) pH of acidic buffer solution increases if more salt is added.

(c) pH of basic buffer decreases if more salt is added.

(d) pH of basic buffer increases if more salt is added.

5. Which of the following mixtures will act as buffer ?

(a) $H_2CO_3 + NaOH$ (1.5 : 1 molar ratio) (b) $H_2CO_3 + NaOH$ (1.5 : 2 molar ratio)

(c) $NH_4OH + HCl$ (5 : 4 molar ratio) (d) $NH_4OH + HCl$ (4 : 5 molar ratio)

6. Degree of hydrolysis for a salt of strong acid and weak base is

(a) independent of dilution (b) increases with dilution

(c) increases with decrease in K_b of the bases (d) decreases with decrease in temperature.

7. Which of the following is/are correct regarding buffer solution?

(a) It contains weak acid and its conjugate base

(b) It contains weak base and its conjugate acid

(c) It shows large change in pH on adding small amount of acid or base.

(d) All of the above.

8. The salt having pH independent of its concentration is are :

1. $(CH_3COO)C_5H_5NH$ 2. NaH_2PO_4 3. Na_2HPO_4 4. NH_4CN

(a) 1 (b) 2 (c) 3 (d) 4

9. A solution of pH = 6.5 can be

(a) Acidic (b) basic (c) neutral (d) None of these

10. Which of the following is true for alkaline aqueous solution?

(a) $pH > \frac{pk_w}{2}$ (b) pH > pOH (c) $pOH < \frac{pk_w}{2}$ (d) pH < pOH

EXERCISE - III

Numerical Answer Type

1. Calculate $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}.

2. Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to $\frac{1}{100}$ times. [Given $K_a = 1.8 \times 10^{-5}$]

3. The pH of a blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$. What volume of 5 M $NaHCO_3$ ***Solution*** should be mixed with 10ml of a sample of ***Solution*** which is 2.5 M in H_2CO_3 (assume no $NaHCO_3$), in order to maitain a pH = 7.4.(pK_a for H_2CO_3 = 6.7, log 2 = 0.3)

4. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

Calculate the pH of a solution made by mixing 50.0 ml of 0.2M NH_4Cl & 75.0 ml of 0.1 M NaOH. $[K_b(NH_3) = 1.8 \times 10^{-5}]$

6. A solution was made up to be 0.01 M in chloroacetic acid, $ClCH_2COOH$ and also 0.002 M in sodium chloroacetate $ClCH_2COONa$. What is $[H^+]$ in the solution ? $K_a = 1.5 \times 10^{-3}$.

7. Find out pH, h (degree of hydrolysis) and $[OH^-]$ of milli molar solution of KCN 10^{-3} M, if the dissociation constant of HCN is 10^{-7}.

8. Calculate the pH and h (degree of hydrolysis) of 0.01 M solution of NaCN, K_a for HCN is 6.2×10^{-12}.

9. Calculate the pH of a 2.0 M solution of NH_4Cl. $[K_b(NH_3) = 1.8 \times 10^{-5}]$

10. Calculate the percent hydrolysis in a 0.0100 M solution of KCN. $(K_a = 6.2 \times 10^{-10})$

$K_h = \frac{K_w}{K_a}$

11. 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 $= 1.9 \times 10^{-5}$.

12. Calculate the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40M HCl.

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. A weak base (50.0mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

15. What $[H^+]$ must be maintained in a saturated H_2S (0.1 M) to precipitate CdS but not ZnS, if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially ?
$K_{sp}(CdS) = 8 \times 10^{-27}$; $K_{sp}(ZnS) = 1 \times 10^{-21}$; $K_a(H_2S) = 1.1 \times 10^{-21}$

EXERCISE - IV

Previous Year Questions

IIT-JAM Previous Year Questions

1. At 25°C, the solubility product (K_{sp}) of CaF_2 in water is 3.2×10^{-11}. The solubility (in mole per kg of water) of the salt at the same temperature (ignore ion pairing) is
(a) 4.0×10^{-6} (b) 3.2×10^{-4} (c) 2.5×10^{-4} (d) 2.0×10^{-4}

2. At 298 K 0.1 mol of ammonium acetate and 0.14 mol of acetic acid are dissolved in 1 L of water. The pH of the resulting solution is
[Given: pK_a of acetic acid is 4.75]
(a) 4.9 (b) 4.6 (c) 4.3 (d) 2.3

3. The minimum concentration of silver ions that is required to start the precipitation of Ag_2S ($K_{sp} = 1 \times 10^{-51}$) in a 0.1 M solution of S^{2-} is
(a) 1×10^{-49} M (b) 1×10^{-50} M (c) 1×10^{-26} M (d) 1×10^{-25} M

4. The hydrolysis constant (K_h) of NH_4Cl is 5.6×10^{-10}. The concentration of H_3O^+ in a 0.1 M solution of NH_4Cl at equilibrium is

(a) $\sqrt{5.6\times10^{-11}}$ (b) $\sqrt{5.6\times10^{-10}}$ (c) 5.6×10^{-10} (d) 2.8×10^{-5}

5. The acid dissociation constant (K_a) for HCOOH, CH_3COOH, $CH_2ClCOOH$ and HCN at 25°C are 1.8×10^{-4}, 1.8×10^{-5}, 1.4×10^{-3} and 4.8×10^{-10}, respectively. The acid that gives highest pH at the equivalence point when 0.2 M solution of each acid is titrated with a 0.2 M solution of sodium hydroxide is

(a) HCOOH (b) CH_3COOH (c) $CH_2ClCOOH$ [✓ (d) HCN] Correct 6PF.

6. If K_{sp} is the solubility product of a sparingly soluble salt A_3X_2, then its solubility is

(a) $(K_{sp}/108)^{1/5}$ (b) $(K_{sp})^{1/5}$ (c) $(K_{sp}/72)^{1.5}$ (d) $(K_{sp})^{1/2}$

7. Solubility product constant (K_{sp}) of slats 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) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

8. The pH of a 1×10^{-8} M HCl solution is close to

(a) 8.0 (b) 7.1 (c) 6.9 (d) 6.0

9. The pH of a 1.0×10^{-3} M solution of weak acid HA is 4.0. The acid dissociation constant K_a is

(a) 1.0×10^{-3} (b) 1.0×10^{-4} (c) 1.0×10^{-5} (d) 2.0×10^{-5}

10. The pH of the solution prepared from 0.005 mole of $Ba(OH)_2$ in 100 cc water is

(a) 10 (b) 12 (c) 11 (d) 13

11. The pK_a values of H_3PO_4 are 2.12, 7.21 and 12.67. The pH of a phosphate buffer containing 0.2 M NaH_2PO_4 and 0.1 M Na_2HPO_4 is ______.

12. A 50 mL solution of 0.1 M monoprotic acid ($K_a = 1 \times 10^{-5}$ at 298 K) is titrated with 0.1 M NaOH at 298 K. Calculate the (H^+) of the solution after the addition of 50 mL of NaOH at this temperature. (given: $K_w = 1 \times 10^{-14}$ at 298 K).

13. Calculate the pH of a solution obtained by mixing 50.00 mL of 0.20 M weak acid HA ($K_a = 10^{-5}$) and 50.00 mL of 0.20 M NaOH at room temperature.

IIT-JEE Previous Year Questions

14. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution? What will be the H^+ concentration in the solution?

(a) 8×10^{-2} M (b) 8×10^{-11} M (c) 1.6×10^{-11} M (d) 8×10^{-5} M

15. Select the correct alternative .

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}

16. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is

(a) 6 y^2 (b) 64 y^4 (c) 36 y^5 (d) 108 y^5

17. The pH of 0.1 M solution of the following salts increases in the order

(a) $NaCl < NH_4Cl < NaCN < HCl$ (b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$ (d) $HCl < NaCl < NaCN < NH_4Cl$

18. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is

(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

19. For sparingly soluble salt ApBq, the relationship of its solubility product (Ls) with its solubility (S) is

(a) $Ls = S^{p+q}, p^p. q^q$ (b) $Ls = S^{p+q}, p^p. q^p$ (c) $Ls = S^{pq}, p^p. q^q$ (d) $Ls = S^{pq}, (p.q)^{p+q}$

20. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16}M sulphide ion. If K_{sp}, MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first?

(a) FeS (b) MnS ✓ (c) HgS (d) ZnS

21. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is
NaOH

✓ (a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%

22. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ 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

23. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$, $K_c = 6.2 \times 10^{-8}$ & K_{sp} of AgCl $= 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

24. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ?

✓ 25. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

26. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C. Calculate the degree of dissociation of acetic acid in the resulting solution.
[K_a of acetic acid $= 1.8 \times 10^{-5}$]

27. Will the pH of water be same at 4°C and 25°C ? Explain.

28. 50 mL 0.2 M of HA is titrated with 0.2 M NaOH, calculate the pH at end point. Given $Ka(HA) = 5 \times 10^{-6}$ and $\alpha << 1$.

ANSWER KEY

EXERCISE - I

1. b   2. b   3. b   4. b   5. d   6. b   7. b

8. c   9. c   10. d   11. c   12. b   13. d   14. d

15. d   16. d   17. a   18. c   19. c   20. b   21. a

22. a   23. c   24. c   25. d   26. b   27. d   28. a

29. b   30. a   31. b   32. c   33. a   34. d   35. b

36. d   37. b   38. c   39. c   40. a   41. d   42. b

43. c   44. b   45. b   46. c   47. c   48. b   49. a

EXERCISE - II

1. c,d   2. b,c,d   3. a,b,d   4. b,c   5. a,b,c   6. b,c,d   7. a,b

8. a,b,c,d   9. a,b,c   10. a,b,c

EXERCISE - III

1. 7.13×10^{-3} M   2. 10

3. V = 25 ml   4. 0.05 mol

5. 9.7324   6. $[H^+] = 7.5 \times 10^{-3}$

7. pH = 9, h = 10^{-2}, $[OH^-] = 10^{-5}$ 8. pH = 11.6020, h = 4×10^{11}.

9. pH = 4.477   10. 4.0%

11. 5.12×10^{-6} M   12. 4.98

13. 2.37×10^{-6} 14. $K_b = 1.8 \times 10^{-5}$, 5.27

15. $[H^+] \geq 0.105$

EXERCISE - IV

1. d   2. b   3. d   4. a   5. c   6. a   7. d

8. c   9. c   10. d

11. 6.9 to 7.0   12. $10^{-8.85}$

13. pH = 9

14. b   15. c   16. d   17. b   18. a   19. a   20. b

21. a   22. d

23. $[Ag(NH_3)_2^+] = 0.0539$ 24. pH = 11.3010

25. S = 1.203×10^{-3}M   26. 0.018%

27. No, pH will be > 7 because K_w is a function of a temperature and as temperature increases K_w increases. Since ΔH = +ve

28. pH = 9.15

CHAPTER

8

PHASE EQUILIBRIUM

INTRODUCTION

Phase rule gives the relation between the condition which must be specified to describe the state of a system at equilibrium. This rule is equally important for both chemical and physical heterogeneous equilibria.

Phase Rule

The rule is stated in terms of the number of phases (P), the number of components (C) and the degrees of freedom (F) of a heterogeneous system. Mathematically it is expressed as

$$F = C - P + 2 \qquad \text{...(i)}$$

Explanation of the terms used in Phase Rule

Before Studying the phase rule, it is necessary to explain the meaning of phase, component and degree of freedom.

Phase: The homogeneous, physically distinct and mechanical separable parts of the heterogeneous system in equilibrium are called phases.

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

There are three phases in equilibrium state two solids and one is gas (CO_2), water system can be expressed as

$$\underset{\text{Ice}}{H_2O(s)} \rightleftharpoons \underset{\text{Water}}{H_2O(l)} \rightleftharpoons \underset{\text{vapours}}{H_2O(g)}$$

In this system there are three phases viz solid, liquid and vapours.

Component: In a heterogeneous system, in equilibrium the minimum number of variables which are necessary to explain the chemical composition of a phase, by a chemical equation, is called component, the meaning of component can be understood by taking following examples:

(a) Ice - water - vapours system

$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$$

This system has three phases i.e. solid (ice) liquid (water) and gas (vapour). Chemical composition of each phase can be expressed by H_2O in the form of chemical equation :

Phase		Component
$H_2O(s)$	=	H_2O
$H_2O(l)$	=	H_2O
$H_2O(g)$	=	H_2O

Thus water system is a one component system.

(b) When solid NH_4Cl is heated in a closed vessel, following equilibrium establishes :

$$NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$$

This system has two phases i.e. solid NH_4Cl and mixture of gases NH_3 and HCl. Here, although system has three components, but chemical composition of both phases can be expressed by single component i.e. NH_4Cl. Since NH_3 and HCl are in equimolar ratio

Phase		Component
$NH_4Cl(s)$	=	NH_4Cl
$NH_3(g) + HCl(g)$	=	NH_4Cl

Thus, this system is also a one component system.

Note: If some additional amount of either $NH_3(g)$ or HCl(g) is added in this system at equilibrium then each phase can be not expressed by NH_4Cl, then one more component will be required and number of components will be two in the system.

(c) When solid $CaCO_3$ is heated in a closed vessel, following hetergeneous equilibrium establishes :

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

This system consists of three phases i.e. solid $CaCO_3$, solid CaO and gaseous CO_2. Although system has three components but they are not independent of each other. Any of these two can be independently variable. Thus out of three, two components may be selected to express the composition of any phase. Thus number of components in this system are two

(i) When $CaCO_3$ and CaO are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaCO_3 + CaO$
$CaO(s)$	=	$CaCO_3 + CaO$
$CO_2(s)$	=	$CaCO_3 - CaO$

(ii) When CaO and CO_2 are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaO + CO_2$
$CaO(s)$	=	$CaO + CO_2$
$CO_2(g)$	=	$CaO + CO_2$

(iii) When CaO and CO_2 are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaCO_3 + CO_2$
$CaO(s)$	=	$CaCO_3 - CO_2$
$CO_2(s)$	=	$CaCO_3 + CO_2$

Therefore minimum number of components which are required to express any phase is two and the system is bi-component system

(d) Sodium Sulphate - water system may have different phases as $Na_2SO_4.7H_2O$, $Na_2SO_4.10H_2O$, Na_2SO_4 solution, ice, vapurs etc. Any phase can be expressed by chemical formulae of Na_2SO_4 and H_2O.

Therefore it is also a two component system.

(e) In $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ system also the number of components are two.

Number of components may also be calculated by the following formula

(1) When components do not ionize

$$C = C' - m$$

where C = number of components

C' = total number of undissociated components

m = number of chemical equations which correlate undissociated species with each other

Degree of Freedom: The degree of freedom or variance of a system is defined as the smallest number of independent variables such as pressure, temperature and concentration that must be specified in order to describe completely the state of a system.

Following examples will illustrate the meaning of degree of freedom in a better way :

(i) A system of aqueous solution of KCl has two degrees of freedom i.e. temperature and composition (Concentration of solution). If the solution is saturated, then only one variable temperature is necessary to express the system. Thus saturated solution of KCl is monovariant and unsaturated solution is bivariant.

(ii) Let there be a gas enclosed in a closed chamber. Two variables temperature and pressure aare required to express this system. Third variable (composition) is not required since container has only one gas. If system has a mixture of gases then third variable i.e. composition is also required and system becomes a trivariant system.

Advantages of Phase Rule

(i) It gives a simple method of classifying equilibrium states of system.

(ii) Physical as well as chemical equilibria can be studied by this rule.

(iii) The phase rule is applicable to macroscopic systems. Therefore, it is not necessary to take into account about their molecular structures.

(iv) It confirms that the different systems having the same number of degree of freedom behave in like manner.

(v) Phase rule takes no account of nature of the reactants or products in phase reactions.

(vi) It predicts the behaviour of systems when subjected to changes in the variables such as pressure temperature and volume.

Limitations of Phase Rule

(i) In phase rule only three variables temperature, pressure and composition are considered. Phase rule does not consider the variable like electric, magnetic and radiation influence.

(ii) As the phase rule is applicable to a single equilibrium state, it does not tell about the number of other equilibria possible in the system.

(iii) Gravitational force is not considered in phase rule.

(iv) No liquid or solid phases should be finely divided otherwise their vapour pressure and surface tension will differ from their normal values.

(v) Certain limitations are to be imposed on phase rule in some circumstances. In this state it is called phase rule under restricted condition.

APPLICATION OF PHASE RULE

1. One component system

Examples of one component system are water system, sulphur system, carbon dioxide system, carbon system, phosphorus system etc. Here we will discuss only first three systems.

In one component system C = 1, so phase rule

F = C – P + 2 reduces to F = 1 – P + 2 or F = 3 – P

Minimum number of phases in a system is 1(P = 1) so maximum number of degrees of freedom is 2(F = 2) for a one component system. Thus maximum number of variables which are required to express the system are two and those are pressure and temperature. Since minimum number of degree of freedom may be 0(F = 0), so maximum number of phases in equilibrium are 3(P = 3)

Two important conclusions may be drawn from above facts :

(i) One component system may be expressed by two variables i.e., phase diagram can be expressed by two axis pressure and temperature. This diagram is called temperature pressure diagram.

(ii) Maximum three phase can remain in equilibrium. If one is carried out at a constant temperature and pressure it is required to add component system.

2. Two Component System

For a two-component system, the phase rule becomes F = 4 – P

Since the minimum number of phases, P, in any system is 1, the maximum number of degrees of freedom, F, is 3. Thus, three variables would be necessary to describe a system. Since three variables are difficult to graph, it is customary to hold one of them say, the pressure, constant on a diagram of temperature plotted versus concentration. This reduces the degree of freedom of the system by one and the phase rule equation is then written as $F' = 3 - P$.

This is known as the reduced phase rule equation.

For the two component solid-liquid equilibria, we come across the following cases: 1. The two components are miscible in the liquid state. 2. The two components are only partially miscible in the liquid state. We shall restrict ourselves to the former case. Under this category, we shall discuss the following cases:

(i) The two components are not miscible in the solid state and form a eutectic mixture.

(ii) The two components form a stable compound with congruent melting point.

(iii) The two components form a compound with incongruent melting point.

Examples Considered for Two component system

Lead Silver System

These metals are completely miscible in liquid state and do not give rise to any compound formation. The equilibrium diagram, therefore, is similar to that shown in Figure. The various features are illustrated in Figure.

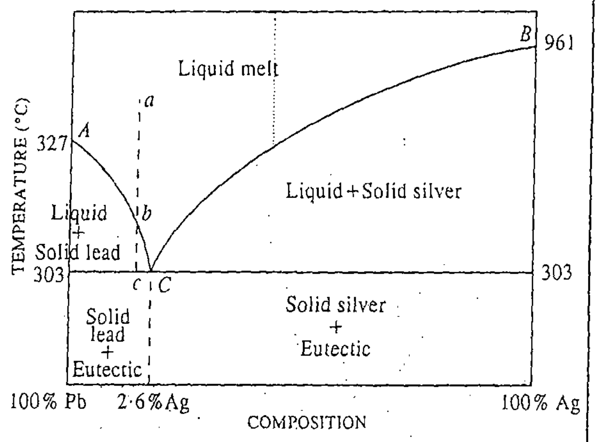


Fig. The phase diagram for lead-silver caption system.

Pure lead melts at 327°C and the addition of silver lowers its melting point along AC. Thus, AC is the freezing point curve of lead containing varying amounts of silver. Pure silver melts at 961°C and the addition of lead lowers its melting point along BC. Thus, BC is the freezing point curve of silver. Along AC, solid lead and solution (melt) coexist while along BC, solid silver and solution (melt) coexist. The system, at constant pressure, is monovariant along AC as well as along BC.

C is the eutectic point where the three phases, solid lead, solid silver and their liquid solution (melt), coexist. It is an invariant point. The temperature of the eutectic is 303°C and the composition of the solution phase is 2.6 per cent silver, as shown in the figure. The phases coexisting in the various areas or regions are also shown in the figure.

Table. Pb-Ag system

Phases present in equilibrium	Position in phase diagram	Degree of freedom
One phase equilibrium		
Solution (l)	Area above curve AOB	$F = C - P + 1$
(Ag + Pb)		$= 2 - 1 + 1 = 2$
Two phase equilibrium		
Pb(s) $\rightleftharpoons$ solution (l)	Curve AO and area ACO	$F = C - P + 1$
Ag(s) $\rightleftharpoons$ solution (l)	Curve BO and area BDO	$= 2 - 2 + 1$
Ag(s) + Pb(s)	Area below line COD	$= +1$

Desilverisation of Lead-Pattinson's Process : The phase diagram is used in the separation of silver from lead in Pattinson's process for desilverisation of lead. Suppose x represents the molte argentiferous lead containing a small amount of silver (0.25%) in it. Allow it to cool. Only temperatu of liquid melt fall with no change in composition till the point y on the curve AO reached. On further cooling lead starts to crystallise out and the solution become richer in silver. On furth cooling lead continuous to separate out and is constantly removed by means of loads. The liquid melt continuous to be richer and richer in silver till the point a is reached where an alloy having 2.6% of silver (from 0.25% to 2.6%) is obtained.

The above process of increasing the percentage of silver in argentiferous lead is known as Pattinson's process.

Bismuth Cadmium System (Bi-Cd System)

The fully labelled phase diagram for the bismuth-cadmium system is shown in Figure. The characteristic features of this system are similar to those of lead-silver described above.

Pure bismuth melts at 317°C and the addition of cadmium to molten bismuth lowers its freezing point along the curve AC which is the freezing point curve of bismuth containing varying amounts of cadmium. Similarly, addition of bismuth to molten cadmium lowers the freezing point of cadmium along the curve BC which is the freezing point curve of cadmium containing varying amounts of bismuth. In the region above the curves AC and CB, bismuth and cadmium are present in the form of a melt. Since in the region, P = 1, F = 2, i.e., the system is bivariant. The two degrees of freedom are the temperature and the composition. Thus in the region, temperature and composition can be varied without changing the number of phases. Along the curve AC, bismuth freezes out and along the curve AC, bismuth freezes out and along the curve BC, cadmium freezes out. Thus, in the area below AC and down to the eutectic point there are two phases, viz., bismuth and liquid whose composition is determined by the temperature. Similarly, in the area below BC down to the eutectic, the two phases in equilibrium are cadmium and liquid. Since in these regions, P = 2, F = 1, i.e., the system is univariant.

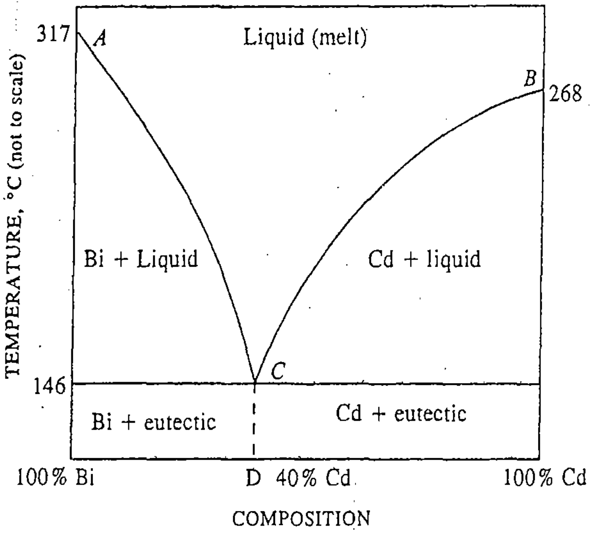


Fig. The phase diagram for the bismuth–cadmium sytem

At the eutectic point C, three phases coexist; these are bismuth, cadmium and liquid. The composition of the eutectic is 40% cadmium. At the C, P = 3 so that F = 0, i.e., the system is invariant. The eutectic temperature is 146°C. The area below the eutectic point is a two-phase region as labelled in the phase diagram. Since in this region P = 2, F = 1. Thus, only the temperature need be specified to describe the system completely.

Potassium Iodide-Water System (KI-H_2O system)

The potassium iodide-water system is a typical example of two component system which forms a eutectic mixture. Figure show the phase diagram of KI – H_2O system.

It is almost same as that of Pb-Ag system except one difference that point B can not be extended upto the melting point of pure KI since water can not exist in liquid state upto the m.p. of KI.

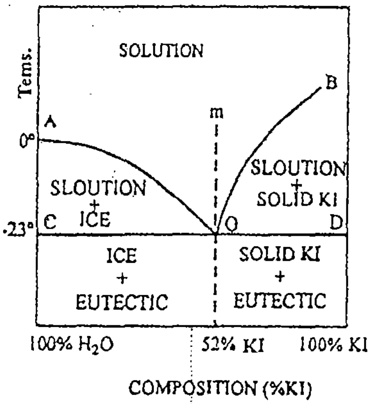


Fig. Graphical representation of Bismuth Potassium iodide-water system.

Main feature of this system are

Curve AO : Point A represents the freezing point of water at 1 atm pressure. This temperature is 0°C. When increased quantities of KI or KI is added, the freezing point of water goes on decreasing along the curve AD. Therefore AD is called freezing point curve of water. Along the curve AD, the solution of KI in H_2O is in equilibrium with ice. Thus it is a two phase system and degree of freedom is calculated by condensed phase rule.

$F = C - P + 1$

$F = 2 - 2 + 1 = 1$

Thus the system is monovariant. It means the composition of the system is fixed corresponding to each temperature.

Curve BO : This is known as the solubility curve of KI in water at different temperatures. The solubility of KI increases with rise of temperature and becomes maximum at the point B which is the boiling point of the saturated solution. Along the curve BO, solid KI is in equilibrium with solution. Again it is a monovariant system along BO.

Point 'O' : It is the eutectic or cryohydric point. Curves AO and OB intersect. At this point corresponding to a definite temperature (–23°C) and fixed composition (52% KI + 48% ice). The temperature is known as cryohydric temperature and composition is called cryohydric composition. At this point 'O', ice, solution and solid KI are in equilibrium. This point has no degree of freedom which is also clear from the condensed phase rule.

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

Area ACO : Two phases (i) ice (solid) and (ii) solution of KI in water (liquid) are in equilibrium in this area. Thus, it is a monovariant system. Composition of liquid state can be determined by drawing a tie line at any given temperature.

Area BOD : this area also has two phases namely solid KI and solution (melt) in equilibrium. Therefore P = 2, C = 2 which follows F = 1. Thus, it is also a monovariant system.

Area above curve AOB : Only one phase i.e. aqueous solution of KI exists in this area. System is bivaraint in this region. Temperature and composition both have to be fixed to describe the system at any point in this area.

Area below horizontal line COD : In this region liquid state does not exist. Solid KI and solid water (ice) are present in this area. The system is monovariant (F = 1) in this area. Cryohydric mixture is found in this area with a composition of 52% KI and 48% ice.

Let us take a point 'm' above the eutectic point O in the phase diagram. this region has only a solution of KI in water. When this solution is cooled slowly, point m shifts towards without any change in composition.

At 'O' ice and solid KI separate out simultaneously. Whole of the solution converts into cryohydric mixture below the point 'O'.

Table. Main features of KI-H_2O system

Phases present in equilibrium	Position in phase diagram	Degree of freedom
One phase equilibrium		
Solution (l)	Area above curve AOB	F = C – P + 1
(KI in water)		= 2 – 1 + 1 = 2
Two phase equilibrium		
Ice (s) $\rightleftharpoons$ Solution (l)	Curve AO and area ACO	F = C – P + 1
KI (s) $\rightleftharpoons$ Solution (l)	Curve BO and area BOD	= 2 – 2 + 1 = 1
Three phase equilibrium		
Ice (s) $\rightleftharpoons$ KI (S)	Point 'O' cryohydric point	F = C – P + 1
$\rightleftharpoons$ Solution (l)	(–23°C and 52% KI)	= 2 – 3 + 1 = 0

Calculation of Eutectic Point and Eutectic Composition

When a two-component solution is cooled to a low temperature, the component which is present in excess separates out as solid at the freezing point of the solution. The variation of the freezing point with composition is given by the following expressions:

$$d\ln x_A = (\Delta H_{fus,A}/RT^2)dT \qquad \text{....(1)}$$

$$d\ln x_B = (\Delta H_{fus,B}/RT^2)dT \qquad \text{....(2)}$$

where the ΔH_{fus}s are the enthalpies of fusion of the two components and x_A and x_B are their mole fractions. Assuming that the components A and B behave ideally and ΔH_{fus} is independent of temperature, we can integrate Eq. 1 and 2 for the limits $T = T_{fus}$, the melting point and $T = T_e$, the eutectic point, to obtain

$$-\ln(x_A)_e = \frac{\Delta H_{fus,A}}{R}\left(\frac{1}{T_e} - \frac{1}{T_{m,A}}\right) \qquad \text{....(4)}$$

and $$-\ln(x_B)_e = \frac{\Delta H_{fus,B}}{R}\left(\frac{1}{T_e} - \frac{1}{T_{fus,B}}\right) \qquad \text{....(5)}$$

Using Eqs. 4 and 5, we can calculate T_e, the eutectic point as well as the eutectic composition, viz., $(x_A)_e$ and $(x_B)_e$.

Illustration: Calculate the eutectic temperature and eutectic composition for a binary solid-liquid system if $\Delta H_{fus,A} = 500$ cal mol^{-1}, $\Delta H_{fus,B} = 1000$ cal mol^{-1} and the melting points of pure A and B are 400°C and 600°C, respectively.

Solution: From Eq. 4 and 5,

$$\ln(x_A)_e = \frac{(500\text{ cal mol}^{-1})(4.184\text{ J cal}^{-1})}{8.314\text{JK}^{-1}\text{mol}^{-1}}\left(\frac{1}{673\text{K}} - \frac{1}{T_e}\right)$$

$$\ln(x_B)_e = \frac{(1000\text{ cal mol}^{-1})(4.184\text{ J cal}^{-1})}{8.314\text{JK}^{-1}\text{mol}^{-1}}\left(\frac{1}{873\text{K}} - \frac{1}{T_e}\right)$$

These two equations can be solved simultaneously with $x_A + x_B = 1$ to give $(x_A)_e = 0.647$, $(x_B)_e = 0.352$ and $t_e = 38°C$.

Illustration: For a two-component system, $\Delta H_{fus,A} = 500$ cal mol^{-1} and $T_{fus,A} = 400°C$. If the eutectic temperature is 350°C, calculate the solubility in terms of the fractions of B in A at 350°C.

Solution: According to Eq. 4,

$$\ln(x_A)_e = \frac{\Delta H_{fus,A}}{R}\left(\frac{1}{T_{fus,A}} - \frac{1}{T_e}\right) = \frac{(500\text{ cal mol}^{-1})(4.184\text{ J cal}^{-1})}{8.314\text{ J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{673\text{K}} - \frac{1}{623\text{K}}\right)$$

$$\therefore \quad (x_A)_e = 0.9333 \qquad \text{and} \qquad (x_B)_e = 1 - 0.9333 = 0.0667$$

Typical Solved Examples for Two-Component Systems

Illustration: Draw schematic phase diagram for the following:

(a) A temperature-composition phase diagram for a binary system A – B having a single eutectic, a single peritectic (corresponding to the incongruently melting compound AB) and no solid solutions. Label all the areas.

(b) A pressure-composition phase diagram at a given temperature for a binary salt system A – W (where A is the anhydrous salt and W is water) having compounds A, AW, A.2W, A.4W and A.6W present as solids in equilibrium with vapour. Assume that no liquid phases are formed. Label the lines.

Solution: The requisite phase diagrams are shown in Figure (a) and (b). The diagram are self-explanatory.

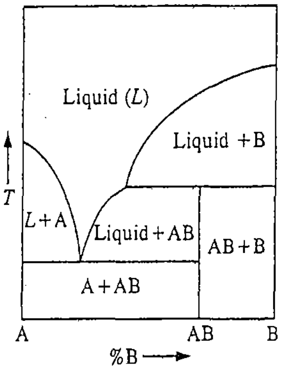


Fig. (a) Phase diagram for the binary system A-B corresponding to the given data.

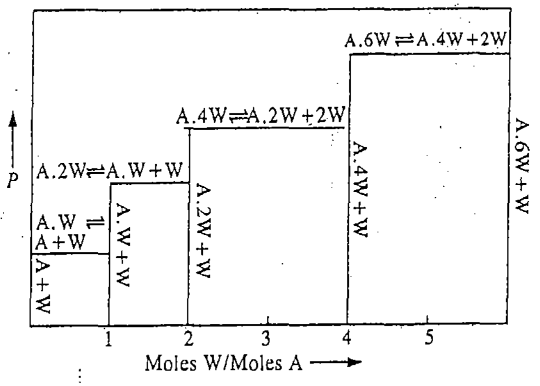


Fig. (b). Phase diagram for the binary system A-W corresponding to the given data.

Illustration: Compare the phase diagram shown in Figure (a) and (b) below and comment briefly.

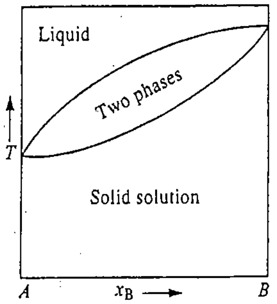


Fig. (a)

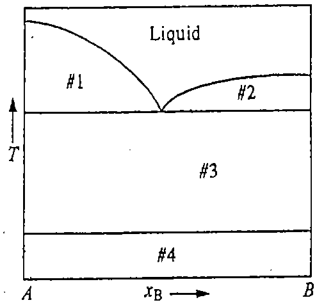
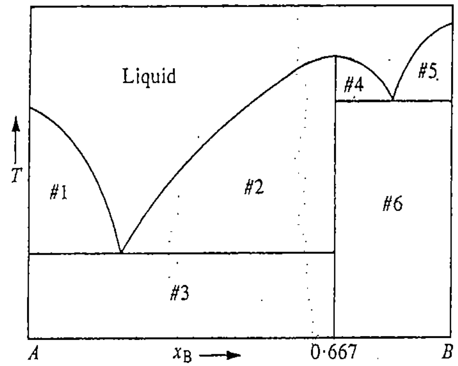


Fig. (b)

Solution: Figure (a) shows complete miscibility of the materials in the solid phase. There are two one-phase areas and one two-phase area. This type of diagram results from the ability of one substance to substitute freely for the other in the crystal lattice because of similarity in the size of molecules (atoms or ions), charge (if any), etc.

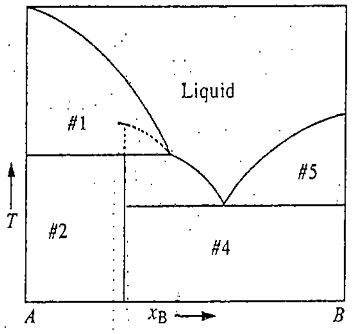
Figure (b) shows that the two substances are completely immiscible in the solid phase. There are four two-phase areas and one one-phase area. The horizontal 'tie lines' indicate that in area market #1. The two phases in equilibrium/are solid A and liquid; in area marked #2, solid B and liquid and in areas marked #3 and #4, solid A and solid B with one of the materials undergoing a phase transition to a second solid.

Illustration: Identify the phase present in the numbered areas of Figure.



Solution: From the figure we see that a congruently-melting compound is formed at $x_B = 0.667$ which means that there are two moles of B for every mole of A so that the compound has the empirical formula AB_2. Horizontal 'tie lines' indicate that in area #1, solid A and liquid are in equilibrium; in areas #2 and #4, liquid and solid AB_2; in area #3, solid A and solid AB_2; in area #5, solid B and liquid and in area #6, solid B and solid AB_2 are in equilibrium.

Illustration: Identify the phases present in the numbered areas of Figure



Solution From the above figure we see that an incongruently melting compound is formed at x_B = 0.250 which means that it has an empirical formula of A_3B. Horizontal 'tie lines' indicate that in area #1, solid A and liquid are in equilibrium; in #2, solid A and solid A_3B; in #3, liquid and solid A_3B; in #4, solid B and solid A_3B and in #5, solid B and liquid.

Zn-Mg SYSTEM

It is an example of a two component system in which two metals form a compound having $Mg(Zn)_2$ having congruent melting point Melting point of pure Zn is 420°C (point A), and that of pure Mg is 650°C (point B) whereas m.p. of compound $Mg(zn)_2$ is 590°C (point D) which is in between the melting point of two metals. This system has four phases i.e. solid Zn, solid Mg, solid compound $Mg(Zn)_2$ and melt of Zn and Mg.

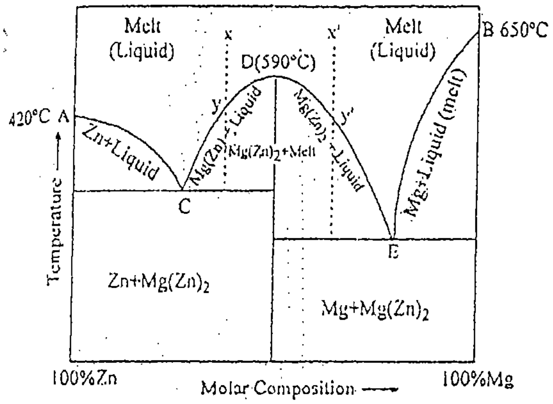


Fig. Graphical representation of Zn-Mg system.

Important features of the phase diagram are :

Point A : It represents the m.p. of pure Zn (420°C)

Curve AC : When Mg is added to Zn gradually the m.p. of Zn is lowered along the curve AC. Along this curve solid Zn is in equilibrium with melt (liquid). Thus there are two phases along this curve and on applying the condensed phase rule F = C – P + 1 = 2 – 2 + 1 = 1 we see that it is a monovariant system. It means only the composition varies along this curve.

Point B : This represents the melting point of pure Mg (650°C)

Curve BE : When Zn is added to Mg gradually, m.p. of Mg is lowered along the curve BE. Aong the curve BE solid Mg is in equilibrium with melt (liquid). Again this is also a monovariant curve having one degree of freedom.

Curve DC : This curve represents the freezing point curve of solid $Mg(Zn)_2$ when Zn is added, the m.p. of compound $Mg(Zn)_2$ lowers along this curve.

Curve DC : This curve represents the freezing point curve of solid Mg $(Zn)_2$ when zn is added, the m.p. of compound $Mg(Zn)_2$ lowers along this curve.

Curve DE : This curve represents the melting point curve of $Mg(Zn)_2$ when Mg is added in it.
Point D. At this point, the liquid and solid have the same composition i.e. $Mg(Zn)_2$. Thus point D is the congruent point and temperature (590°C) corresponds to this point is known as congruent melting point of $Mg(Zn)_2$.

Point C : Two curves AC and DC intersect at point C. Three phases i.e. solid Zn, compound $Mg(Zn)_2$ and melt are in equilibrium at this point.

Thus, on applying phase rule F = C – P + 1 = 2 – 3 + 1 = 0 we see that point C is non variant point C is known as eutectic point.

Point E : This is the point where curves DE and BE intersect. Here also three phases i.e. solid Mg, compound $Mg(Zn)_2$ and melt are in equilibrium at this point. Again it is invariant and known as eutectic point.

Cooling : When liquid melt is cooled at point X, it follows the path xy and $Mg(Zn)_2$ separates out at y and two phases i.e. solid $Mg(Zn)_2$ and liquid are in equilibrium and the degree of freedom is one. On further cooling curve follows the path yC and at C, solid Zn also separtes out. Thus there will be three phases at point C. These phases are solid Zn, solid $Mg(Zn)_2$ and melt. Therefore C is monovariant.

$NaCl-H_2O$ System

Phase diagram of $NaCl – H_2O$ system is shown in fig.

$$\underset{\text{Solid}}{NaCl.2H_2O} \rightleftharpoons \underset{\text{Solid}}{NaCl} + \text{solution}$$

Area ABCD consists of saturated solution of NaCl and area ABE has two phases, viz., ice and saturated solution. Solid NaCl + saturated solution are found in area CDHG and area CBFG have two solid phases $NaCl.2H_2O$ + saturated solution.

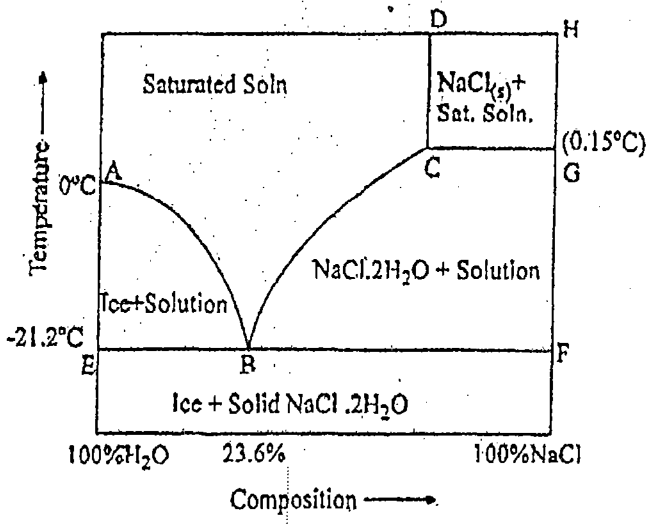


Fig. Graphical representation of $NaCl-H_2O$ system

FERRIC CHLORIDE-WATER SYSTEM

The phase diagram has four maxima corresponding to the formation of four hydrates. Point C(37°C), E(32.5°C), G(56°C) and I(78.5°C) represent the congruent melting points of dodeca, hepta, penta and tetra hydrates respectively. The congruent melting point of a salt hydrate is also known as the dyestectic point.

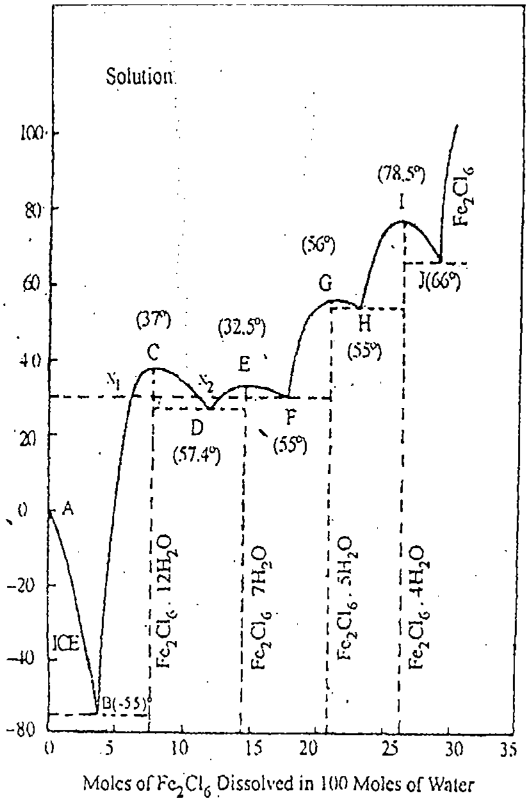


Fig. Graphical representation of Ferric Chloride-Water system

COPPER SULPHATE WATER VAPOUR SYSTEM

Phase diagram of this system in shown in figure.

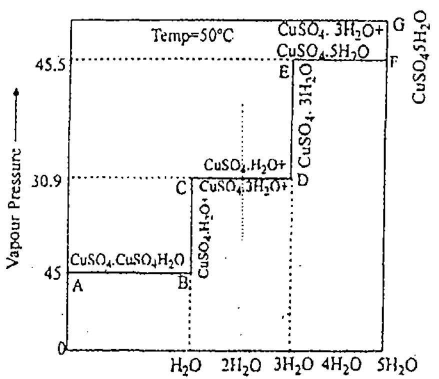


Fig. Graphical representation of Copper sulphate water vapour system

Liquid-Liquid Mixtures

When a liquid is mixed with another liquid three possible situations may arise.

(i) Both liquids are miscible with each other in all proportions. For example water and alcohol are miscible with each other in all proportions. These liquids are called completely miscible liquids

(ii) Liquid are compoletely immiscible with each other. For example water and nitrobenzene are completely imiscible with each other and form different layers with each other. These liquid are called immiscible liquids.

(iii) There are some liquids which are partially miscible with each other. For example water and phenol are partially miscible at room temperature. These liquids are called partially miscible liquids.

EXERCISE - I

Single Answer Correct Type

1. The number of components in a system containing 1 mole of NH_4Cl, 0.5 mole of NH_3 and 0.5 mole of HCl are
(a) One (b) Two (c) Three (d) Four

2. For the system; $H_2O(s) \rightleftharpoons H_2O(g)$
under equilibrium, the number of degrees of freedom is
(a) zero (b) 1 (c) 2 (d) 3

3. The maximum number of triple points occuring in the one component sulphur system are
(a) 1 (b) 2 (c) 3 (d) 4

4. The number of degrees of freedom at the triple point for a phase diagram for one component system is
(a) 1 (b) 2 (c) 3 (d) zero

5. When a liquid is in equilibrium with its vapour the thermodynamic criteria for the equilibrium is
(a) Entropy of the liquid phase is greater than entropy in the vapour phase.
(b) Enthalpy of the liquid phase is less than enthalpy in the vapour phase.
(c) Chemical potential in the liquid phase is equal to the chemical potential in the vapour phase
(d) Gibbs free energy of the two phases is different

The system $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ contains:
(a) two components (b) one component (c) three phases (d) one phase

7. The temperature at which a compound melts into a liquid of the same composition as the solid is called the:
(a) Congruent melting point (b) Incongruent melting point
(c) Peritectic point (d) Eutectic point

8. A system is said to be homogeneous if it consists only:
(a) One phase (b) One state (c) One component (d) One molecules

9. A system consisting of calcium carbonate in equilibrium with calcium oxide and carbondioxide has .... phases:
(a) six (b) two (c) three (d) four

10. The number of degrees of freedom of a mixture of three gases enclosed ~~in a~~ cylinder is:
(a) 3 (b) 4 (c) 5 (d) 6

sulphur?

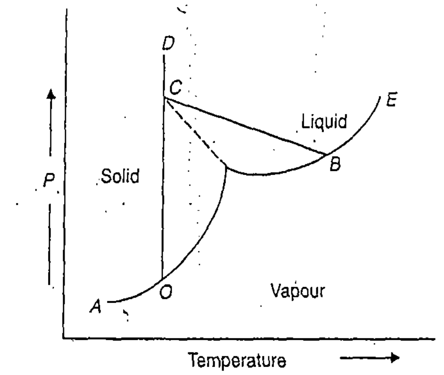


Fig. The sulphur system

(a) AO (b) OB (c) BE (d) OC

12. A triple point is

(a) Trivariant (b) Invariant (c) Univariant (d) Bivariant

13. Number of phase at the transition point in sulphur system is

(a) 2 (b) 3 (c) 4 (d) 5 → plastic

14. Number of phases in a mixture of ten pieces of ice and water in an ice tray at 0°C is

(a) 3 (b) 2 (c) 4 (d) 1

15. Temperature at which the two allotropic forms of the same solid substance change into each other at constant pressure is called

(a) Congruent m.pt (b) Transition temperature

(c) Incongruent m.pt. (d) None of the above

16. The vapour of a pure substance, when cooled under a pressure less than its triple-piont pressure,

(a) Liquiefies (b) Liquifies first and then solidifies

(c) Solidifies directly (d) Remains unchanged.

17. For the equilibrium $H_2O(\ell) \rightleftharpoons H_2O(g)$. If volume of container is doubled at constant temperature

(a) Pressure of container reduces to half of original value

(b) Pressure of container becomes double of original value

(c) More water will form (d) More vapour will form

18. Which of the following statements are incorrectly matched

(a) Water $\rightleftharpoons$ steam (One component system)

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (Two component system)

(c) A system containing 1 mole of NH_4Cl, 0.5 mole of NH_3 and 0.5 mole of HCl. (2 component system)

(d) A gaseous mixture of He and N_2 (Two component system)

19. Calculate maximum degree of freedom for three component system at constant pressure.

(a) 1 (b) 2 (c) 3 (d) 4

20. The number of degrees of freedom of a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose.

(a) 1 (b) 2 (c) 3 (d) 4

21. The number of degrees of freedom in the homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure, is :

(a) 0 (b) 1 (c) 2 (d) 3

22. The maximum number of phases that can co-exist in equilibrium for a one component system is

(a) 1 (b) 2 (c) 3 (d) 4

23. For the equilibrium, $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$

What are the number of components, phases and degrees of freedom respectively?

(a) 3, 2, 3 (b) 2, 3, 3 (c) 3, 3, 2 (d) 2, 2, 3

24. Which of the following statements is/are not correct?

(1) The phase diagram of a substance shows the regions of pressure and temperature at which the various phases are kinetically stable.

(2) The freezing point when the pressure is 1 bar is called standard freezing point.

(3) The normal and standard freezing points are negligibly different for most of the cases.

Select the correct answer using the code given below

(a) 1 only (b) 2 and 3 (c) 1 and 3 (d) 2 only

25. Solid carbon reacts with oxygen in presence of a catalyst to form the gaseous oxides CO and CO_2. What is the number of degrees of freedom (variance) for the system once equilibrium has been attained?

(a) 0 (b) 1 (c) 2 (d) 3

26. Consider the following statements

(1) For a one component system, the maximum number of phases that can exist in equilibrium is three.

(2) A system can have negative degrees of freedom.

(3) The number of phases in a system does not depend on the amounts of the various substances present at equilibrium.

Which of the statements given below above is/are correct?

(a) 1 and 3 (b) 1 only (c) 3 only (d) 2 and 3

27. For a pure substance, the triple point in a phase diagram has

(a) One degree of freedom (b) Two degrees of freedom

(c) Three degree of freedom (d) Zero degree of freedom

28. Sulfur can exist in four phases. The possible number of triple point is

(a) 1 (b) 2 (c) 3 (d) 4

29. In a system, when the chemical potential of each component is the same for all the phases, the equilibrium is said to be

(a) Metastable equilibrium (b) Thermal equilibrium

(c) Composition equilibrium (d) Mechanical equilibrium

30. The triple point of water is at

(a) 273.16 K (b) 273.16 K and 760 Torr

(c) 273.16 K and 4.58 Torr (d) 760 Torr

31. Solid CO_2 is called 'dry ice' because

(a) At 25°C and 1 atm, only solid and vapour phases of CO_2 are in equilibrium

(b) The critical temperature of CO_2 is above 25°C

(c) The boiling point of liquid CO_2 is above 100°C

(d) The melting point of solid CO_2 is 0°C

32. The lowest pressure at which the liquid phase of a pure substance can exist is known as

(a) Critical point pressure (b) super-incumbent pressure

✓(c) Triple-point pressure (d) saturation vapour pressure

33. The number of phases, components and degrees of freedom, when Ar is added to an equilibrium mixture of NO, O_2 and NO_2 in gas phase are, respectively

(a) 1, 3, 5 (b) 1, 4, 5 (c) 1, 3, 4 (d) 1, 4, 4

34. A system consists of gaseous H_2, O_2, H_2O and CO_2 where the amount of CO_2 is specified and the equilibrium constant for the reaction $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ is known. The number of degrees of freedom of the system is

(a) 2 (b) 3 (c) 4 (d) 5

EXERCISE - II

Numerical Answer Type

1. For each of the following systems, determine the number of components:

(a) $NH_4Cl(s)$, $NH_4^+(aq)$, $Cl^-(aq)$, $H_2O(liq)$, $H_3O^+(aq)$, $H_2O(g)$, $NH_3(g)$, $OH^-(aq)$, $NH_4OH(aq)$

(b) $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$, where the partial pressure of NH_3 is equal to the partial pressure of HCl as is the case when the gaseous mixture is formed by the sublimation of $NH_4Cl(s)$.

(c) $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$, where the partial pressure of NH_3 is not necessarily equal to the partial pressure of HCl.

(d) $CH_3COONH_4(s)$, $CH_3COO^-(aq)$, $NH_4^+(aq)$, $H_3O^+(aq)$, $NH_3(g)$, $OH^-(aq)$, $CH_3COOH(aq)$, $H_2O(l)$, $H_2O(g)$, assuming hydrolysis to take place.

(e) $NaCl(s)$, $KBr(s)$, $K^+(aq)$, $Na^+(aq)$, $Cl^-(aq)$, $Br^-(aq)$, $H_2O(l)$, $H_2O(g)$.

(f) $NaCl(s)$, $KCl(s)$, $Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$, $H_2O(g)$.

(g) $CaCl_2.6H_2O(s)$, $Ca^{2+}(aq)$, $Cl^-(aq)$, $H_2O(l)$, $H_2O(g)$.

(h) $CaCO_3(s)$, $CaO(s)$, $CO_2(g)$, when CaO and CO_2 in the system are formed exclusively by the decomposition of $CaCO_3$.

2. Determine the number of degrees of freedom in each of the following systems. Suggest the variables that could correspond to these degrees of freedom.

(a) Liquid water and water vapour in equilibrium.

(b) Liquid water and water vapour in equilibrium at a pressure of 1 atm.

3. Calculate the number of components and the number of the degrees of freedom in:

(a) an aqueous solution of glucose (b) an aqueous solution of acetic acid

(c) an aqueous solution of sodium chloride (d) a mixture of $H_2(g)$, $O_2(g)$ and $H_2O(g)$

(e) a mixture of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$

4. At 100°C, the specific volumes of water and steam are, respectively, 1 c.c. and 1673 c.c. Calculate the change in vapour pressure of the system by 1°C change in temperature. The molar heat of vaporisation of water in this range may be taken as 40584.8 J mol^{-1}.

5. The vapour pressure of water at 95°C is found to be 634 mm. What would be the vapour pressure at a temperature of 100°C? The molar heat of vapourisation in this range of temperature may be taken as 40593 J mol^{-1}.

6. The specific volumes of ice and water at 0°C are 1.0907 cm^3 and 1.0001 cm^3, respectively. What would be the change in melting point of ice per atm increase of pressure? Molar heat of fusion of ice = 6009.9 J mol^{-1}.

7. Rhombic sulphur changes into monoclinic form at a temperature of 95.6°C at 1 atm pressure. What would be the change in the transition temperature per atm change of pressure? Given: heat absorbed in the change = 2499.94 J mol^{-1} per mole, density of rhombic sulphur = 2.05 g/c.c. and density of monoclinic sulphur is 1.95 g/c.c.

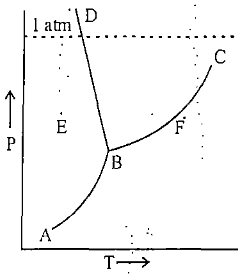
8. As heat is removed from a liquid which tends to supercool, its temperature drops below the freezing point and then rises suddenly to its freezing point. What is the source of heat which causes the temperature to rise?

9. Calculate the eutectic temperature and eutectic composition for a binary solid–liquid system if $\Delta H_{fus,A} = 500$ cal mol^{-1}, $\Delta H_{fus,B} = 1000$ cal mol^{-1} and the melting points of pure A and B are 400°C and 600°C, respectively.

10. For a two component system, $\Delta H_{fus,A} = 500$ cal mol^{-1} and $T_{fus,A} = 400$°C. If the eutectic temperature is 350°C, calculate the solubility in terms of the fraction of B in A at 350°C.

11. Explain why KCl-NaCl-H_2O system should be regarded as a 3-component system whereas KCl-NaBr-H_2O system should be regarded as a 4-component system.

12. For the phase diagram for the water system shown in figure answer the following questions :



(a) What feature represents the equilibrium of solid water (ice) and water vapour ?

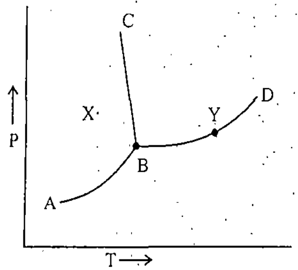
(b) What phase changes occur when a sample at point E is heated at constant pressure until point F is reached ?

(c) What is the temperature at which the line BD intersects the 1 atm line called ?

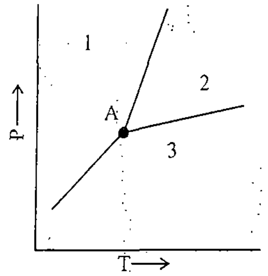
13. Consider the phase diagram for a one-component system shown in figure.

(a) Calculate the number of degrees of freedom at point B, X and Y.

(b) How many phases exist along AB, BC and BD ?



14. Consider the phase diagram of a one-component system shown in figure. Indicate the relative magnitudes of the specific entropies and the molar volumes of phase in the neighbourhood of point A which is the 1–2–3 triple point.



Phase diagram of a one-component system.

15. Using the following data for the iodine system, draw the phase diagram for the system : Triple point 113°C, 0.12 atm; Critical point 512°C, 116 atm; Normal melting point 114°C; Normal boiling point 184°C. Also ρ (solid) > ρ (liquid)

16. A substance exists in two solid modifications α and β and also as liquid and vapour. At a pressure of 1 atm, α melts at a lower temperature than β which melts at a higher temperature to form the liquid. Also, α is denser than the liquid but β is less dense than the liquid. Assuming that no metastable equilibria are observed, sketch the pressure-temperature phase diagram showing the significance of each point, line and region. Also, show in the diagram all the triple point that can be observed.

17. Compute the number of component in the following systems :

(i) A solution containing Na^+, Cl^-, Ag^+, NO_3^-, AgCl(s) and H_2O

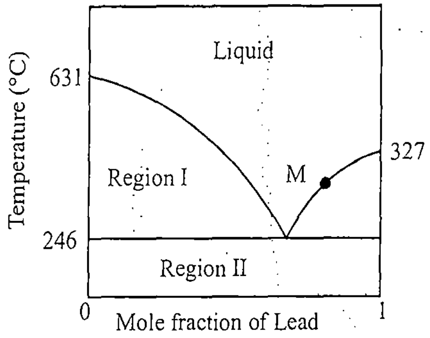
(ii) A solution containing H^+, OH^-, Na^+, Cl^-, Ag^+, NO_3^-, AgCl(s) and H_2O

(iii) A solution containing H_2O, Na^+, Cl^-, K^+, NO_3^-, NH_4^+, NH_3, H^+ and OH^-

(iv) A aqueous solution containing H_3PO_4, H_2PO_4, HPO_4^-, PO_4^{3-}, Na^+ and H^+ at 1 atm pressure.

(v) $NH_4Cl(s)$, $NH_4^+(aq)$, $Cl^-(aq)$, $H_2O(l)$, $H_3O^+(aq)$, $H_2O(g)$, $NH_3(g)$, $OH^-(aq)$, and $NH_4OH(aq)$.

18. The phase diagram for the lead-antimony system at a certain pressure is given below.



(i) Identify the phases and components in region I and region II.

(ii) Calculate the number of degrees of freedom (variance) at point M.

✓ 19. Na and K melt at 90°C and 65°C, respectively. They form one compound NaK which decomposes at 10°C to give a solid and a melt containing 60 mol % K. There is an eutectic at –5°C and the eutectic composition is 75 mol % of K.

(a) Identify the phases in the respective region

(d) Identify the points in the diagram that are non-variant.

20. A lady weighing 50 kg is standing on ice wearing shoes with sole area of 60 cm^2 per shoe. Calculate the temperatue at which the ice will melt under her feet.

21. The following equations give the vapour pressures of ice and water :

$$\ln P_{vapour}\ (ice) = -(6140.1/T) + 24.00$$
$$\ln P_{vapour}\ (water) = -(5432.8/T) + 21.41$$

where P is in mm Hg. Calculate (a) the temperature and pressure at the triple point of water (b) the molar enthalpies of sublimation, vaporization and fusion at the triple point.

22. The melting point of mercury is 234.5 K at 1.01325 bar pressure and it increase 5.033×10^{-3} K per bar increase in pressure The densities of solid and liquid mercury are 14.19 and 13.70 g cm^{-3}, respectively, (a) Determine the molar enthalpy of fusion, (b) Calculate the presure required to raise the melting point to 273 K.

23. At 373.15 K and 1 bar, the specific volume of water vapour of water vapour is 1 696 $cm^3\ g^{-1}$ and the value of dp/dT is 0.0362 2 bar K^{-1}. Calculate $\Delta_{vap}H_m$.

24. The vapour pressure of toluene is 0.078 bar at 313.75 K and 0.398 bar at 353.15 K. Calculate the molar enthalpy of vaporization.

25. The mean enthalpy of vaporization of water in the temperature range between 363.15 K and 373.15 K is 2 268 J g^{-1}. Calculate the vapour pressure of water at 363.15 K, its value at 373.15 K is being 76.0 cm Hg.

26. The vapour pressures of solid and liquid white phosphorus are given by the expression

$$\log\left(\frac{p_2}{atm}\right) = -\frac{(2\,875\ K)}{T} + 5.36 \text{ and } \log\left(\frac{p_1}{atm}\right) = -\frac{(2\,740\ K)}{T} + 4.95$$

respectively. Calculate (a) the temperature and pressure of the triple point of phosphorus, and (b) the molar enthalpy and molar entropy of fusion of phosphorus at the triple point.

27. The vapour pressure of a liquid changes with temperature according to the expression

$$\log\left(\frac{p}{\text{mmHg}}\right) = 11.36 - \frac{273\text{K}}{T}$$

Calculate the enthalpy of vaporization per mole of the liquid.

28. The specific volume of monoclinic sulphur which is stable above the transition temperature is greater than that of rhombic sulphur by 0.0126 $cm^3\ g^{-1}$. The transition point at one atm pressure is 368.65 K and it increases at the rate of 0.035 K atm^{-1}. Calculate the molar enthalpy of transition.

EXERCISE - III

Previous Year Questions

IIT-JAM Previous Year Questions

1. The number of degrees of freedom in the homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure, is:

(a) 0 (b) 1 (c) 2 (d) 3

2. The vapour pressure of benzene is 5333 Pa at 7.6°C and 53330 Pa at 60.6°C. Calculate the heat of vapourization of benzene and the normal boiling point of benzene. Trouton's rule

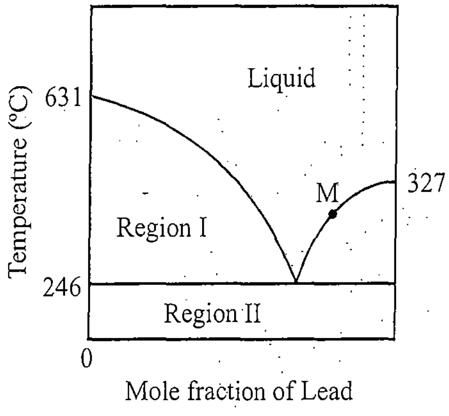
3. The vapour pressures of solid and liquid chlorine are given by

$$\log_e P^{solid} = 24 - \frac{3900}{T} \text{ and}$$

$$\log_e P^{liq} = 18 - \frac{2600}{T},$$

Where P^{solid} and P^{liq} are the vapour pressures (in Torr) of solid and liquid chlorine near the triple point, respectively and T is the absolute temperature. The ratio of the slope of the solid-gas curve to the slope of the liquid-gas curve at the triple point in the P-T diagram is......

4. The phase diagram for the lead-antimony system at a certain pressure is given below



(i) Identify the phases and components in region I and region II.

(ii) Calculate the number of degrees of freedom (variance) at point M.

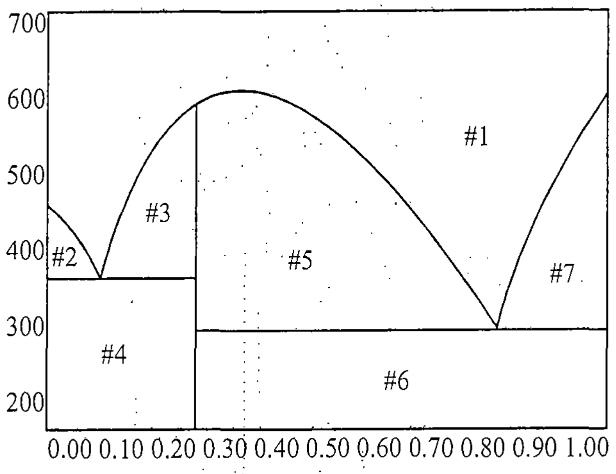
5. (i) Draw the P-T phase diagram of water.

(ii) Label the different regions in this diagram

6. The maximum number of phases that can co-exist in equilibrium for a one component system is

(a) 1 (b) 2 (c) 3 (d) 4

7. The solid-liquid phase diagram for the Mg-Zn system is shown in the figure below where the vertical line at x(Mg) = 0.33 represents the formation of a congruent melting compound $MgZn_2$. The figure is divided into seven regions depending upon the physical state of the system. The composition of the region #6 represents



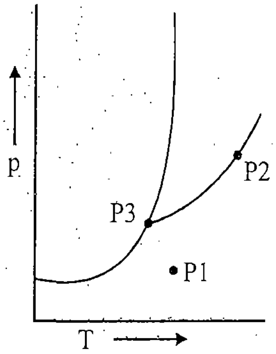
(a) Single phase of a solution of Mg and Zn

(b) two phase region between the solid Zn and solid $MgZn_2$

(c) two phase region between the liquid and solid $MgZn_2$

[✓ (d) two phase region between solid Mg and solid $MgZn_2$]

8. The phase diagram of a pure substance is sketched below.



The number of degrees of freedom at points P1, P2 and P3, respectively, are

[✓ (a) 2, 1, 0] (b) 1, 2, 0 (c) 2, 0, 1 (d) 0, 2, 1

9. For the following system in equilibrium

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

the number of components (C), phases (P) and degrees of freedom (F), respectively, are

(a) 2, 2, 2 (b) 1, 3, 0 (c) 3, 3, 2 (d) 2, 3, 1

10. The number of degrees of freedom of liquid water in equilibrium with ice is

(a) 0 (b) 1 (c) 2 (d) 3

11. The number of degrees of freedom in the homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure, is:

(a) 0 (b) 1 (c) 2 (d) 3

12. The phase diagram of CO_2 and H_2O differ in that

(a) The slope of the solid-liquid equilibrium curve is positive for the former and negative for the latter.

(b) The slope of the solid-liquid equilibrium curve is negative for the former and positive for the latter.

(c) The slope of the solid-vapour equilibrium curve is negative for the former and positive for the latter.

(d) The slope of the solid-vapour equilibrium curve is positive for the former and negative for the latter.

13. The number of degree of freedom for a system consisting of NaCl(s), Na^+(aq) and Cl^-(aq) at equilibrium is

(a) 2 (b) 3 (c) 4 (d) 5

14. The triple point for water is

(a) Unique (b) Depends on p but is independent of T

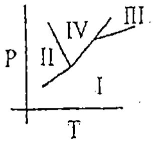
(c) Depends on T but is independent of p (d) Depends on both p and T

15. An aqueous mixed solution of NaCl and HCl is exactly neutralized by an aqueous NaOH solution. The number of components in the final mixture is

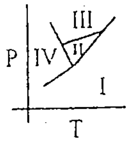
(a) 1 (b) 2 (c) 3 (d) 4

16. A certain substance is known to exist in four phase. Which of the following is definitely NOT the phase diagram?

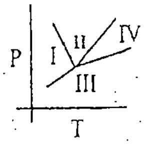
(a)



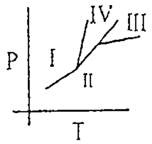
(b)



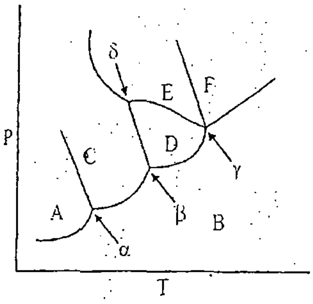
(c)



(d)



17. A pure substance can exist in several different phases A, B, C, ... Its partial phase diagram is shown below.



Which of the following statements is correct about the above diagram?

(a) The diagram is correct in all respects

(b) The diagram is wrong as it has more than one triple point

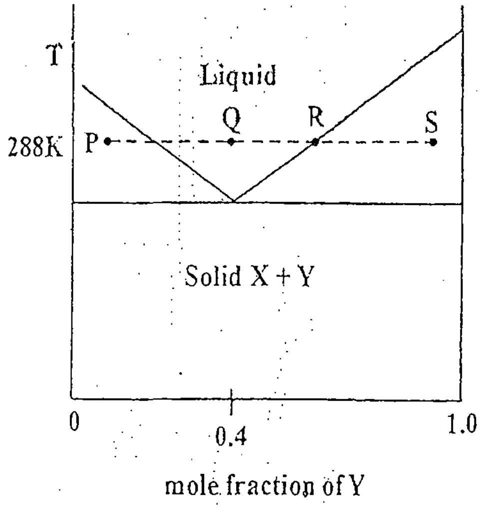
(c) A phase diagram cannot have an island, such as D

(d) The point γ cannot be present in any phase diagram

18. The temperature-dependence of the vapour pressure of solid A can be represented by $\log p = 10.0 - \frac{1800}{T}$, and that of liquid A by $\log p = 8.0 - \frac{1400}{T}$. The temperature of the triple point of A is

(a) 200 K (b) 300 K (c) 400 K (d) 500 K

19. The temperature-composition (T-x) phase diagram of the two-component system made of X and Y is given below. At a temperature of 288 K and starting at the point P, Y is added until the composition reaches S. Which of the following statements is Not True?



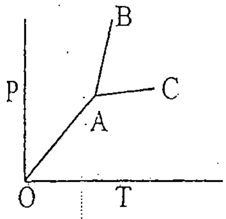
(a) At P, the solid and liquid are present in almost equal proportions

(b) At Q, the system is all liquid

(c) At S, the system has more solid than liquid

(d) At R, the liquid is pure X

20. Phase diagram of a compound is shown below



The slopes of the lines OA, AC and AB are $\tan\frac{\pi}{4}$, $\tan\frac{\pi}{6}$ and $\tan\frac{\pi}{3}$, respectively. If melting point and ΔH of melting are 300 K and 3 kJ mole^{-1} respectively, the change in the volume on melting is

(a) $10\tan\frac{\pi}{3}$ (b) $10\tan\frac{\pi}{4}$ (c) $10\cot\frac{\pi}{3}$ (d) $10\cot\frac{\pi}{4}$

ANSWER KEY

EXERCISE - I

1\. a 2. b 3. d 4. d 5. c 6. a 7. a

8\. a 9. c 10. b 11. a 12. b 13. b 14. a

15\. b 16. c 17. d 18. c 19. c 20. b 21. c

22\. c 23. c 24. a 25. d 26. a 27. d 28. d

29\. c 30. c 31. a 32. a 33. c 34. b

EXERCISE - II

1\. (a) 3, (b) 1, (c) 2, (d) 4, (e) 4, (f) 3, (g) 2, (h) 2

2\. (a) 1, That is, only one variable T or P need to be specified.

(b) 0, The system under the given conditions is thus invariant.

3\. (a) 3, (b) 3, (c) 3,

(d) 4, This means that T, P and the concentrations of two of the three components must be specified.

(e) 2

4\. 27.08 mm of Hg

5\. 759.8 mm

6\. –0.0075 K

7\. 0.011 K

8\. The enthalpy of fusion

9\. $(x_A)_e = 0.647$, $(x_B)_e = 0.352$ and $T_e = 38°C$

10\. 0.0667

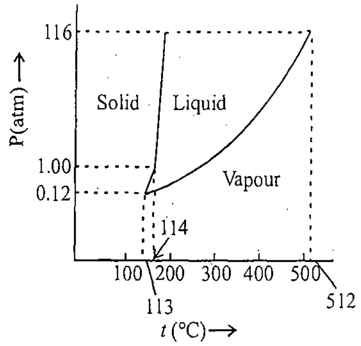
11\. explain

12\. **a.** line AB, **b.** E-melting F-vapourisation, **c.** normal freezing point

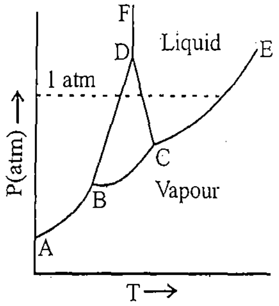
13\. **a.** B–0, X–2, Y–1, **b.** 2

14\. $S_3 > S_2 > S_1$, $V_3 > V_2 > V_1$

15\.



16\.



Triple point B, C, D

The partial phase diagram of the substance conforming to the data.

17. (i) 4, (ii) 4, (iii) 6, (iv) 3, (v) 3

18. (i) I-antimony (solid) + melt, II-solid antimony + solid lead, (ii) 1

19. **a.** 1-melt, 2-Na + melt, 3-NaK + melt, 4-Na + NaK, 5-K + melt, 6-NaK + K
b. 4, 6; **c.** A; **d.** B, D

20. $-0.003°C$

21. 5.88 kJ mol^{-1}

22. 2.33 kJ mol^{-1}, 7501 bar

23. 41237 J mol^{-1}

24. 37675 J mol^{-1}

25. 52.9 cm Hg

26. **a.** 329.3 K, 4.246×10^{-4} atm, **b.** 2585 J mol^{-1}, 7.85 JK^{-1} mol^{-1}

27. 5227 J mol^{-1}

28. 430.3 J mol^{-1}

EXERCISE - III

1. c
2. $\Delta H = 33.85$ kJ mol^{-1}; 111.35°C
3. 3/2
4.
5.
6. c
7. c
8. a
9. d
10. b
11. c
12. a
13. a
14. a
15. b
16. c
17. d
18. a
19. d
20. c

CHAPTER

9

CHEMICAL KINETICS

It is a branch of physical chemistry which deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval.

For a general reaction carried out at constant volume.

$$aA + bB \longrightarrow cC$$

$$\text{The rate of disappearance of } A = \frac{\text{Decrease in conc. of A}}{\text{Time taken}} = -\frac{d[A]}{dt} \text{ or } \frac{\Delta[A]}{\Delta t}$$

$$\text{Rate of disappearance of B} = \frac{\text{Decrease in conc. of B}}{\text{Time taken}} = -\frac{d[B]}{dt} \text{ or } \frac{\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of C} = \frac{\text{Increase in conc. of C}}{\text{Time taken}} = \frac{d[C]}{dt} \text{ or } \frac{\Delta[C]}{\Delta t}$$

The positive sign shows that concentrations of C and D increases with time and the negative sign indicates that concentrations of A and B decreases with time.

***Units of Rate** are unit of concentration divided by the unit of time (mol $L^{-1}s^{-1}$ or mol $L^{-1}min^{-1}$ or so on).*

$$\text{Rate of reaction : } -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}.$$

Rate of disappearance / Rate of appearance / Rate of reaction are different quantities which may be related for a reaction.

FACTORS AFFECTING RATE CONSTANT

The value of rate constant depends on: (i) nature of reactent (ii) temperature (iii) Catalyst

ORDER OF REACTION

The order of a reaction is obtained from the experimentally determined rate law and may be zero, an integer or a fraction.

TBR

MOLECULARITY:

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Bimolecular reactions involve collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \longrightarrow H_2 + I_2$$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2NO + O_2 \longrightarrow 2NO_2$$

Molecularity of a reaction is :

The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

TBR

Table Differences between molecularity and order of reaction order can be zero

	Molecularity		Order of reaction
1	It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change	1	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction
2	It is always a whole number	2	It may be a whole number, zero fractional,(positive or negative)
3	It is a theoritical concept	3	It is experimentally determined
4	It is meaningful only for simple reaction or individual steps of a complex reaction	4	It is meant for the reaction and not for individual step

Thus, from the above discussion we can conclude the following:

(a) Order is defined to elementary as well as complex reactions whereas molecularity is defined only for elementary reactions. For complex reaction molecularity has no meaning.

(b) For an elementary reaction order and molecularity are same.

ZERO ORDER REACTIONS

Consider of general reaction.

$nA \longrightarrow$ products

Rate = $k\,[A]^{\circ}$

$[A]_t = [A]_0 - kt.$

Characteristics of zero order reactions:

(i) *Concentration of reactant decreases linearly with time.*

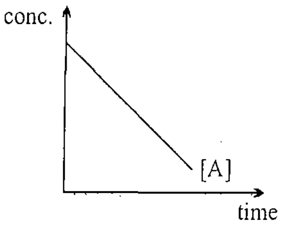
(ii) *Units of k are* ***mol l^{-1} time^{-1}***.

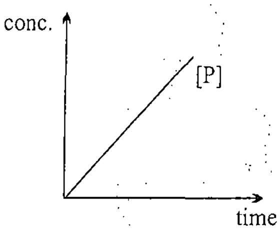
(iii) *Time required for the 100% completion of reaction is* $\frac{[A]_0}{k}$

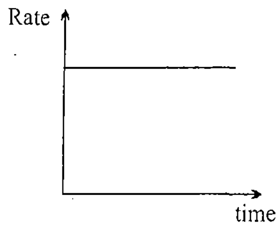
(iv) $t_{1/2} = \frac{[A]_0}{2k}$

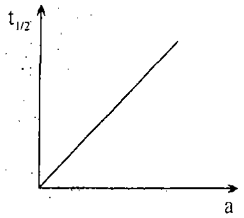
(v) *Zero order reaction must be complex reaction*

(vi) *Graph related with zero order reactions.*









Examples :

(i) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$

(ii) $N_2O(g) \xrightarrow[\text{Surface}]{\text{hot Pt.}} N_2(g) + \frac{1}{2} O_2(g)$

(iii) $2NH_3(g) \xrightarrow[\text{surface}]{\text{Mo or W.}} N_2 + 3H_2$

(iv) Enzyme catalysed reaction

Substrate(S) $\xrightarrow{\text{Enzyme(E)}}$ product(P).

FIRST ORDER REACTIONS

Consider a general reaction.

nA ⟶ products

at time t = 0 concentration of A = a or $[A]_0$

at time t = t concentration of A = (a – x) or $[A]_t$

Rate α [A]

$$-\frac{d[A]}{dt} = k[A] \text{ or } \frac{dx}{dt} = k(a-x)$$

Exponential form of 1st order equation is $[A]_t = [A]_0 e^{-kt}$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}.$$

The constant obtained above is not w.r.t. to reaction rather it is w.r.t. disappearance of A.

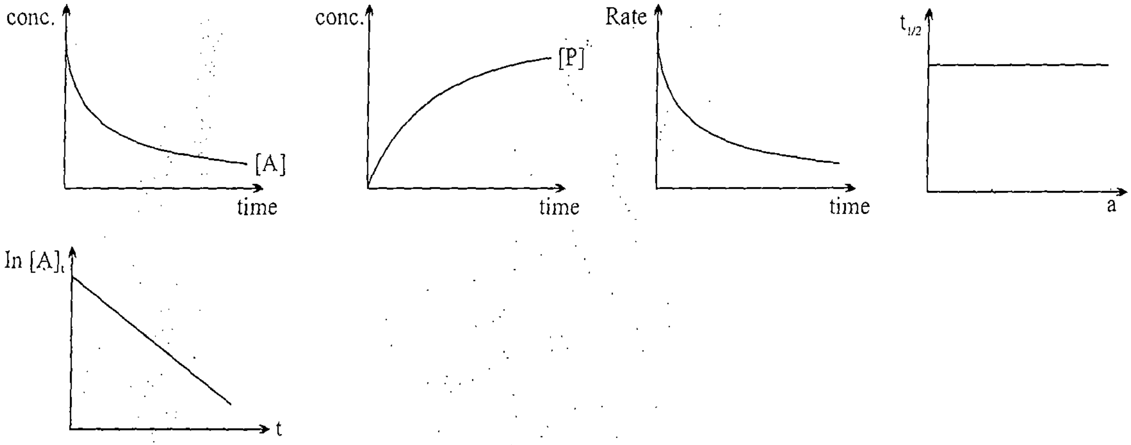
Characteristics of First Order Reaction :

(i) *Unit of rate constant is* $time^{-1}$.

(ii) $t_{1/2} = \frac{0.693}{k}$ *(Half-life)*

(iii) $\log (a-x)$ *v/s t is a straight line with slope* $-\frac{k}{2.303}$.

(iv) *Graph related with first order reactions.*



Examples:

(i) Radioactive disintegration is a first order reaction.

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} C_6H_{12}O_6 + C_6H_{12}O_6$.
(glucose) (fructose)

(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

CALCULATION OF FIRST ORDER RATE CONSTANT USING DIFFERENT PARAMETERS

(I) Decomposition of H_2O_2 in aqueous solution (In terms of volume of reagent $KMnO_4$ required in titration against H_2O_2).

$$H_2O_2 \longrightarrow H_2O + O_2$$

$$k = \frac{2.303}{t}\log\frac{V_0}{V_1}$$

where

V_0 = Volume of $KMnO_4$ required in titration of H_2O_2 sample taken initially

V_t = Volume of $KMnO_4$ required in titration of same volume of H_2O_2 sample at time 't'.

(II) Oxide layer formation:

$$k = \frac{1}{t}\ln\frac{\tau_{max}}{\tau_{max} - \tau}$$

τ_{max} = Thickness of oxide layer after ∞ times

τ = Thickness of oxide layer at time 't'.

(III) Bacterial Growth:

$$k = \frac{1}{t}\ln\frac{a+x}{a}$$

SECOND ORDER REACTION:

(i) For the given reaction.

$nA \longrightarrow$ products

Differential rate equation $\frac{dx}{dt} = k(a-x)^2$

Integrated rate equation $k = \frac{1}{t}.\frac{x}{a(a-x)}$ *or* $kt = \frac{1}{a-x} - \frac{1}{a}$.

(ii) For the given reaction.

	A	+	B $\longrightarrow$ products
at time t = 0	a		b
at time t = t	a – x		b – x

differential rate equation $\frac{dx}{dt} = k(a-x)(b-x)$.

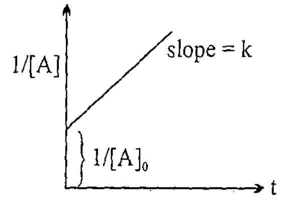
Integrated rate equation $k = \frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$

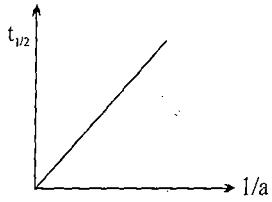
Characteristics of Second Order Reaction :

(i) Unit of rate constant L mol^{-1} time^{-1}.

(ii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iii) 2nd order reaction converts to first order when one of the reactant is in excess.





Examples:

(i) Saponification (hydrolysis of esters catalysed with alkali).

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(ii) Hydrogenation of ethane $C_2H_4 + H_2 \xrightarrow{100°C} C_2H_6$.

(iii) $2\,O_3 \longrightarrow 3\,O_2$.

Third order reactions

A reaction is said to be a third order if its rate is determined by the variation of three concentration terms.

When the concnetration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given by

$3A \rightarrow$ products or $A + B + C \rightarrow$ products

$$\frac{dx}{dt} = k(a-x)^3$$

On solving this equation, $k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$

Characteristics of third order reactions

1. Half life period

$$= \frac{1}{k} \cdot \frac{0.5a(2a-0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a} = \frac{3}{2a^2k}$$

Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k.
3. The unit of k is expressed as $(\text{mol/litre})^{-2}$ time^{-1} or litre^2 mol^{-2} time^{-1}.

Examples of third order reactions

1. Reaction between nitric oxide and oxygen

$2NO + O_2 \rightarrow 2NO_2$

2. Reaction between nitric oxide and chlorine.

$2NO + Cl_2 \rightarrow 2NOCl$

3. Reduction of $FeCl_3$ by $SnCl_2$.

$2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$

PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions, e.g.

(i) $RCl + H_2O \xrightarrow{\text{acid}} ROH + HCl$

Expected rate law :

Rate = $k[RCl]\,[H_2O]$ expected order = 1 + 1 = 2

Actual rate law :

Rate = $k'[RCl]$; Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, **pseudo first order.** Similarly, the acid catalyzed hydrolysis of ester, viz.,

$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$

follow first order kinetics : Rate = $k[RCOOR']$

It is also a pseudo-first order reaction.

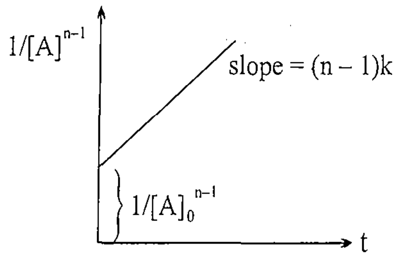
nth ORDER REACTION.

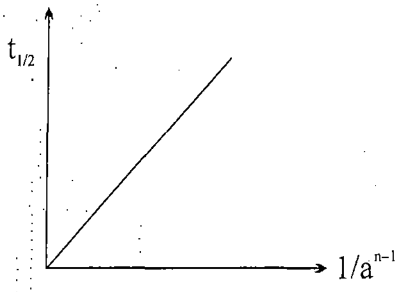
Consider the reaction

$nA \rightarrow \text{Product}$

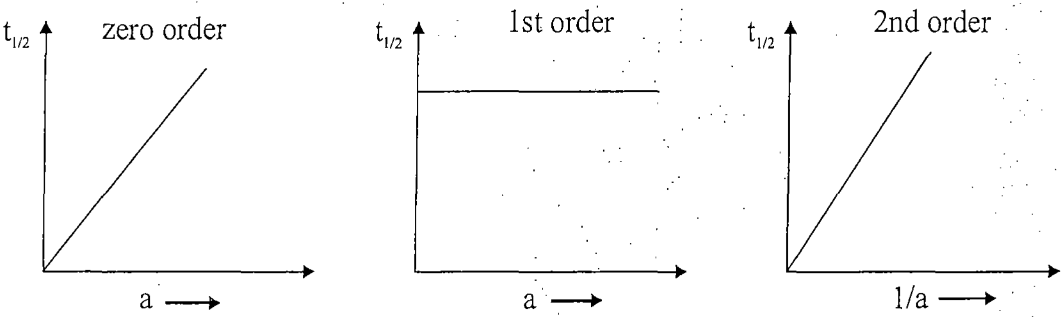
$$kt = \frac{1}{n-1}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} \qquad [n \neq 1,\ n = \text{order}]$$

$$t_{1/2} = \frac{1}{k(n-1)} \cdot \left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$





Plots of $t_{1/2}$ vs. Conc.



INFLUENCE OF TEMPERATURE ON REACTION RATES :

Temperature coefficient :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}.$$

If no temperature is specified in T.C. then it can be taken as 25°C

Arrhenius Equation :

Main characteristics of Arrhenius Equation

The main characteristics of Arrhenius equation are described below.

(1) Larger the activation energy, smaller is the value of rate constant.

(2) Larger the activation energy, greater is the effect of a given temperature rise on k. This follows $\frac{k_{T+10}}{k_T}$ will be larger for a large value of E_a.

(3) At lower temperatures, increase in temperature causes more change in the value of k than that at higher temperatures.

A quantitative relationship was proposed by Arrhenius

$$k = A.\, e^{-Ea/RT}$$

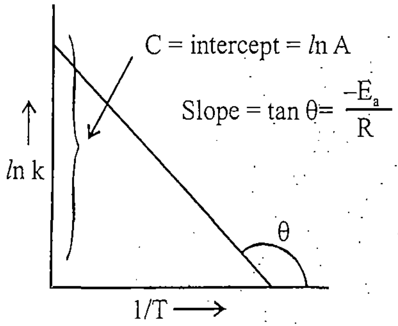
where

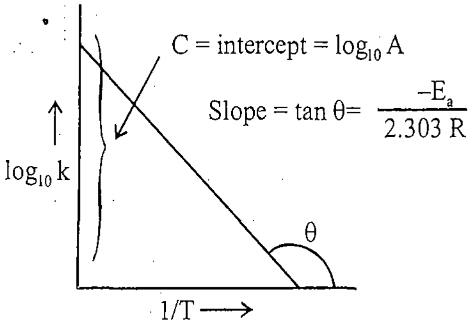
k = rate constant ; A = frequency factor (or pre – exponential factor);

R = gas constant ; T = Temperature (kelvin) ; E_a =Activation energy.

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\,R}\left[\frac{1}{T}\right]$$

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$





A → a constant (frequency factor)

E_a → energy of activation

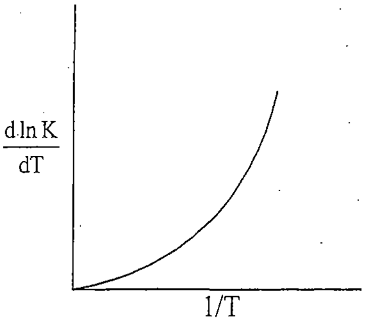
Reactions on the basis of influence of temperature are classified into five types. These are shown in the graphs.

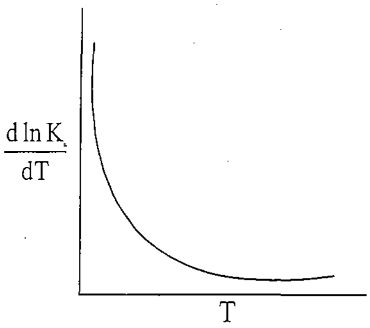
(d) Plots of $\frac{d \ln K}{dT}$ vs Temperature

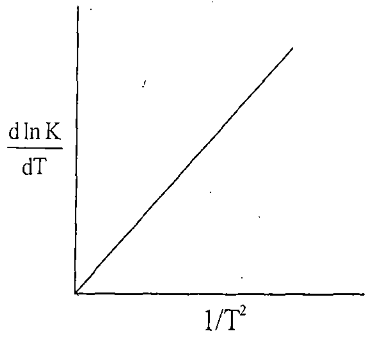
$$\ln k = \ln A - \frac{Ea}{RT}$$

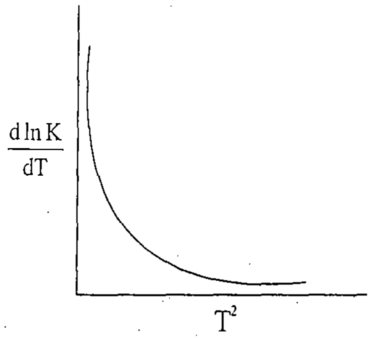
Differentiating w.r.t. to T

$$\frac{d \ln k}{dT} = \frac{d \ln A}{dT} - \frac{Ea}{R}\frac{d}{dT}\left(\frac{1}{T}\right); \quad \frac{d \ln k}{dT} = \frac{-Ea}{R}\left[\frac{-1}{T^2}\right]; \quad \frac{d \ln k}{dT} = \frac{Ea}{RT^2}$$









Relation between $t_{1/2}$ and temperature:

$$\boxed{\ell n\ t_{1/2} = \ell n\ A' + \frac{E_a}{RT}}$$

COLLISION THEORY OF REACTION RATE

(i) This theory was given by Arrhenius and Von't Hoff.

(ii) This theory is mainly applicable for the bimolecular gaseous reactions.

(iii) A chemical reaction takes place due to the collisions between the reactant molecules. Bond cleavage as well as bond formation takes place at the time of collision between the molecules.

(iv) The number of molecular collisions taking place per second perunit volume of the reaction mixture is known as collision frequency (Z_{11} or Z_{12}).

(v) Under normal conditions, the value of Z_{11} or Z_{12} is about 10^6 mol l^{-1} s^{-1}. Normally, the reactions are not so fast. It represents that all molecular collisions do not response reaction. Reaction occurs due to a very small fraction of collisions.

(vi) The collisions that actually produce products are called effective collision. For a collision to be effective, the following two barriers should be crossed by the molecules.

Reaction, $A + B \rightarrow$ Products

The expression of biomolecular collisions is given by

$$Z_{AB} = \pi n_A n_B d_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

k_B is Boltz mann constant, μ is reduced mass.

d_{AB} is the average collision diameter.

n_A and n_B are the number of atoms/volume of A and B respectively.

Note: for identical molecules i.e., $A + A \rightarrow$ Products

$$Z_{AA} = \frac{1}{\sqrt{2}} \pi n_A n_B d_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

$$\boxed{A = pN_A d_{AB}^2 \left(\frac{8\pi k_BT}{\mu}\right)^{\frac{1}{2}}} \quad \text{or} \quad \boxed{A = p\pi N_A d_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}}}$$

Transition state theory/Activated complex theory:

This theory was established by Eyring and Polanyi and based on following postulates.

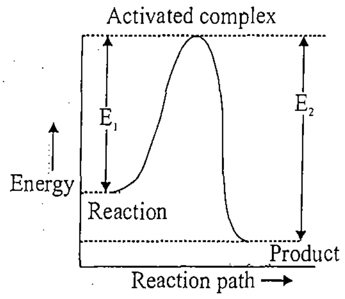
1. As the reactant molecules approach each other, there are continuous changes in bond distances. These changes are accompanied by energy change.
2. The reactant molecules are transformed into an energy rich intermediate called activated complex or transition state.
3. The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy. or if it be a unimolecular reaction, the reactant molecule may produce the activated complex by rearrangement of atoms and redistribution of energy.

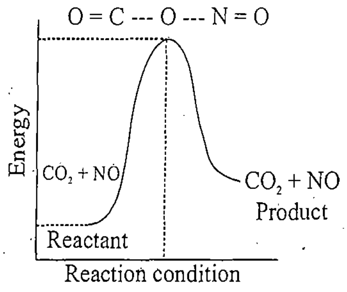
   Partition function of loose vibration: $\frac{kT}{h\nu}$

   Frequency of loose vibration: $\frac{kT}{h}$
4. The activated complex, though unstable, has transient existence. The activated complex is in equilibrium with the reactants. The potential energy of activated complex is maximum.

   Reactants $\rightleftharpoons$ Activated complex
5. The activated complex decomposes into products.

   Reactants $\rightleftharpoons$ Activated complex $\rightarrow$ Products
6. The activation energy, in the light of transition state theory, is defined as the additional energy which the reacting molecules must acquire to form the activated complex.





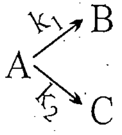
(i) $\Delta H_{rxn} = E_a - E_b$

(ii) $E_a = \Delta H + RT$ (Unimolecular gaseous Reaction)

(iii) $E_a = \Delta H + 2RT$ (Bimolecular reaction)

MISCELLENEOUS REACTIONS

(i) Parallel Reactions



$$ln\frac{[A]_0}{[A]_t} = (k_1 + k_2)\,t$$

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

$$[A] = [A_0]\,e^{-kt}$$

$$[B] = \frac{k_1[A_0]}{k_1 + k_2}(1 - e^{-kt})$$

$$[C] = \frac{k_2[A_0]}{k_1 + k_2}(1 - e^{-kt})$$

where $k = k_1 + k_2$

{Initial concentration of [B] and [C] is taken zero}

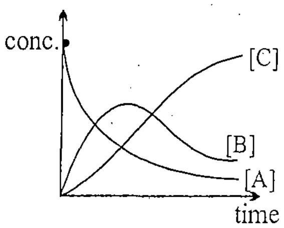
(ii) Consecutive Reaction

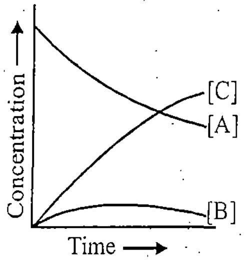
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

{at t = 0 $[A] = [A_0]$, $[B] = 0$, $[C] = 0$}

$$[A]_t = [A]_0 e^{-k_1 t} \quad , \; [B]_t = \frac{k_1[A]_0}{(k_2 - k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right] , \quad [C]_t = [A_0] - ([A]_t + [B]_t)$$

$$t_{max} = \frac{1}{(k_1 - k_2)}\, ln\left(\frac{k_1}{k_2}\right) \quad ; \quad [B]_{max} = [A_0].\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}}$$





Steady-State Approximation: In this section, we will see how the use of steady-state approximation helps in deriving the differential rate expression from the proposed reaction mechanism of a given reaction.

Many of reactions fall into the following four categories of simple reaction mechanisms.

Type 1: First step is the rate-determining slow step and is followed by rapid subsequent reactions.

Type 2: First step is a rapid equilibrium which produces an intermediate which reacts slowly in the rate determining step.

Type 3: Reactions involving more than one step with comparable rate constants (or whether the steps are slow or fast are not known).

The differential rate law for the first two types of mechanisms can be derived without the use of the steady-state approximation. Nevertheless, the steady-state approximation can be equally applied to derive the differential rate law of a reaction belong to these categories. We now describe a few typical reactions belonging to the types listed above.

Illustration: Reaction exhibiting this type of mechanism may, in general, be represented as

$$A \xrightarrow{k_1} B \qquad \text{(slow)}$$

$$B \xrightarrow{k_2} \text{Products} \qquad \text{(fast)}$$

Since the fist step is slow and is the rate-determining step, the rate at which products are formed will depend only on this reaction irrespective of the number and nature of subsequent fast reactions. Thus, we have

$$\frac{dx}{dt} = k_1[A]$$

A example is given below

Decomposition of Ozone:

The decomposition reaction

$$2O_3 \rightarrow 3O_2 \qquad \dots (1)$$

follows the first order differential rate law

$$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad \dots (2)$$

Equation (2) suggests that the rate-determining step involves one molecule of ozone. The proposed mechanism is

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

It is expected that $k_1 << k_2$ since the second reaction involves atomic oxygen which is very reactive. Thus, the rate law would be

$$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad \dots (2)$$

(Note the division by 2 on the left hand side. This is done as two molecules of O_3 are removed in the over-all reaction mechanism).

The use of steady-state approximation also yields the rate expression of Eq. (2). Applying the approximation to the reactive intermediate oxygen atom, we get

$$\frac{d[O]}{dt} = 0 = k_1[O_3] - k_2[O][O_3]$$

Hence, $[O] = \frac{k_1}{k_2}$ ... (3)

The rates of decomposition of O_3 will be given as

$$r_1 = -\frac{d[O_3]}{dt} = k_1[O_3]$$

$$r_2 = -\frac{d[O_3]}{dt} = k_2[O_3][O]$$

The total rate of disappearance of O_3 will be given by

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_2[O_3][O] \qquad \dots (4)$$

Substituting the concentration of O from Eq. (3), we get

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_2[O_3]\frac{k_1}{k_2} = 2k_1[O_3]$$

or $$-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3] \qquad \dots (2)$$

(iii) Reversible reaction

Consider the reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

At time t = 0 $\quad a \quad\quad b$

At time t = t $\quad a - x \quad\quad x$

At time $t = t_{eq}$ $\quad a - x_{eq} \quad\quad x_{eq}$

$$ln\left(\frac{x_{eq}}{x_{eq} - x}\right) = (k_f + k_b)\,t \quad ; \quad \frac{x_{eq}}{a - x_{eq}} = \frac{k_f}{k_b}$$

These expressions are derived for first order reactions.

CATALYSIS

A catalyst may be defined as the substance which when present in a chemical reaction accelerates its speed & is recovered unchanged in amount & chemical characteristics when the reaction is over. The process involving the use of catalyst in a chemical reaction is known as catalysis.

Characteristics of Catalyst:

- A catalyst can't initiate a chemical reaction. It can increase or accelerate the speed of a reaction already in progress. Thus a catalyst can catalyse a spontaneous reactions with negative ΔG.
- Catalyst are required only in small amount.
- A catalyst remains unchanged in amount as well as in chemical characteristics at the end of the reaction only state & colour may be changed.
- A catalyst is of specific nature, i.e. different catalysts are needed for different reaction.
- A catalyst does not influence the equilibrium constant of an equilibrium reaction. However, it can only influence the extent of attainment of equilibrium.

ENZYME CATALYSIS

Enzyme reaction forms an important type of heterogeneous catalytic reactions occuring in aqueous solutions. Enzymes are naturally occurring living cells of animals and plants. Enzymes are specific, colloidal catalysts. Enzymes belong to the class of organic substances called proteins, having the dimension of 100 – 1000 Å in a diameter. Enzyme catalysis, hence lies between the homogeneous and heterogeneous catalysis and is sometimes known as micro-heterogeneous, e.g., hydrolysis of urea in presence of urease, hydrolysis of maltose in presence of maltase, inversion of cane sugar is presence of invertase and sucrase. Each enzyme is specific for a given reaction. e.g. urease will hydrolyse urea but not methyl urea. Enzymes also catalyse both the forward and backward reactions, without affecting the final state of equilibrium. They can be activated and poisoned like ordinary catalysts.

1. Factors Affecting Enzyme Catalysed Reactions

(i) **Temperature:** With the rise in termperaure the enzymes are coagulated and hence the activity of an enzyme decreases. Thus, there is in general, an optimum temperature at which the catalytic efficiency of an enzyme is maximum. The enzyme is most effective between 35° and 50°C.

(ii) **Concentration:** The rate increases with the increase in the concentration of enzyme.

(iii) **pH:** Within moderate pH, enzymes are effective.

(iv) **Electrolytes:** Being colloidal in nature, the enzymes are coagulated by addition of electrolytes, resulting in the loss of their catalytic activity.

(v) **Ultraviolet rays:** These rays also tend to destroy enzymes.

2. **Kinetics of Enzyme Catalysis**

A reactant in an enzyme catalysed reaction is known as **substrate**. The enzyme combine with the substrate to form a complex, and this complex remains in equilibrium with the enzyme and the substrate.

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \text{ (Fast)} \qquad ES \xrightarrow{k_3} E + P \text{ (Slow)}$$

$$\frac{d[P]}{dt} = \frac{k_3[E]_0[S]}{k_m + [S]} = \text{Rate}$$

Equation is known as Michaelis-Menton equation.

for maximum rate: $[E]_0 = [ES]$

$r_{max} = v_{max} = k_3[E]_0$

where v_{max} refers to maximum rate, using the notation of enzymology. So, Michaelis-Menton equation can also be written as, $r = \dfrac{v_{max}[S]}{k_m + [S]}$

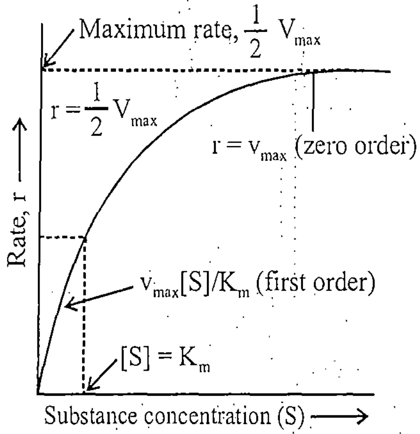
If $r = \dfrac{v_{max}}{2}$, then $K_m = [S]$

Thus, Michaelis constant is equal to that concentration of substrate, S at which the rate of formation of the product is half the maximum rate obtained at a high concentration of substrate.

From equation, we can draw the following conclusions :

(i) If [S] is very small as compared to K_m, the factor $\dfrac{K_m}{[S]}$ will be very large as compared to unity and so the rate of formation of P, i.e., $\dfrac{d[P]}{dt}$ will be directly proportional to [S]. In other words, the reaction will be of the first order with respect to S.

(ii) If [S] is very large compared to K_m, the factor $\dfrac{K_m}{[S]}$ will be negligibly small as compared to unity and so the rate of formation of P, i.e., $\dfrac{d[P]}{dt}$ will be independent of the concentration [S]. In other words, the reaction will be zero order with respect to S.



(iii) If [S] is very small or very large, the reaction remains first order with respect to the total concentration, $[E]_0$ of the enzyme.

TURNOVER NUMBER

It is the number of molecules of substrate converted into product by one molecule of enzyme per unit time.

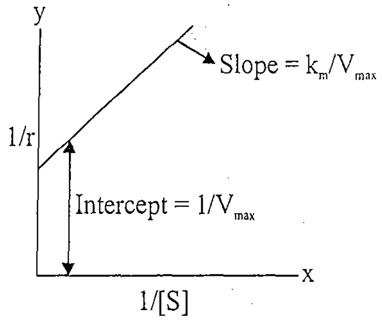
$$\text{Turn over number} = \frac{\text{Number of molecules of substrate reacted}}{\text{Number of molecules of enzyme} \times \text{time taken}}$$

The Lineweaver-Burk plot:

The Michaelis-Menten equation may be rearranged.

$$r = \frac{V_{max}[S]}{k_m + [S]}$$

Or, $$\frac{1}{r} = \frac{k_m + [S]}{V_{max}[S]} = \frac{1}{V_{max}} + \frac{k_m}{V_{max}} \times \frac{1}{[S]}$$



Lineweaver-Burk Plot

A plot of $\frac{1}{r}$ against $\frac{1}{[S]}$ gives a straight line whose $\boxed{\text{Slope} = (k_m / V_{max})}$ and $\boxed{\text{Intercept} = \frac{1}{V_{max}}}$

TURNOVER FREQUENCY AND CATALYTIC EFFICIENCY

The turnover frequency or catalytic constant (k_{cat}) is the number of catalytic cycles performed by active site in a given interval divided by the duration of interval.

In terms of Michaelis-Menten mechanism, T.O.F. is numerically equal to k_3 is rate constant for release of product from enzyme substrate complex.

$$\boxed{\text{T.O.F.} = k_{cat} = k_3 = \frac{v_{max}}{[E]_0}}$$

The catalytic efficiency ($\in$) of an enzyme is the ratio of T.O.F and Michaelis constant.

$$\boxed{\in = \frac{\text{T.O.F}}{k_m} = \frac{k_3}{k_m} = \frac{V_{max}}{[E]_0} \times \frac{1}{k_m}}\ ; \ \boxed{\in = \frac{k_1 k_3}{k_1 + k_3}}$$

PHOTOCHEMISTRY

Studies the reaction of those molecules, which absorb light radiation of spectrum in the UV and visible regions and become electronically excited.

Photochemistry provides a phenomenon of fluorescence and phosphorescence which is collectively known as photophysical phenomenon.

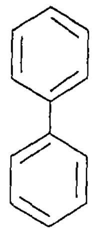
FLUORESCENCE

When the light radiation is observed by a compound, its electron goes to higher energy level from lower energy level. From that level, electron returns to the normal position either directly or in steps with the emission of light energy. When this emission of light is instantaneous (10^{-8} sec.), the phenomenon is known as florescence.

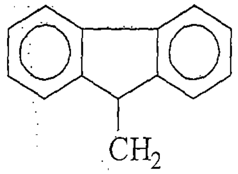
In other words, remission as radiation of all the part of radiant energy is known as fluoresence.

Factors affecting fluorescence

1. Fluoresence is produced by those molecules which are able to absorb U-V light or visible radiation.
2. Molecules which have conjugated double bond or π-bonds give fluorescence.
3. Substitution frequency affects the fluorescence efficiency.
4. Some electron donating groups enhance fluoresence. These groups are $-NH_2$, $-OH$ etc. while electron withdrawing groups, such as $-COOH$, $-NO$, etc. decrease or destroy fluorescence.
5. Rigid structure and aromatic compound increase the fluoresence.



biphenyl



Fluorescence

6. Certain organic chelating agents increase fluorescence.
7. On increasing the temperature, fluorescence gets decreased.
8. By decreasing the viscosity of the solvent, fluorescence increases.
9. Polarity of the solvnet also affects fluorescence.
10. pH also affects fluorescence e.g., Neutral or alkaline solution of aniline shows fluorescence in the visible region, but in the acidic solution, fluorescence disappears in the visible region and appears in the U-V region.

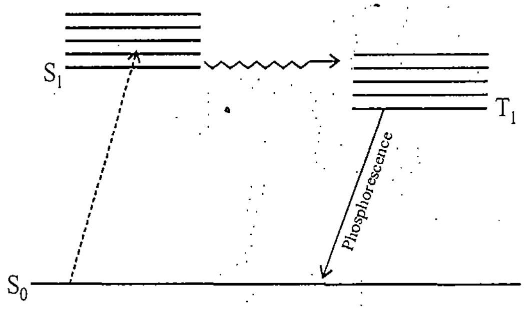
PHOSPHORESCENCE

The molecules with relatively stable excited state may undergo transition to metastable triplet state and after some time return to the ground state by the emission of U-V or visible photon. this process is called phosphorescence or stepwise fluorescence.

If the excited state is a p → p* triplet, the lower probability of a spin transition back the ground state causes the emission of light and the result is the phosphorescence.

Factors affecting phosphorescence

1. Only those molecules which are able to absorb UV and visible radiation can show phosphorescence.
2. The polarity of the solvent also affects phosphorescence.
3. Compounds containing heavy atoms are frequently incorporated in solution, then increased phosphorescence is required.
4. Temperature also affects phosphorescence, but good phosphorescence is obtained at room termperature.



LAWS OF PHOTOCHEMISTRY

1. **Lambert's law:** "Equal fraction of the incident radiation are absorbed by successive layers of equal thickness of the light absorbing substances."

$$-\frac{dI}{I} \propto [d\ell] \qquad \text{.... (1)}$$

k = absorption coefficient and depends on the material & wavelength of radiation. It can also be given as "The rate of decreases of intensity with thickness of medium is proportional to the intensity of the medium."

$$-\frac{dI}{d\ell} = kI$$

From equation (1), $-\int_{I_0}^{I} \frac{dI}{I} = k\int_{0}^{\ell} d\ell \quad \Rightarrow \quad \ell n\frac{I}{I_0} = -k\ell$ .... (2)

$$\boxed{I = I_0.e^{-k\ell}}$$

from equation (2) $\log\frac{I}{I_0} = \frac{-k}{2.303}.\ell \quad \therefore \quad \boxed{I = I_0.10^{-al}}$

where, $a = \frac{k}{2.303}$ = absorption coefficient/extinction coefficient

2. **Beer's law: (Lambert's law to solution):** For a solution of Conc. 'c' according to Beer's law

$$-\frac{-dI}{I} \propto c \qquad \text{.... (3)}$$

combining equation (1) and (3)

$$-\frac{-dI}{I} = k(d\ell).c \qquad \text{.... (4)}$$

Equation (4) is known as Lambert's Beer law.

on integrating.

$$\log\frac{I}{I_0}=\frac{-k}{2.303}Cl=-\in Cl \quad\Rightarrow\quad \boxed{I=I_0.10^{-\in Cl}} \qquad ....(5)$$

$$\in=\frac{k}{2.303}=\text{molar absorption coefficient/molar extinction coefficient}$$

It has unit (Conc.) $(\text{length})^{-1}$. Beer's law is applicable for dilute solutions only.

Absorbance of a solution:

$$\because \quad \log\frac{I}{I_0}=-\in Cl \qquad \Rightarrow I=I_0.10^{-\in Cl}$$

The exponents is called as absorbance (A) or optical density

$$\boxed{A=\in Cl} \qquad \text{Or} \qquad \boxed{A=-\log\frac{I}{I_0}=\log\frac{I_0}{I}}$$

Transmittance (T): The ratio I / I_0 called Transmittance

⇒ Absorbance of a solution is additive i.e.

$$A=\ell\sum_i \in_i c_i=\sum_i \in_i c_i l=\sum_i A_i$$

⇒ If absorbance of a solution is additive transmittance will be multiplicative.

Law of Photochemical equivalence:

- **The first law of photochemistry, the Grotthuss-Draper law,** states that light must be absorbed by a compound in order for a photochemical reaction to take place.
- **The second law of photochemistry, the Stark-Einstein law,** states that for each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction. This "photoequivalence law" was derived by Albert Einstein during his development of the quantum (photon) theory of light.

Primary and secondary processes: Primary processes are light absorbing process & follows law of photochemical equivalence.

The photon absorbed by a molecule causes the electronic excitation. The electronic excitation follows the Franck Condon Principle.

In secondary process the products of primary reaction undergoes subsequency thermal reaction. THey may involve one step or many.

Quantum efficiency: It is defined as the number of light absorbing molecules reacted per photon of light absorbed.

$$\text{i.e.} \qquad \phi=\frac{\text{no. of molecules reacted}}{\text{no. of photons absorbed}}=\frac{\text{Amount of substance reacted}}{\text{Amount of photon absorbed}}$$

according to law of photochemical equivalence, the quantum efficiency (ϕ) will always be equal to 1 but secondary process alters ϕ from 1.

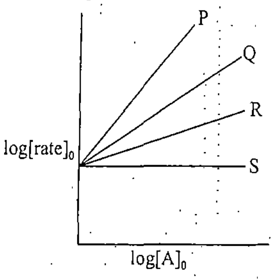
EXERCISE - I

Single Answer Correct Type

1. Rate of reaction and Rate law.

1. For the nth order reaction, $\frac{dx}{dt} = \text{Rate} = k[A]_0^n$

Graph between log (rate) against log $[A]_0$ is of the type



Lines P, Q, R, S are for the order

	P	Q	R	S		P	Q	R	S
(a)	0	1	2	3	(b)	3	2	1	0
(c)	1	2	3	0	(d)	0	3	2	1

2. For reaction system:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

volume is suddenly reduced to half of its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will

(a) diminish to one-fourth of its initial value (b) diminish to one-eight of its initial value

(c) increase to eight times of its initial value (d) increase to four times of its initial value

3. The equilibrium constant K is for the reaction $HA + B \rightleftharpoons BH^+ A^-$. The rate constant for forward reaction and backward reaction is 2.38×10^{-4} and 8.15×10^{-5} respectively will be

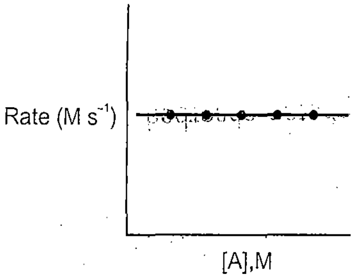
(a) 4.77 (b) 2.92 (c) 3.92 (d) 0.392

4. For a given reaction $A \rightarrow$ Product, rate is 1×10^{-4} M s^{-1} when [A] = 0.01 M and rate is 1.41×10^{-4} M s^{-1} when [A] = 0.02 M. Hence, rate law is :

(a) $-\frac{d[A]}{dt} = k[A]^2$ (b) $-\frac{d[A]}{dt} = k[A]$ (c) $-\frac{d[A]}{dt} = \frac{k}{4}[A]$ (d) $-\frac{d[A]}{dt} = k[A]^{1/2}$

5. Following reaction can take place in both direction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$,

It is given that for the forward reaction :



and for the backward reaction

[B]	Rate
0.01 M	1×10^{-2} Ms^{-1}
0.02 M	2×10^{-2} Ms^{-1}

Hence, net reaction rate of B is :

(a) $= k_1[A] - k_2[B]$ (b) $= k_1 - k_2[B]$ (c) $= k_1[A] - k_2$ (d) $= k_1 - k_2$

6. In the reaction between NO and H_2 the following data are obtaiend

Experiment I : P_{H_2} = constant

P_{NO} (mm of Hg)	359	300	152
$\frac{-dP_{NO}}{dt}$	1.50	1.03	0.25

Experiment II : P_{NO} = constant

P_{H_2} (mm of Hg)	289	205	147
$\frac{-dP_{H_2}}{dt}$	1.60	1.10	0.79

The orders with respect of H_2 and NO are :

(a) 1 with respect to NO and 2 with respect to H_2

(b) 2 with respect to NO and 1 with respect to H_2

(c) 1 with respect to NO and 3 with respect to H_2

(d) 2 with respect to NO and 2 with respect to H_2

7. For a first order reaction A → products, the plot of $\ln\left(\frac{[A]_t}{[A]_0}\right)$ vs time, where $[A]_0$ and $[A]_t$ refer to concentration at time t = 0 and t respectively, is

(a) a straight line with a positive slope passing through origin

(b) a straight line with a negative slope passing through origin

(c) an exponential curve asymptotic to the time axis

(d) a curve asymptotoic to the $\ln\left(\frac{[A]_t}{[A]_0}\right)$ axis

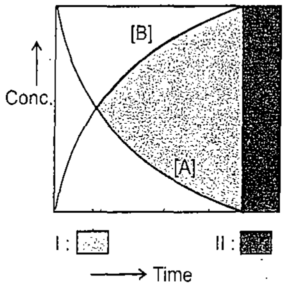
8. For the complex $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$\left(\frac{dx}{dt}\right) = 2 \times 10^7 \, L^2 \, mol^{-2} \, s^{-1} \, [Ag^+][NH_3]^2 - 1 \times 10^{-2} \, s^{-1} \, [Ag(NH_3)_2^+]$$

Hence, ratio of rate constants of the forward and backward reactions is :

(a) 2×10^7 L^2 mol^{-2} (b) 2×10^9 L^2 mol^{-2} (c) 1×10^{-2} L^2 mol^{-2} (d) 0.5×10^{-9} L^2 mol^{-2}

9. In the following graphical representation for the reaction A ⟶ B there are two types of regions:



(a) I and II both represent kinetic region at different interval

(b) I and II both represent equilibrium regions at different time interval

(c) I represents kinetic while II represents equilibrium region

(d) I represents equilibrium while II represents kinetic region

10. For the non-equilibrium process, A + B → products, the rate is first-order w.r.t. A and second-order w.r.t. B. If 1.0 mole each of A and B introduced into a 1.0 L vessel and the initial rate was 1.0×10^{-2} mol L^{-1} s^{-1}, rate when half reactants have been turned into products is :

(a) 1.25×10^{-3} mol L^{-1} s^{-1}
(b) 1.0×10^{-2} mol L^{-1} s^{-1}
(c) 2.50×10^{-3} mol L^{-1} s^{-1}
(d) 2.0×10^{-2} mol L^{-1} s^{-1}

11. The bromination of acetone that occurs in acid solution is represented by

$$CH_3COCH_3\,(aq) + Br_2\,(aq) \longrightarrow CH_3COCH_2Br\,(aq) + HBr\,(aq)$$

Given :

Initial concentrations			Initial Rate of Disapperance of Br_2 , Ms^{-1}
Br_2	$[CH_3COCH_3]$	M $[H^+]$	
0.050	0.30	0.050	5.7×10^{-5}
0.10	0.30	0.050	5.7×10^{-5}
0.10	0.30	0.10	1.2×10^{-4}
0.050	0.40	0.20	3.1×10^{-4}

Based on the above data , rate law is :

(a) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]\,[H^+]$
(b) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[H^+]$
(c) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]$
(d) $\left(\frac{dx}{dt}\right) = k\,[CH_3COCH_3]\,[Br_2]\,[H^+]^2$

12. The rate law for the dimerisation of NO_2 is

$$-\frac{d[NO_2]}{dt} = k\,[NO_2]^2$$

which of the following changes will change the value of the specific rate constant , k :

(a) Doubling the total pressure on the system
(b) Doubling the temperature
(c) Both of (a) and (b)
(d) None of the above

13. In the following reaction, how is the rate of appearance of the underlined product related to rate of disappearance of the underlined reactant :

$$BrO_3^-\,(aq) + 5\,\underline{Br^-}\,(aq) + 6\,H^+\,(aq) \longrightarrow 3\,\underline{Br_2}\,(\ell) + 3\,H_2O\,(\ell)$$

(a) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\,\frac{d[Br^-]}{dt}$
(b) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$
(c) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$
(d) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\,\frac{d[Br^-]}{dt}$

14. Imp The rate law for a reaction between the substances A and B is given by rate = $K[A]^n [B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as :

(a) $1/2^{m+n}$ (b) $(m + n)$ (c) $(n - m)$ (d) $2^{(n-m)}$

Comprehension (Q. 15-17)

Study the following experiment and answer the questions at the end of it.

The following reactions was studied at 25⁰C in benzene solution containing 0.10 M pyridine

$$\underset{A}{CH_3OH} + \underset{B}{(C_6H_5)_3CCl} \longrightarrow \underset{C}{(C_6H_5)_3C.OCH_3} + HCl$$

The following sets of data were observed : [c)

Set	Initial concentration		time difference	Final concentration [C]
	$[A]_0$	$[B]_0$		
I	0.10 M	0.05 M	25 min	0.0033 M
II	0.10 M	0.10 M	15 min	0.0039 M
III	0.20 M	0.10 M	7.5 min	0.0077 M

15. Rates $\frac{d[C]}{dt}$ in sets I, II and III are respectively (in M min^{-1}) :

	I	II	III
(a)	1.30×10^{-4}	2.6×10^{-4}	1.02×10^{-3}
(b)	0.033	0.0039	0.0077
(c)	0.02×10^{-4}	0.04×10^{-4}	0.017

(d) None of above

16. Rate law of the above experiment is :

(a) $r = k [A] [B]$ (b) $r = k [A]^2 [B]$ (c) $r = k [A] [B]^2$ (d) $r = k [A]^2 [B]^0$

Rate constant of the above experiment is :

(a) 1.3×10^{-1} (b) 2.6×10^{-2} (c) 2.6×10^{-1} (d) 1.3×10^{-2}

Comprehension (Q.18 - 19)

The thermal decomposition of N_2O_5 occurs as : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Experimental studies suggest that rate of decomposition of N_2O_5, rate of formation of NO_2 or rate of formation of O_2 all becomes double if concentration of N_2O_5 is doubled.

18. If rate constants for decomposition of N_2O_5, formation of NO_2 and formation of O_2 are K_1, K_2 and K_3 respectively, then :

nice ques (a) $K_1 = K_2 = K_3$ (b) $2K_1 = K_2 = 4K_3$ (c) $K_1 = 2K_2 = K_3$ (d) $K_1 = K_2 = 2K_3$

19. If rate of formation of O_2 is 16 g/hr, then rate of decomposition of N_2O_5 and rate of formation of NO_2 respectively is :

(a) can not be calculated without knowing rate constants

(b) 108 g/hr, 92 g/hr

(c) 32 g/hr, 64 g/hr (d) 54 g/hr, 46 g/hr concentration of substance at same temperature. Find out order of reaction.

(a) 1 (b) 2 (c) 0 (d) 3

21. Match order of the reaction (in List - I) with the unit of rate constant (in List-II) :

	List I (order)		List II (unit)
(A)	Zero	(p)	$L^2\ mol^{-2}\ s^{-1}$
(B)	First	(q)	$L\ mol^{-1}\ s^{-1}$
(C)	Second	(r)	$mol\ L^{-1}\ s^{-1}$
(D)	Third	(s)	s^{-1}

(a) A-r, B-s, C-q, D-p (b) A-r, B-q, C-s, D-p (c) A-s, B-r, C-q, D-p (d) A-s, B-r, C-p, D-q

22. For the reaction, $P + Q + R \rightarrow S$, experimental data for the measured initial rates is given below:

Expt.	Initial conc. P (M)	Initial conc. Q (M)	Initial conc. R (M)	Initial rate (m/s)
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0.4	1.28×10^{-3}
4	0.1	0.25	1.6	4.0×10^{-5}

The order of the reaction with respect to P, Q and R respectively, is

(a) 2, 2, 1 (b) 2, 1, 2 (c) 2, 1, 1 (d) 1, 1, 2

23. Rate = K[A][B]; If the volume of reaction vessel is suddenly reduced to ¼th of initial value. The new rate will be effected by:

(a) $\frac{1}{10}$ (b) $\frac{1}{8}$ (c) 8 (d) 16

24. The rate constant of a reaction does not depend upon:

(a) temperature (b) activation energy

(c) catalyst (d) concentration of reactants and products

25. The rate of reaction, $A + B \rightarrow$ Products, is given by the equation, $r = k[A][B]$. If B is taken in large excess, the order of reaction would be

(a) 2 (b) 1 (c) zero (d) unpredictable

26. In a reaction, $2A_2 + B_2 \rightarrow 2A_2B$, the reactant A will disappear at:

(a) half the rate that B will decrease (b) the same rate that B will decrease

(c) double the rate that A_2B will form (d) twice the rate that B will decrease

27. The rate of reaction that does not involve gases, is not dependent on:

(a) pressure (b) temperature (c) concentration (d) catalyst

2. Order

28. For the first order reaction $(C = C_0 e^{-k_1 t})$ and $T_{av} = k_1^{-1}$. After two average lives, concentration of the reactant is reduced to

(a) 25% (b) 75% (c) $\frac{100}{e}\%$ (d) $\frac{100}{e^2}\%$

29. Which is not true for a second order reduction?

(a) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}

(b) Its half-life is inversely proportional to its initial concentration

(c) Time to complete 75% reaction is twice of half-life

(d) $T_{50} = \frac{1}{k_a . A_0}$

$\frac{a_0}{2} \propto \frac{V_\infty - V_0}{2}$

$x \propto V_t - V_0$

as, here $x = \frac{a_0}{2}$

30. Acid hydrolysis of ester in first order reaction and rate constant is given by

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

where, V_0, V_t and V_∞ are the volume of standard NaOH required to neutralise acid present at a given time, if ester is 50% neutralized then

(a) $V_\infty = V_t$ (b) $V_\infty = (V_t - V_0)$ (c) $V_\infty = 2V_t - V_0$ (d) $V_\infty = 2V_t + V_0$

31. For the reaction, A(g) + 2B(g) → C(g) + D(g)

$$\frac{dx}{dt} = k[A][B]^2$$

Initial pressure of A and B are respectively 0.60 atm and 0.80 atm. At a time when pressure of C is 0.20 atm, rate of the reaction, relative to the initial value is

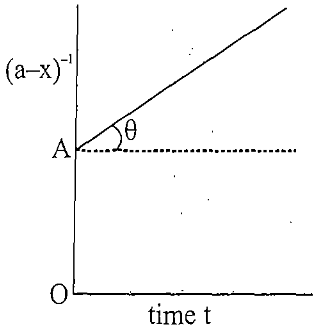
(a) $\frac{1}{6}$ (b) $\frac{1}{48}$ (c) $\frac{1}{4}$ (d) $\frac{1}{24}$

very

32. Following is the graph between $(a-x)^{-1}$ and time t for a second order reaction

$\theta = \tan^{-1}(0.5)$

OA = 2L mol^{-1}



Hence, rate at the start of the reaction is

(a) 1.25 mol^{-1} min^{-1} (b) 0.5 mol L^{-1} min^{-1}

(c) 0.125 mol L^{-1} min^{-1} (d) 1.25 mol L^{-1} min^{-1}

// 33. For the second order reaction, concentration (x) of the product at time t starting with initial concentration $[A]_0$ is

(a) $\frac{kt[A_0]^2}{1+kt[A_0]}$ (b) $\frac{k+[A_0]^2}{1+kt}$ (c) $\frac{1+kt[A_0]^2}{k+[A_0]^2}$ (d) None of these

34. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for the first order k_1 and zero order (k_0) of the reaction is

(a) 0.5 mol^{-1} dm^{-3} (b) 1.0 mol dm^{-3} (c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^3

35. The gas phase decomposition of NOBr is second order in [NOBr], with k = 0.810 M^{-1} s^{-1} at 10°C. We start with 4.00×10^{-3} M NOBr in a flask at 10°C. How many seconds does it take to use up 1.50×10^{-3} M NOBr?

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

Rate = $k[NOBr]^2$

(a) 92.6 s (b) 9.26 s (c) 926 s (d) 0.926 s

36. The following data were obtained for the decomposition of a compound at 580°C

a_0(mol dm^{-3})	0.50	1.10	2.48
$t_{1/2}$(s)	4280	885	174

The order of reaction and the rate constant are

(a) zero order, $k = 1.40 \times 10^{-3}$ dm^6 mol^{-2} s^{-1} (b) 1st order, $k = 3.36 \times 10^{-3}$ dm^6 mol^{-2} s^{-1}

(c) 2nd order, $k = 3.36 \times 10^{-3}$ dm^6 mol^{-2} s^{-1} (d) 3rd order, $k = 1.40 \times 10^{-3}$ dm^6 mol^{-2} s^{-1}

37. Inversion of sucrose is studied by measuring angle of rotation at any time t

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_3O^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

It is found that $(r_\infty - r_0) \propto a$ and $(r_\infty - r_t) \propto (a - x)$ where, r_0, r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively. From the following values calculate rate constant and the time at which solution is optically inactive

Time/Min.	0.0	46.0	∞
Rotation of polarized light/degree	24.1	10.0	−10.7

(a) $k = 0.011$ min^{-1}, t = 107.2 min (b) $k = 0.11$ min^{-1}, t = 107.2 min

(c) $k = 1.1 \times 10^2$ min^{-1}, t = 304 min (d) $k = 2.1 \times 10^2$ min^{-1}, t = 304 min

38. Which among the following plots are linear? (a − x) is the concentration of reactant remaining after time, t.

(a) (a − x) vs t, for a first order reaction (b) (a − x) vs t, for a zero order reaction

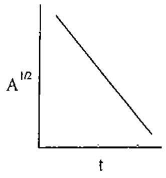
(c) (a − x) vs t, for a second order reaction (d) $\left(\frac{1}{a-x}\right)$ vs t, for a first order reaction

39. For the reaction A → B, the rate law expression is $-\frac{d[A]}{dt} = K[A]^{1/2}$

If initial concentration of A is A_0, then

(a) the integrated rate expression $k = \frac{2}{t}(A_0 - A)$

(b) the graph of $A^{1/2}$ vs t will be



(c) The half life period $t_{1/2} = \frac{K}{2[A_0]^{1/2}}$

(d) The time taken for 75% completion will be $t_{3/4} = \frac{K}{[A_0]}$

40. The time taken for 10% completion of a first order reaction is 20 mins. Then, for 19% completion, the reaction will take

(a) 40 min. (b) 60 min. (c) 30 min. (d) 50 min.

41. Ammonia and oxygen react at higher temperatures as

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O\ (l)$

In an experiment the concentration of NO increases by 1.08×10^{-2} moles litre^{-1} in 3 seconds. Which of the following is not correct.

(a) The rate of reaction is 9×10^{-4} moles litre^{-1} seconds^{-1}.

(b) The order of the reaction is 2.

(c) The rate of disappearance of NH_3 is 36×10^{-4} mol L^{-1} s^{-1}.

(d) The rate of appearance of H_2O is 54×10^{-4} mol L^{-1} s^{-1}.

42. If a reaction is of nth order the half life period .... of the initial concentration of reactants.

(a) is independent (b) varies inversely as (n – 1) th power

(c) varies inversely at nth power (d) varies directly as (n – 1) th power

43. The decomposition of gaseous acetaldehyde at T(K) follows second order kinetics. The half-life of this reaction is 400 s when the initial pressure is 250 Torr. What will be the rate constant (in Torr^{-1} s^{-1}) and half-life (in s) respectively, if the initial pressure of the acetaldehyde is 200 Torr at the same temperature?

(a) 10^5 and 500 (b) 10^{-5} and 400 (c) 10^{-4} and 400 (d) 10^{-5} and 500

44. The concentrations of a species A undergoing the reaction A → P is 1.0, 0.5, 0.33, 0.25 mol dm^{-3} at t = 0, 1, 2 and 3 seconds, respectively. The order of the reaction is

(a) two (b) one (c) zero (d) three

45. Select the correct statements out of I, II and III for zero order reaction

I : Quantity of the product formed is directly proportional to time

II : Larger the initial concentration of the reactant, greater the half-life period

III : If 50% reaction takes place in 100 minutes, 75% reaction take place in 150 minutes.

(a) I only (b) I and II only (c) II and III only (d) I, II and III

46. A reaction of first-order completed 90% in 90 minutes, hence, it is completed 50% in approximately

(a) 50 min (b) 54 min (c) 27 min (d) 62 min

47. T_{50} (Half-life period) of first-order reaction is 10 minute. Starting with 10 mol L^{-1}, rate after 20 minute is :

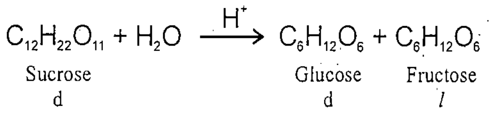
(a) 0.0693 mol L^{-1} min^{-1} (b) 0.0693 × 2.5 mol L^{-1} min^{-1}

(c) 0.0693 × 5 mol L^{-1} min^{-1} (d) 0.0693 × 10 mol L^{-1} min^{-1}

48. For the first-order reaction T_{av} (average life), T_{50} and T_{75} in the increasing order are :

(a) $T_{50} < T_{av} < T_{75}$ (b) $T_{50} < T_{75} < T_{av}$ (c) $T_{av} < T_{50} < T_{75}$ (d) $T_{av} = T_{50} < T_{75}$

49. Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first-order reaction and is studied by measuring angle of rotation at different instant of time



$$\underset{\substack{\text{Sucrose}\\ d}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\ d}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ l}}{C_6H_{12}O_6}$$

If $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = (a - x)$ (where r_0, r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively, then there is 50% inversion when :

(a) $r_0 = 2r_t - r_\infty$ (b) $r_0 = r_t - r_\infty$ (c) $r_0 = r_t - 2r_\infty$ (d) $r_0 = r_t + r_\infty$

50. If $\left(\frac{dx}{dt}\right) = k\,[H^+]^n$ and rate becomes 100 times when pH changes from 2 to 1. Hence, order is :

(a) 1 (b) 2 (c) 3 (d) 0

51. Consider following reaction,

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$$

Half–life period is independent of concentration of Zn at constant pH. At constant Zn concentration, half–life is 10 minutes at pH = 2 and half–life is 100 minutes at pH = 3. Hence , rate law is :

(a) $k\,[Zn][H^+]$ (b) $k\,[Zn][H^+]^2$ (c) $k\,[Zn]^0\,[H^+]$ (d) $k\,[Zn]^0\,[H^+]^2$

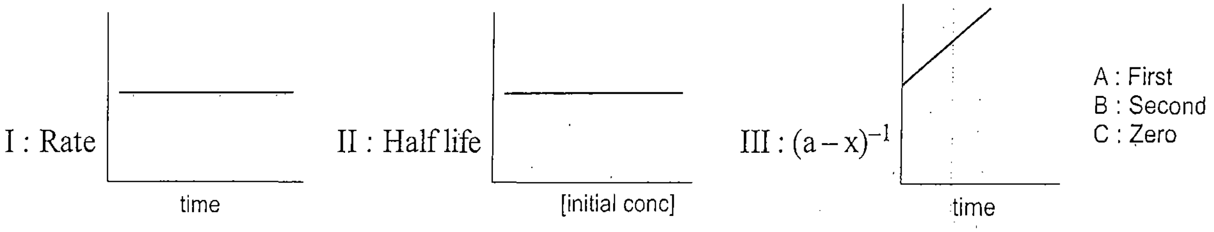
52. If the fermentation of sugar in an enzymatic solution that is 0.12 M , the concentration of the sugar is reduced to 0.06 M in 10 h and to 0.03 M in 20 h. What is the order of the reaction ?

(a) 1 (b) 2 (c) 3 (d) 0

53. Number of natural life times (T_{av}) required for a first-order reaction to achieve 99.9% level of completion is :

(a) 2.3 (b) 6.9 (c) 9.2 (d) 0.105

54. Match the graphical study with the order of the reactions :



	I	II	III		I	II	III
(a)	A	B	C	(b)	B	C	A
(c)	C	B	A	(d)	C	A	B

55. $3A \longrightarrow B + C$

It would be a zero order reaction when :

(a) the rate of reaction is proportional to square of concentration of A

(b) the rate of reaction remains same at any concentration of A

(c) the rate remains unchanged at any concentration of B and C

(d) the rate of reaction doubles if concentration of B is increased to double

Comprehension (Q. 56)

The thermal decomposition of N_2O_5 occurs as : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Experimental studies suggest that rate of decomposition of N_2O_5, rate of formation of NO_2 or rate of formation of O_2 all becomes double if concentration of N_2O_5 is doubled.

56. The container of 2 litre contains 4 mole of N_2O_5. On heating to 100°C, N_2O_5 undergoes complete dissociation to NO_2 and O_2. Select the correct answers if rate constant for decomposition of N_2O_5 is 6.2×10^{-4} sec^{-1}.

1. The mole ratio before and after dissociation is 4 : 2.
2. Half life of N_2O_5 is 1117 sec and it is independent of temperature.
3. Time required to complete 40% of reaction is 824 sec.
4. If volume of container is doubled, the rate of decomposition becomes half of the initial rate :

(a) 1, 3, 4 (b) 1, 2, 3, 4 (c) 3, 4 (d) 2, 3, 4

57. The value of the rate constant for the gas phase reaction, $2NO_2 + F_2 \rightarrow 2NO_2F$ is 38 $dm^3\ mol^{-1}\ s^{-1}$ at 300 K. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

58. A reaction follows second order rate law, $-\frac{d[A]}{dt} = k[A]^2$, if

(a) a plot of [A] versus t is a straight line (b) a plot of 1/[A] versus t is a straight line

(c) a plot of ln[A] versus t is a straight line (d) a plot of $e^{[A]}$ versus t is a straight line

59. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half-life of 28.4 min. The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is

(a) 56.8 min (b) 170.4 min (c) 85.2 min (d) 227.2 min

60. 1g of ^{90}Sr gets converted to 0.953 g after 2 yr. The half-life of ^{90}Sr, and the amount of ^{90}Sr remaining after 5 yr are

(a) 1.44 yr and 0.916 g (b) 57.6 yr and 0.75 g

(c) 28.8 yr and 0.887 g (d) 100 yr and 0.982 g

61. The half-life of a first order reaction varies with temperature according to

(a) $\ln t_{1/2} \propto 1/T$ (b) $\ln t_{1/2} \propto T$ (c) $t_{1/2} \propto 1/T^2$ (d) $t_{1/2} \propto T^2$

62. The half-life time for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200 s and 50 s respectively. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

63. Which one of the following statement is incorrect about order of reaction ?

(a) Order of reaction is determined experimentally

(b) Order of reaction is equal to sum of the power of concentration terms in differential rate law

(c) It is not affected with stoichiometric coefficient of the reactants

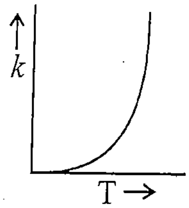
(d) Order cannot be fractional

64. Under the same reaction conditios, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_2}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is

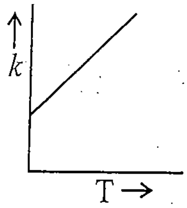
(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol dm^3 (c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^3

65. Plots showing the variation of the rate constant (k) with tempeature (T) are given below. The plot that follows Arrhenius equation is

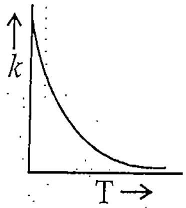
(a)



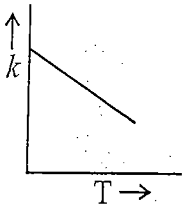
(b)



(c)



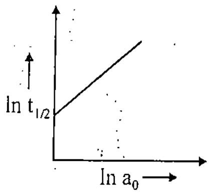
(d)



66. 75% of first order reaction was completed in 32 min. 50% of reaction was completed in

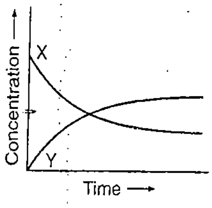
(a) 24 min. (b) 8 min. (c) 16 min. (d) 4 min.

67. The slope of the curve is +1. Predict the order of reaction



(a) 0 (b) 1 (c) 2 (d) 3

68. The curve depicts the change in concentration of species X and Y as a function of time. The point of intersection of the two curves represents:



(a) $t_{1/2}$ (b) $t_{3/4}$ (c) $t_{2/3}$ (d) data insufficient to predict

3. **Arrhenius + Theories**

69. At a certain temperature, the first order rate constant k_1 is found to be smaller than the second order rate constant k_2. If the $E_a(1)$ of the first order reaction is greater than $E_a(2)$ of the second order reaction, then as temperature is raised

Imp

(a) k_2 will increase faster than k_1

(b) k_1 will increase faster than k_2 but will always remain less than k_2

(c) k_1 will increase faster than k_2 and become equal to k_2

(d) k_1 will increase faster than k_2 and become greater than k_2

70. Rate constant k varies with temperature as given by equation

$$\log k(\text{min}^{-1}) = 5 - \frac{2000\text{K}}{T}$$

Consider the following about this equation

I. Pre-exponential factor is 10^5

II. E_a is 9.212 kcal

III. Variation of log k with $\frac{1}{T}$ is linear

Select the correct statement.

(a) I, II, III (b) I, III (c) II, III (d) I, II

71. The energies of activation for forward and reverse, reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lower the activation energy of both (forward and reverse) reaction by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1})

check

(a) – 300 (b) –120 (c) +280 (d) –20

72. In the temperature range of 250 K to 450 K, the pre-exponential factor, A, for the reaction. $Cl(g) + H_2(g) \rightarrow HCl(g) + H(g)$ is found to be equal to 1.20×10^{10} $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. If M(Cl) = 35.453 g mol^{-1}, $M[H_2] = 2.016$ g mol^{-1}, d(Cl) = 200 pm and $d[H_2] = 150$ pm, the value of the steric factor, P is

(a) 0.11 (b) 0.33 (c) 0.55 (d) 0.77

73. Select the incorrect statement

(a) Larger the value of E_a, smaller the value of rate constant (k).

(b) Larger the value of E_a, greater is the effect on the value of k for a given temperature change.

(c) At lower temper~~ature, increase~~ in temperature causes more change in the value of k than at higher temperature.

(d) k is affected by change in concentration.

74. The increase in rate of a reaction with rise in temperature is mainly due to

(a) increase in collision frequency (b) lowering of activation energy

(c) increase in number of effective collisions (d) increase in activation energy

75. The rate constant of a unimolecular reaction was $2.66 \times 10^{-3}\ s^{-1}$ and $2.2 \times 10^{-1}\ s^{-1}$ at T = 120 K and 360 K respectively. The rate constant (in s^{-1} units) at 240 K would be

(a) 2.4×10^{-2} (b) 2.4×10^{-1} (c) 4.8×10^{-2} (d) 1.8×10^{-3}

76. The rate law of rone of the mechanism of the pyrolysis of CH_3CHO at 520°C and 0.2 bar is

$$\text{Rate} = -\left| k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} \right| [CH_3CHO]^{3/2}$$

The overall activation energy E, in terms of the rate law is

(a) $E_a(2) + E_a(1) + 2E_a(4)$ (b) $E_a(2) + \frac{1}{2}E_a(1) - E_a(4)$

(c) $E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)$ (d) $E_a(2) - \frac{1}{2}E_a(1) + \frac{1}{2}E_a(4)$

77. The arrhenius parameters for the thermal decomposition of NOCl, $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$, are $A = 10^{13} M^{-1}\ s^{-1}$, $E_a = 105\ kJ\ mol^{-1}$ and $RT = 2.5\ kJ\ mol^{-1}$. The enthalpy (in $kJ\ mol^{-1}$) of the activated complex will be

(a) 110 (b) 105 (c) 102.5 (d) 100

78. In the Lindeman mechanism of unimolecualr reactions, the observed order at low concentration is

(a) 0.5 (b) 1 (c) 1.5 (d) 2

79. According to Arrhenius equation (K = rate constnat and T = temperature)

(a) ln K decreases linearly with 1/T (b) ln K decreases linearly with T

(c) ln K increases linearly with 1/T (d) ln K increases linearly with T

80. A first order gaseous reaction is 25% complete in 30 minutes at 227°C and in 10 minutes at 237°C. The activation energy of the reaction is closest to ($RT = 2\ cal\ K^{-1}\ mol^{-1}$)

(a) $27\ kcal\ mol^{-1}$ (b) $110\ kcal\ mol^{-1}$ (c) $55\ kcal\ mol^{-1}$ (d) $5.5\ kcal\ mol^{-1}$

81. A reaction $A + B + C \rightarrow D$ follows the mechanism

$A + B \rightleftharpoons AB$

$AB + C \rightarrow D$

in which first step remain essentially in equilibrium. If ΔH is the enthalpy change for the first reaction and E_0 is the activation energy for the second reaction, the activation energy ofthe overall reaction wil be given by

(a) E_0 (b) $E_0 - \Delta H$ (c) $E_0 + \Delta H$ (d) $E_0 + 2\Delta H$

82. Following are the values of E_a and ΔH for three reactions carried out at the same temperature :

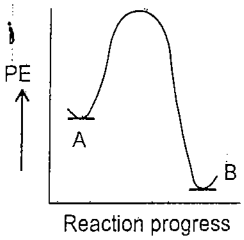
I : $E_a = 20\ kJ\ mol^{-1}$, $\Delta H = -60\ kJ\ mol^{-1}$ II : $E_a = 10\ kJ\ mol^{-1}$, $\Delta H = -20\ kJ\ mol^{-1}$

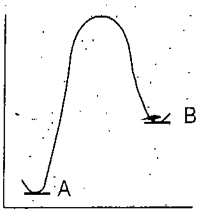
III: $E_a = 40\ kJ\ mol^{-1}$, $\Delta H = +15\ kJ\ mol^{-1}$

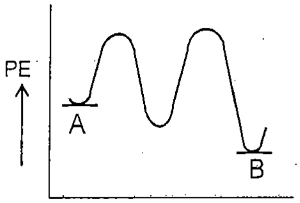
If all the three reaction have same frequency factor then fastest and slowest reactions are :

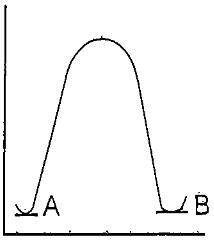
	Fastest	Slowest
(a)	I	II
(b)	II	III
(c)	I	III
(d)	can't be predicted.	

83. for a reaction $A \rightarrow B$, $E_a = 10\ kJ\ mol^{-1}$, $\Delta H = 5\ kJ\ mol^{-1}$. Thus, potential energy profile for this reaction is :

(a) 

(b) 

(c) 

(d) 

84. Milk turns sour at 40^0C three times as faster as 0^0C. Hence E_a in cal of process of turning of milk sour is :

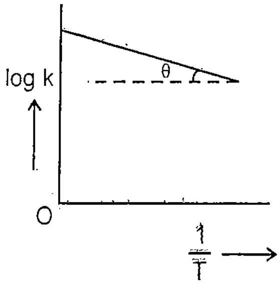
(a) $\frac{2.303 \times 2 \times 313 \times 273}{40} \log 3$

(b) $\frac{2.303 \times 2 \times 313 \times 273}{40} \log\left(\frac{1}{3}\right)$

(c) $\frac{2.303 \times 2 \times 40}{273 \times 313} \log 3$

(d) None of the above

85. Graph between log k and $\frac{1}{T}$ (k is rate constant in s^{-1} and T is the temperature in K) is a straight line. As shown in figure if OX = 5 and slope of the line $= -\frac{1}{2.303}$ then E_a is :



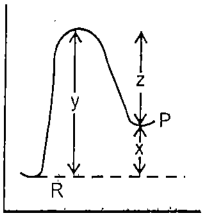
(a) 2.303×2 cal

(b) $\frac{2}{2.303}$ cal

(c) 2 cal

(d) None of these

86. The potential energy diagram for a reaction $R \longrightarrow P$ is given below :



ΔH^0 of the reaction corresponds to the energy –

(a) x (b) y (c) z (d) (x+y)

87. At room temperature, the reaction between NO and O_2 to give NO_2 is fast, while that between CO and O_2 is slow. It is due to :

(a) CO is smaller in size that of NO

(b) CO is poisonous

(c) The activation energy for the reaction, $2NO + O_2 \longrightarrow 2NO_2$ is less then $2CO + O_2 \longrightarrow 2CO_2$.

(d) None of the above

88. In gaseous reactions important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1}, then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is :

(a) 3 kJ mol^{-1} (b) 4 kJ mol^{-1} (c) 5 kJ mol^{-1} (d) 7 kJ mol^{-1}

Comprehension (Q. 89-90)

The instantaneous rate of an elementary chemical reaction : $aA + bB \rightleftharpoons cC + dD$ can be given by:

rate = $Kf[A]^a [B]^b - K_b [C]^c [D]^d$ where, K_f and K_b are rate constants for forward and backward reactions respectively for the reversible reaction. If the reaction is an irreversible one, the rate is expressed as : rate = $K[A]^a [B]^b$ and (a + b) is order of reaction. It is also evident from the stoichiometry of reaction that rate of disappearance of A is $\frac{a}{b}$ times the rate of disappearance of B.

$K = Ae^{-E_a/RT}$ whereas the ratio $\frac{K_f}{K_b}$ is expressed in terms of van't Hoff isochore :

$\frac{K_f}{K_b} = Ae^{-\Delta H/RT}$, where E_a and ΔH are energy of activation and heat of reaction respectively.

very nice

89. For a chemical reaction $aA \rightarrow bB$;

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3,$$

then the ratio of a and b is approximately :

(a) 3 (b) 0.3 (c) 2 (d) 0.5

90. The variation of K_{eq} (equilibrium constant) and $\frac{K_f}{K_b}$ with increase in temperature shows the following effects :

(i) For endothermic reaction, K increase, $\frac{K_f}{K_b}$ also increases

(ii) For endothermic reaction, K decreases, $\frac{K_f}{K_b}$ also decreases.

(iii) For exothermic reaction, K and $\frac{K_f}{K_b}$ both increases.

(iv) For exothermic reaction, K increases and $\frac{K_f}{K_b}$ decreases

(v) For exothermic reaction, K and $\frac{K_f}{K_b}$ both decreases.

(a) i, v (b) iii, v (c) ii, iii (d) ii, iii, v

91. The specific rate constant of decomposition of a compound is represented by

$$\ln k = 5.0 - \frac{12000}{T}$$

The activation energy of decomposition for this compound at 300 K is

(a) 24 kcal/mol (b) 12 kcal/mol (c) 24 cal/mol (d) 12 cal/mol

92. The rate constant of as reaction depends on

(a) temperature (b) initial concentration of the reactants

(c) time of reaction (d) extent of reaction

93. A catalyst is a substance which

(a) increases the equilibrium concentration of the product

(b) change the equilibrium constant of the reaction

(c) shortens the time to reach equilibrium

(d) supplies energy to the reaction

94. For a first order reaction A → P, the temperature (T) dependent rate constnat (k) was found to follow the equation :

$$\log k = \frac{2000}{T} + 6.0$$

The pre-exponential factor A and the activation energy E_a, respectively, are

(a) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1} (b) $6.0\ s^{-1}$ and 16.6 kJ mol^{-1}

(c) $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1} (d) $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

95. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ mol^{-1}, the Ea will be:

(a) $Ea < \Delta H$ (b) Zero (c) $Ea > \Delta H$ (d) $Ea = \Delta H$

96. If the rate of reaction grows 15.6 times on increasing the temperature by 30K; η = ? (temperature coefficient)

$\boxed{\frac{30}{10} = 3}$ Nice $\eta^3 = 15.6$ $\eta = ?$

(a) 2 (b) 2.5 (c) 3 (d) 3.5

97. Imp A reaction takes place in three steps; the rate constants are k_1, k_2 and k_3. The overall rate constant $k = \frac{k_1 k_3}{k_2}$. If energies of activation are 40, 30 and 20 kJ, the overall energy of activation is

(a) 10 (b) 15 (c) 30 (d) 60

98. Imp The activation energy for a hypothetical reaction A → Product is 12.49 kcal/mol. If temperature is raised from 295 to 305, the rate of reaction increases by:

(a) 60% (b) 100% (c) 50% (d) 20%

99. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to

(a) greater number of collisions (b) higher velocity of reacting molecules

(c) greater number of molecules having the activation energy

(d) decrease in the activation energy

100. The activation energy for a chemical reaction depends upon:

(a) temperature (b) nature of reacting species

(c) concentration of the reacting species (d) Collision frequency

101. $E_{Threshold}$ can never be:

(a) $> E_R$ (b) $> E_P$ (c) $< E_P$ (d) $> E_R$ as well as $> E_P$

4. Steady state + Enzyme kinetics

102. A hypothetical reaction, $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below,

$$A_2 \rightleftharpoons A + A \text{ (fast)}$$
$$A + B_2 \rightarrow AB + B \text{ (slow)}$$
$$A + B \rightarrow AB \text{ (fast)}$$

The order of the overall reaction is

(a) 2 (b) 1 (c) $1\frac{1}{2}$ (d) 0

103. For an enzyme catalyzed reaction, a Lineweaver-Burk plot gave the following data:

slope = 40 s

intercept = 4 (mol dm^{-3} s^{-1})$^{-1}$.

If the initial concentrations of enzyme is 2.5×10^{-9} mol dm^{-3}, what is the catalytic efficiency (in dm^{-3} mol^{-1} s^{-1}) of the reaction?

(a) 10^5 (b) 10^6 (c) 10^7 (d) 10^4

Imp

Equil

104. The overall rate of the following complex reaction,

$$2A \underset{}{\overset{K_1}{\rightleftharpoons}} A_2 \quad \text{(fast equilibrium)}$$
$$A + B \overset{K_2}{\rightleftharpoons} C \quad \text{(fast equilibrium)}$$
$$A_2 + C \xrightarrow{k_3} P + 2A \quad \text{(slow) would be}$$

K_1 ⇒ Equilibrium constants

Check..

(a) $K_1K_2k_3[A]^3[B]$ (b) $K_2K_1k_3[A][B]^3$ (c) $K_1K_2k_3[A][B]^2$ (d) $K_1K_2k_3[A][B]$

105. In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained is

$$\frac{v}{[E]_0[S]} = 1.4 \times 10^{12} - \frac{10^4\, v}{[E]_0}$$

The value of k_3 (k'_{exp}, mol L^{-1} s^{-1}) and K(Michaelis constant, mol L^{-1}), respectively are

(a) $1.4 \times 10^{12}, 10^4$ (b) $1.4 \times 10^8, 10^4$ (c) $1.4 \times 10^8, 10^{-4}$ (d) $1.4 \times 10^{12}, 10^{-4}$

106. The rate equation for the reaction $2AB + B_2 \rightarrow 2AB_2$ is given by

$$\text{rate} = k[AB][B_2]$$

A possible mechanism consistent with this rate law is

(a) $2AB + B_2 \xrightarrow{slow} 2AB_2$

(b) $AB + AB \rightleftharpoons A_2B_2$ (fast)
$A_2B + B_2 \xrightarrow{slow} 2AB_2$

(c) $AB + B_2 \xrightarrow{\text{slow}} AB_3$

$AB_3 + AB \xrightarrow{\text{fast}} 2AB_2$

(d) $AB + B_2 \rightleftharpoons AB_3$ (fast)

$AB_3 + AB \xrightarrow{\text{slow}} 2AB_2$

107. In radical chain polymerization, the quantity given by the rate of monomer depletion, divided by the rate of propagating radical formation is called

(a) kinetic chain length (b) propagation efficiency

(c) propagation rate constant (d) polymerization time

Eddie –
HO$fee plot

plot

Rs

Line - Burk

Rate

108. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)

$$2\,NO_2\,(g) + O_3\,(g) \longrightarrow N_2O_5\,(g) + O_2\,(g)$$

The reaction can take place by mechanism :

I : $NO_2 + O_3 \xrightarrow{\text{slow}} NO_3 + O_2$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O]$

$NO_2 + O \xrightarrow{\text{slow}} NO_3$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

Select correct mechanism.

(a) I only (b) II only (c) both I and II (d) None of I and II

109. Read the following industrial methods for the preparation of H_2SO_4 and answer the question at the end.

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions :

Proposal A : $H_2O\,(g) + SO_3\,(g) \longrightarrow H_2SO_4\,(g)$

Proposal B : $2\,H_2O\,(g) + SO_3\,(g) \longrightarrow H_2SO_4\,(g) + H_2O\,(g)$

Using simple collision theory, what reaction orders would be expected for proposal B ?

Proposal B is thought to proceed by the following two-step process :

$SO_3 + 2\,H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3.2\,H_2O$ (fast)

$SO_3.2\,H_2O \xrightarrow{k_2} H_2SO_4 + H_2O$ (slow)

($SO_3.2\,H_2O$ is a complex which is stabilized by hydrogen bonds and $k_2 << k_1$ or k_{-1}).

(a) $k\,[H_2O]\,[SO_3]$ (b) $k\,[H_2O]^2\,[SO_3]$ (c) $k\,[SO_3]$ (d) $k\,[H_2O]$

Comprehension (Q. 110 - 112)

Impo

Study the two photochemical reactions and answer the question at the end.

For the overall reaction between A and B to yield C and D , two mechanisms are proposed :

I. $A + B \longrightarrow AB^{*} \longrightarrow C + D$, $k_1' = 1 \times 10^{-5}\ M^{-1}\ s^{-1}$

II. $A \longrightarrow A^{*} \longrightarrow E$, $k_1 = 1 \times 10^{-4}\ s^{-1}$

$E + B \longrightarrow C + D$, $k_2 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$

(species with * are short-lived)

110. Rate according to mechanism I when concentration of each reactant is 0.1 M will be:
(a) $1 \times 10^{-7}\ Ms^{-1}$ (b) $1 \times 10^{-6}\ Ms^{-1}$ (c) $1 \times 10^{-5}\ Ms^{-1}$ (d) $1 \times 10^{-4}\ Ms^{-1}$

111. Rate according to mechanism II when concentration of each reactant is 1 M will be:
(a) $1 \times 10^{-4}\ Ms^{-1}$ (b) $1 \times 10^{10}\ Ms^{-1}$ (c) $1 \times 10^{-6}\ Ms^{-1}$ (d) $1 \times 10^{-10}\ Ms^{-1}$

112. At what concentration of B, rates of two mechanism are equal :
(a) 1 M (b) 5 M (c) 7 M (d) 10 M

Statement for Linked Answer Questions 113 and 114

The decomposition of ozone to oxygen,

$$2O_3(g) \rightarrow 3O_2(g)$$

occurs by the mechanism

(i) $M(g) + O_3(g) \xrightarrow{k_1} O_2(g) + O(g) + M(g),\ E_{a_1}$

(ii) $O_2(g) + O(g) + M(g) \xrightarrow{k_2} M(g) + O_3(g),\ E_{a_2}$

(iii) $O(g) + O_3(g) \xrightarrow{k_3} 2O_2(g),\ E_{a_3}$

where, M is the catalyst molecule.

k' are rate constants and E_{a_1} is the activation energy for the elementary step.

113. Under the steady state approximation for the intermediates, the rate of decomposition of ozone, $-\frac{d[O_3]}{dt}$, is

Refer Atkin Ques. from Rxn mechanism

(a) $\frac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M]+k_3[O_3]}$ (b) $\frac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M]-k_3[O_3]}$

(c) $\frac{2k_2k_3[O_3][M]}{k_2[O_2][M]+k_3[O_3]}$ (d) $\frac{2k_1k_2[O_3]^2[M]}{k_2[O_2][M]-k_3[O_3]}$

114. Assuming $k_3[O_3] >> k_2[O_2][M]$, the activation energy of the overall reaction is
(a) $\frac{E_{a_1}E_{a_3}}{E_{a_2}}$ (b) $E_{a_3} + E_{a_1} - E_{a_2}$ (c) E_{a_2} (d) E_{a_1}

115. For the reaction, $2X_3 \rightleftharpoons 3X_2$ the rate of formation of X_2 is

(a) $3(-d[X_3]/dt)$ (b) $\frac{1}{2}(-d[X_3]/dt)$ (c) $\frac{1}{3}(-d[X_3]/dt)$ (d) $\frac{3}{2}(-d[X_3]/dt)$

116. In a homogeneous catalytic reaction, 1.0 M of a substrate band 1.0 μM of a catalyst yields 1.0 mM of a product in 10s. The turnover frequency (TOF) of the reaction (s^{-1}) is

(a) 10^{-2} (b) 10^{2} (c) 10^{-3} (d) 10^{3}

117. The reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ proceeds via the following steps:

Good

$$NO + NO \xrightarrow{k_a} N_2O_2$$

$$N_2O_2 \xrightarrow{k_{a'}} NO + NO$$

$$N_2O_2 + O_2 \xrightarrow{k_b} NO_2 + NO_2$$

The rate of this reaction is equal to

(a) $2k_b[NO][O_2]$ (b) $(2K_ak_b[NO]^2[O_2])/(K_a + k_b[O_2])$

(c) $k_b \cdot K[NO]^2[O_2]$ (d) $K_a[NO]^2[O_2]$

118. H_2 and Br_2 react to give HBr by the following steps

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M(\text{fast}) \left(\frac{k_1}{k_{-1}} = K\right)$$

$$Br + H_2 \xrightarrow{k_2} HBr + H(\text{slow})$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br(\text{fast})$$

The probable rate law for the above sequence is

(a) Rate $= k_2(K)^{1/2}[H_2][Br_2]^{1/2}$ (b) Rate $= k_2[H_2][Br_2]$

(c) Rate $= k_2(k_1)^{1/2}[H_2][Br_2]^{1/2}$ (d) Rate $= k_2(K)[H_2]^{1/2}[Br_2]^{1/2}$

119. Nitramide O_2NNH_2 decomposes slowly in aqueous solution according to the reaction:

$$O_2NNH_2 \longrightarrow N_2O + H_2O$$

The experimental rate law is:

$$\frac{d[N_2O]}{dt} = K\frac{[O_2NNH_2]}{[H^+]}$$

Which of the following mechanisms seems most appropriate?

(a) $O_2NNH_2 \xrightarrow{k_1} N_2O + H_2O$ (slow)

(b) $O_2NNH_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH_3^+$ (fast equilibrium)

$O_2NNH_3^+ \xrightarrow{k_2} N_2O + H_3O^+$ (slow)

(c) $O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$ (fast equilibrium)

$O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$ (slow)

$H^+ + OH^- \xrightarrow{k_3} H_2O$ (fast)

(d) Both (b) and (c)

A reaction $A \to B$, involves following mechanism:

I: $A \xrightarrow{k_1} B$ (fast) II: $B \xrightarrow{k_2} C$ (slow)

III. $C \xrightarrow{k_3} D$ (fast)

The rate law of the reaction may be given as:

(a) Rate = $k_1[A]$ (b) Rate = $k_2[B]$ (c) Rate = $k_3[C]$ (d) Rate = $k_1k_2k_3[B][C]$

121. The mechanism of the reaction:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \text{ is:}$$

I. $2NO + H_2 \xrightarrow{\text{slow}} N_2 + H_2O_2$ II. $H_2O_2 + H_2 \xrightarrow{\text{fast}} 2H_2O$

(a) Rate = $k[NO]^2 [H_2]^2$ (b) Rate = $k[H_2O_2][H_2]$

(c) On doubling the conc. of H_2, keeping the conc. of NO constant, the rate will become double.

(d) If the initial conc. of H_2 and NO is Co and after time 't', the conc. of N_2 is x, then rate= $k[Co-2x]^x$.

122. Consider the reaction:

$Cl_2(aq) + H_2S \longrightarrow S(s) + 2H^+(aq.) + 2Cl^-(aq)$

The rate equation for this reaction is

Rate = $k[Cl_2][H_2S]$

Which of these mechanism is/are consistent with this rate equation?

A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^\ominus + Cl^\oplus + HS^-$ (slow)

$Cl^\oplus + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast)

$Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(a) Neither A nor B (b) A only (c) B only (d) Both A and B.

5. Complex Mech

123. For the following sequential reaction,

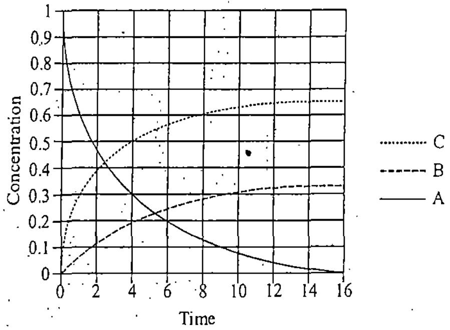
$$A \xrightarrow{k_A} B \xrightarrow{k_B} C$$

$$k_A = 2k_B = 0.1 s^{-1}$$

Time at which [B] is maximum is

(a) 13.9 s (b) 10 s (c) 6.0 s (d) 16.7 s

124. Graphed at right are concentration [A], [B] and [C] from one of the mechanisms below, $k_1 l = 0.1$, $k_2 = 0.2$. Which mechanism matches the graph? ($k_2 > k_1$)



(a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(b) $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C$

(c) $A \xrightarrow{k_1} B,\ A \xrightarrow{k_2} C$

(d) $A \xrightarrow{k_1} B \underset{k_1}{\overset{k_2}{\rightleftharpoons}} C$

125. Observe the following statements

(I) In the H_2—O_2 reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.

(II) The order of the reaction, $nA \rightarrow$ products, is 2.5. For this reaction, $t_{1/2} \propto [A]_0^{-3/2}$

(III) Unimolecular gas phase reactiosn are second order at low pressure but becomes first order at high pressure. (Linaemann mechanism)

Which of the following is correct

(a) I, II and III are correct
(b) Only II is correct
(c) Only III is correct
(d) I and II are correct

126. In the mechanism of reaction, $H_2 + Br_2 \rightarrow 2Br$, the first step is

(a) dissocaition of H_2 into H· radicals
(b) dissociatio of Br_2 into Br· radicals
(c) reaction of H· radical with Br_2
(d) reaction of Br· radical with H_2

127. Examine the following first order consecutive reactions. The rate constant (in s^{-1} units) for each step is given above the arrow mark. The following cases in which the species Q can act as a transient species is/are :

(1) $P \xrightarrow{10^5} Q \xrightarrow{10^8} R$
(2) $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$
(3) $P \xrightarrow{10^7} Q \xrightarrow{10^7} R$
(4) $P \xrightarrow{10^2} Q \xrightarrow{10^6} R$

(a) (2)
(b) (3)
(c) both (2) and (3)
(d) both (1) and (4)

128. In the Lineweaver-Burk plot of (initial rate)$^{-1}$ vs. (initial substrate concentration)$^{-1}$ for an enzyme catalyzed reaction following Michaelis-Menten mechanism, the y-intercept is 5000 M^{-1} s. If the initial enzyme concentration is 1×10^{-9} M, the turnover number is

(a) 2.5×10^3
(b) 1.0×10^4
(c) 2.5×10^4
(d) 2.0×10^5

129. For an enzyme-substrate reaction, a plot between $\frac{1}{v}$ and $\frac{1}{[S]_0}$ yields a slope of 40s. If the enzyme concentration is 2.5 μM, then the catalytic efficiency of the enzyme is

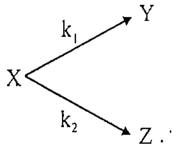
(a) 40 $Lmol^{-1}\ s^{-1}$ (b) 10^{-4} $Lmol^{-1}\ s^{-1}$ (c) 10^{7} $Lmol^{-1}\ s^{-1}$ (d) 10^{4} $Lmol^{-1}\ s^{-1}$

130. Which of the following reaction in the formation of HCl from hydrogen and chlorine would be a chain terminating step?

(a) $Cl + H_2 \rightarrow HCl + H\cdot$ (b) $H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$

(c) $H\cdot + \cdot H \rightarrow H_2$ (d) $Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot$

131. For the reaction shown below



the value of k_1 is $1 \times 10^{-4}\ s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given time during the course of the reaction is found to be $\frac{[Y]}{[Z]} = \frac{1}{4}$. The value of k_2 is

(a) $1 \times 10^{-4}\ s^{-1}$ (b) $2.5 \times 10^{-5}\ s^{-1}$ (c) $4 \times 10^{-4}\ s^{-1}$ (d) $3.5 \times 10^{-4}\ s^{-1}$

132. In a consecutive first order reaction,
(where k_1 and k_2 are the respective rate contants) species B has transient existence. Therefore,

(a) $k_1 = k_2$ (b) $k_1 = 2k_2$ (c) $k_1 >> k_2$ (d) $k_1 << k_2$

133. A reaction proceeds though the formation of an intermediate B in a unimolecular reaction

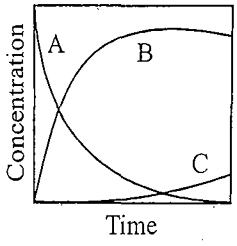
$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

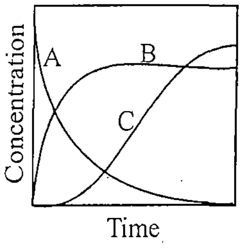
The integrated rate law for this reaction is

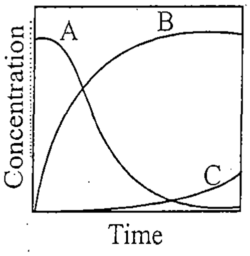
(a) $[A] = [A]_0 e^{-k_a t}$ (b) $[A] = [A]_0 (e^{-k_a t} - e^{-k_b t})$

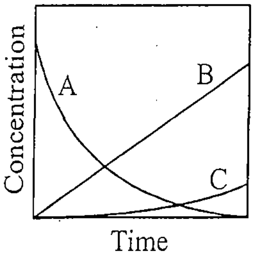
(c) $[A] = \frac{[A]_0}{2}\left(1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_a - k_b}\right)$ (d) $[A] = [A]_0 (1 + e^{-k_a t} - e^{-k_b t})$

134. If $k_a >> k_b$, then concentration versus time plot for the reaction is

(a)


(b)


(c)


(d)


PHOTOCHEMISTRY

6. Jablonskii Diagram

135. High quantum yields of photochemical reactions are due to

(a) lowering of activation energy (b) high frequency of collision

(c) accompanying side reaction (d) formation of free radicals

136. Consider the following processes in the photochemical delay of an excited molecule

I. Fluorescence   II. Quenching   III. Phosphorescence

Which of these processes are radiative?

(a) I and III   (b) I and II   (c) II and III   (d) I, II and III

137. The term used to define the phenomenon of emission of light in a chemical reaction is

(a) chemical luminescence   (b) photosensitisation

(c) both a and b   (d) None of these

138. The phenomenon of fluorescence and phosphorescence are best explained with the help of the

(a) Potential energy diagram   (b) Jablonski diagram

(c) Both a and b   (d) None of them

139. For which one of the following process is intersystem crossing (ISC) essential?

(a) Fluorescence   (b) Phosphorescence   (c) Chemiluminescence   (d) Radioactive decay

140. The light radiations of the visible ultraviolet regions lying between - wavelength are chiefly concerned in bringing about photochemical reactions.

(a) 1000 Å and 2000 Å   (b) 1500 Å and 1000 Å

(c) 8000 Å and 2000 Å   (d) 19000 Å and 12,000 Å

141. Which of the following instruments is used to measure the energy of the monochromatic radiation most accurately?

(a) Photoelectric cell   (b) Thermopile

(c) The potential detector   (d) The chemical actinometer

142. Match List I with list II and choose the correct answer using the codes given below:

List I		List II
(A) Primary absorption	1.	$S + h\nu \rightarrow S^*$
(B) Fluorescence	2.	$S^* \rightarrow S + h\nu$
(C) Intersystem crossing	3.	$S^* \rightarrow T^*$

Codes:

	A	B	C		A	B	C
(a)	1	2	3	(b)	2	3	1
(c)	1	3	2	(d)	1	2	3

143. Match the list I with list II and choose the correct answer using the codes given below

List I		List II
(A) Phosphorescence	1.	$T^* \rightarrow S + h\nu$
(B) Internal conversion	2.	$S^* \rightarrow S$
(C) Collision-induced emission	3.	$S^* + M \rightarrow S + M + h\nu$
(D) Excited state absorption	4.	$S^* + h\nu \rightarrow S^*$

A - 1
B → 2
D → 4
C - 3

Codes:

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	4	3	1	2	(d)	3	4	1	2

144. Match list I with list II and choose the correct answer using the codes given below:

List I		List II
(A) Singlet - Singlet	1.	$S^* + S \rightarrow S + S^*$
(B) Triplet - Triplet	2.	$T^* + T \rightarrow T + T^*$
(C) Phosphorescence	3.	$T^* \rightarrow S + h\nu$
(D) Collision deactivation	4.	$S^* + M \rightarrow S + M$

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	2	1	3	4
(c)	4	3	2	1	(d)	3	4	2	1

145. Which of the following is secondary effect?
(a) Fluorecence (b) Phosphorescence (c) Both a and b (d) None of these

146. Which of the following is not secondary effect
(a) Excitation of molecules (b) Rise in temperature
(c) Fluorescence (d) Phosphorescence

147. Which of the following photochemical reactions does an excited atom undergo?
(a) Emission of resonance radiations (b) Fluorescence
(c) Collision with other molecules (d) All of the above

148. Which type of electronic transition can be seen in saturated aldehyde and ketones?
(a) $\sigma \rightarrow \sigma^*$ (b) $n \rightarrow \sigma^*$
(c) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (d) Only $\pi \rightarrow \pi^*$

149. Which of the following decay with the change in multiplicity known as ISC?
(a) $S_1 \rightarrow S_0$ (b) $S_2 \rightarrow S_1$ (c) $T_2 \rightarrow T_1$ (d) $S_1 \rightarrow T_1$

150. In flourescence, which one of the following decay of excited state takes place?
(a) $S_1 \rightarrow S_0$ (b) $T_1 \rightarrow S_0$ (c) $T_2 \rightarrow T_1$ (d) $S_0 \rightarrow S_1$

151. Which one of the following excited state has a long life?
(a) S_1 (b) S_2 (c) T_1 (d) T_2

152. Which one of the following decay takes place in phosphorescene?
(a) $S_1 \rightarrow S_0$ (b) $T_1 \rightarrow S_0$ (c) $T_2 \rightarrow T_1$ (d) $T_2 \rightarrow S_1$

153. How many types of electronic transition are taking place in visible and UV regions?
(a) 1 (b) 2 (c) 3 (d) 4

154. Consider the following statements:

(I) In aldehyde both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition can be possible

(II) The order of energy required for various electronic transition is $\sigma \rightarrow \sigma^* > n \rightarrow \pi^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^*$.

(III) In fluorescene, $S_1 \rightarrow S_0$ decay of excited state takes place.

Select the correct statement:

(a) I, II (b) I, II, III (c) I, III (d) II, III

155. Match:

(A) $S_1 \rightarrow S_0 + h\nu$ (1) IC
(B) $S_1 \rightarrow S_0$ (2) Phosphorescence
(C) $S_1 \rightarrow T_1$ (3) Flourescence
(D) $T_1 \rightarrow S_0 + h\nu$ (4) ISC

A → 3
B → 1

Codes:

	A	B	C	D
(a)	2	1	4	3
(b)	3	1	4	2
(c)	2	4	1	3
(d)	3	4	1	2

156. The free energy change in a photochemical reaction is

(a) Always zero (b) Always –ve

(c) Always +ve (d) may be positive or negative

7. Lambert Beer's Law and Quantum yield

157. The molar extinction coefficeint of B (MW = 180) is 4×10^3 lit mol^{-1} cm^{-1}. One liter solution of C which contains 0.1358 g pharmaceutical preparatio of B, shows an absorbance of 0.411 in a 1 cm quartz cell. The percentage (w/w) of B in the pharmaceutical preparation is :

(a) 10.20 (b) 14.60 (c) 20.40 (d) 29.12

158. Appropriate reasons for the deviation form the Beer's law among the following are

(a) Monochromativity of light (b) Very high concentration of analyte

(c) Association of analyte (d) Dissocaition of analyte

(a) A, B and D (b) B, C and D (c) A, C and D (d) A, B and C

159. A 0.1 M solution of compound A shows 50% transmittance when a cell of 1 cm width is used at λ_1 nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at λ_1 nm.

What will be the transmittance of a solution that is simultaneously 0.1 M in A and 0.1 M in B using the same cell and at the same wave length ?

[log 20 = 1.301; log 30 = 1.4771; log 50 = 1.699]

(a) 33.3% (b) 50% (c) 66.7% (d) 70%

Transmittance is multiplicative property.

160. Which of the following will result in deviation from Beer's law :

(A) Change in refractive index of medium (B) Dissociation of analyte on dilution

(C) Polychromatic light (D) Path length of cuvette

(a) A, B and C (b) B, C and D (c) A, C and D (d) A, B and D

161. A 10 cm long cell filled with 0.002 M $KMnO_4$ solution absorbs 20% of incident light. The concentration of $KMnO_4$ solution absorbing 80% of incident light is equal to

(a) 0.0144 M (b) 0.0288 M (c) 0.0432 M (d) 0.0576 M

162. Consider the following statements:

I. Photosynthesis in plants proceeds with an increase in energy

II. Quantum yield is defined as the number of moles reacted or formed per Eintein of light absorbed.

III. Phosphorescence occurs from the lowest vibrational level of triplet state (T_1).

Which of the following statements are correct?

(a) I, II and III (b) II and III (c) I and III (d) I and II

163. Given that Planck' constant = 6.6×10^{-27} erg sec, velocity of light = 3×10^{10} cm/s; the energy of photon of wavelength 3000 Å will be

(a) 6.6×10^{-12} erg (b) 13.2×10^{-12} erg (c) 4.95×10^{-12} erg (d) 3.3×10^{-12} erg

164. The quantum efficiency of a photochemical reaction is defined as

(a) ratio of molecules decomposed in a given time to the number of quanta aborbed in the same time.

(b) number of molecules decompoed in a given time

(c) number of quanta absorbed percent time

(d) ratio of molecules decomposed in a given time to the number of quanta emitted in the same time

165. A substance absorbs 2.0×10^{16} quanta of radiations per second and 0.002 mole of it reacts in 1200 seconds. The quantum yield of the reaction ($N = 6.02 \times 10^{23}$) is

(a) 50 (b) 40 (c) 80 (d) 100

166. According to Lambert-Beer Law

(a) $\ln I = \ln I_0 + Kbc$ (b) $\ln I = \ln I_0 + Kb$ (c) $\ln I = \ln I_0 - Kbc$ (d) None of these

167. Reactions in which molecules absorbing light do not themselves react but induce other molecules to react are called

(a) Free radical reactions (b) Chain reactions

(c) Reversible reactions (d) Photosensitized reactions

168. Which of the following statements is incorrect

(a) Fluorescence is the process of an excited state returning to the ground state of the same multiplicity with the emission of light.

(b) The lower the wavelength of light the greater is the value of einstein corresponding to it.

(c) Reactions in which the molecules absorbing light do not react themselves but can induce other molecules to react are called chain reactions

(d) Quantum yield is the ratio of the number of moles consumed in a process and the number of einstein absorbed by it.

169. The quantum yield of photochemical combination of hydrogen and chlorine is decreased by certain substance called

(a) Photoinhibitors (b) Inhibitors (c) Negative catalysis (d) None of these

170. For a photochemical reaction, the numerical value of einstein varies

(a) Directly as the wave length of the light absorbed

(b) Inversely as the wave length of the light absorbed

(c) Directly as the square of the wave length of the light absorbed.

(d) Inversely as the square of the wave length of the light absorbed.

171. Consider the following statements:

I. According to Einstein law of photochemical Equivalence, each molecule which takes part in a photochemical reaction absorbs only one quantum of radiation.

II. Absorption of a photon by a molecule always leads to a chemical reaction

III. Delayed fluorescence is phosphorescence

Which of the above statement are correct

(a) I and III (b) I and II (c) II and III (d) I, II and III

172. The mechanism for photochemical decomposition of HI into H_2 and I_2 is

1. $HI + h\nu \rightarrow H\cdot + I\cdot$ 2. $H\cdot + HI \rightarrow H_2 + I\cdot$ 3. $I\cdot + I\cdot \rightarrow I_2$

What is the overall quantum yield of the reaction?

(a) 0.5 (b) 1 (c) 2 (d) 4

173. Consider the following photochemical reactions:

$H_2 + Cl_2 \xrightarrow[4000\text{Å}]{h\nu} 2HCl$ $H_2 + Br_2 \xrightarrow[5100\text{Å}]{h\nu} 2HBr$

These reactions are examples of which of the following?

(a) Reactions of low and high quantum yields respectively

(b) Reactions of high and low quantum yields respectively

(c) Reactions with quantum yields equal to one

(d) Reactions with equal quantum yields but not equal to one

174. Match List I (scientist) with list II (contribution) and select the correct answer:

List I		List II
(A) Michaelis menten	1.	Effect of temperature on the reaction rate
(B) Arrhenius	2.	Enzyme catalyst
(C) Erying	3.	Photochemical reactions
(D) Einstein	4.	Transition state theory

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	4	3	2	1
(c)	2	1	4	3
(d)	4	3	1	2

Eadie-Hofstee diagram → (~~Woolf~~ is graphical representation of enzyme kinetics in which reaction rate is ploted as a function of ratio b/w rate & substrate conc.

$$\nu = -K_m \frac{\nu}{[S]} + V_{max}$$

* Derived from Michaelis menton eq.

$$v = \frac{V_{max}[S]}{K_m + [S]}$$ → Invert & multiply by V_{max}, the rearrange to get the above eq.

175. In the primary photochemical process each molecule is activated by the absorption of one quantum of radiation (one proton). This is called as

(a) Beer's law
(b) Lambert's law
(c) Grotthus - Draper law
(d) Stark - Eintein law

176. Match list I with list II and choose the correct answer using the codes given below the list:

List I (Reaction)		List II (Quantum yield)
(A) $H_2 + Cl_2 \rightarrow 2HCl$	1.	$10^4 - 10^6$
(B) $H_2 + Br_2 \rightarrow 2HBr$	2.	0.01
(C) $2HI \rightarrow H_2 + I_2$	3.	2
(D) $2NH_3 \rightarrow N_2 + 3H_2$	4.	0.2

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	3	4	2	1	(d)	4	3	1	2

177. Which of the following is secondary effect

(a) Photosensitization reaction
(b) Delayed photochemical changes
(c) Rise in temperature
(d) All of the above

178. Which of the following reactions represents the rate of reaction for decomposition of HI?

(a) $-\frac{d[HI]}{dt} = 2I_{abs}$ (b) $-\frac{d[HI]}{dt} = 3Iabs$ (c) $-\frac{d[HI]}{dt} = Iabs$ (d) $-\frac{d[HI]}{dt} = 4Iabs$

179. Only the light that is absorbed by a substance is effective in producing a photochemical change. This is called as the

(a) Beer's law (b) Lambert's law (c) Grotths-Draper law (d) Both a and b

180. Equal fractions of the incident light radiations are absorbed by equal change in concentration of absorbing substance in a path of constant length. This is called as the

(a) Lambert's law (b) Beer's law (c) Stark's law (d) None of the above

181. If the quantum yield of a photochemical reaction is unity, then________ process is taking place

(a) Only secondary (b) only primary (c) only tertiary (d) both a and b

182. The fluorescence life time of a molecule in solution in 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is

(a) $1 \times 10^9 s^{-1}$ (b) $1 \times 10^8 s^{-1}$ (c) $1 \times 10^7 s^{-1}$ (d) $9 \times 10^7 s^{-1}$

183. If a photochemical reaction has higher Quantum yield than unity, it indicates

(a) Reversible reaction
(b) Elementary reaction
(c) Chain reaction
(d) None

PBr_5 PBr_4 PBr_5

184. Which one of the following statement is false for a photosensitizer as a donor?

(a) It must have sufficient life time

(b) Able to transfer it's energy to acceptor molecule.

(c) Transfer of energy reaction has higher energy than acceptor

(d) Acceptor has higher energy than donor

PBr_4 Br

$PCl_4^+ + P$

PI_5

PI_3

EXERCISE - II

One or More Than One Correct Type

1. Which of the following statements are correct about half–period.

(a) It is proportional to initial concentration for zero order

(b) Average life = 1.44 half–life for first order reaction.

(c) Time of 75% completion of reaction is thrice of half–life(initial half life) period in second order reaction

(d) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}

2. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half–life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence,

(a) $\frac{dx}{dt} = k[Zn]^0[H^+]^2$

(b) $\left(\frac{dx}{dt}\right) = k[Zn][H^+]^2$

(c) rate is not affected if concentration of zinc is made four times and that of H^+ ion is halved

(d) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration

3. Rate constant k varies with temperature by equation, $\log k(min^{-1}) = 5 - \frac{2000}{T(K)}$. We can conclude:

(a) pre–exponential factor A is 5

(b) E_a is 2000 kcal

(c) pre–exponential factor A is 10^5.

(d) E_a is 9.212 kcal

4. Activation energy of a chemical reaction can be determined by :

(a) evaluating rate constant at standard temperature → as Arhenius constant involved

(b) evaluating velocities of reaction at two different temperatures

(c) evaluating rate constant at two different temperatures

(d) changing concentration of reactants

5. Which of the following statements are correct ?

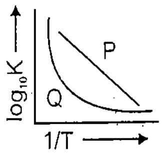
(a) Law of mass action and rate law expressions are same for single step reactions.

(b) Order of the slowest elementary reaction of a complex reaction gives the order of the complex reaction

(c) Both order and molecularity have normally a maximum value of 3

(d) Molecularity of a complex reaction, $A + 2B \longrightarrow C$ is 3.

6. Which of the following statement are true regarding the log K vs. 1/T plot shown in the given diagram ?



$K = Ae^{-E_a/RT}$

(a) Plot P shows that the energy of activation is independent of temperature.

(b) Plot Q describes the behaviour of temperature dependence of energy of activation

(c) Arrhenius behaviour is described by P

(d) The slope of curve P gives the value $-\frac{E_a}{R}$ & Intercept of (P) makes Arrhenius Behaviour

7. If the rate of reaction, $2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3(g)$ is given by :

$$\text{Rate} = K\frac{[SO_2]}{[SO_3]^{1/2}}$$

which statements are correct :

(a) The overall order of reaction is –1/2

(b) The overall order of reaction is +1/2

(c) The reaction slows down as the product SO_3 is build up

(d) The rate of reaction does not depend upon concentration of SO_3 formed

8. For a second order reaction plots are made for $\frac{1}{[A]}$ vs time for the reaction, 2A ⟶ Product. Pick up the correct sentences.

(a) the graph will show straight line with slope 2K

(b) the graph will show straight line with intercept $[A]_0$

(c) the graph will show straight line with slope $[A]_0$

(d) the graph will show straight line with intercept $\frac{1}{[A]_0}$

9. Which is true for a second order reaction ?

(a) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}

(b) Its half-life is inversely proportional to its initial concentration

(c) Time to complete 75% reaction is twice of half-life

(d) $T_{50} = \frac{1}{K \times \text{Initial conc.}}$

10. Which of the following statements are correct

(a) A plot of log Kp vs $\frac{1}{T}$ is linear.

(b) A plot of log [X] vs time is linear for n = 1 for the reaction X → P

(c) A plot of log P vs $\frac{1}{T}$ is linear at constant volume.

(d) A plot of P vs $\frac{1}{V}$ is linear at constant temperature.

11. A catalyst

(a) increases the average kinetic energy of reacting molecules

(b) decreases the activation energy (c) alters the reaction mechanism

(d) increases the frequency of collisions of reacting species

12. $X \rightarrow Y$. Ea, f = 15 kJ mol^{-1}; Ea,b = 9 kJ mol^{-1}. Potential energy of X = 10 kJ mol^{-1}. Then

(a) $E_{threshold} = 25$ kJ (b) P.E.(Y) = 16 kJ (c) $\Delta H = 6$ kJ (d) the reaction is endothermic

13. The activation energy reaction is zero. The rate constant of the reaction:

(a) increases with increase of temperature (b) decreases with decreases of temperature

(c) decreases with increase of temperature (d) is nearly independent of temperature

14. In photophysical process of organic molecule, which of the following process occurs ?

(a) Fluorescence (b) Phosphorescene (c) ISC (d) IC

EXERCISE - III

Numerical Answer Type & Subjective Questions

1. The rate constant for an isomerisation reaction, $A \longrightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1M, calculate the rate of the reaction after 1 hr.

2. A reaction having time-independent stoichiometry follows the equation

$$A + 2B \rightarrow 2Z$$

Suppose that initially there are present 0.28 mol of A, 0.39 mol of B, and 0.13 mol of Z.

(a) After a certain time 0.18 mol of A remains. What is the extent of reaction and what are the amounts of B and Z?

(b) What is the extent of reaction if the process goes to completion?

3. A reaction is of time-independent stoichiometry.

$$2A + B \rightarrow 3Z$$

If the initial rate of consumption of A is 3.36×10^{-4} mol dm^{-3} s^{-1}. What is the rate of consumption of B? What is the rate of formation of Z and what is the rate of reaction?

4. A reaction obeys the stoichiometric equation

$$A + 2B \rightarrow 2Z; \text{Rate} = K[A]^{\alpha}[B]^{\beta}$$

Rates of formation of Z at various concentrations of A and B are given in the table below:

[A]/mol dm^{-3}	[B]/mol dm^{-3}	v_z/mol dm^{-3} s^{-1}
3.5×10^{-2}	2.3×10^{-2}	5.0×10^{-7}
7.0×10^{-2}	4.6×10^{-2}	2.0×10^{-6}
7.0×10^{-2}	9.2×10^{-2}	4.0×10^{-6}

What are α and β in the rate equation

5. A reaction has the stoichiometry

$$2A + 2B \rightarrow Y + 2Z; \text{ Rate} = K[A]^{\alpha}[B]^{\beta}$$

Some results for the rate of consumption of A are shown below:

$[A]/\text{mol dm}^{-3}$	$[B]/\text{mol dm}^{-3}$	$v_A/\text{mol dm}^{-3}\ \text{s}^{-1}$
1.4×10^{-2}	2.3×10^{-2}	7.4×10^{-9}
2.8×10^{-2}	4.6×10^{-2}	5.92×10^{-8}
2.8×10^{-1}	4.6×10^{-2}	5.92×10^{-6}

Deduce α and β.

6. Identify the reaction order from each of the following:

(i) $K = 5.6 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$ (ii) $K = 4.5 \times 10^{-2}\ \text{L mol}^{-1}\ \text{s}^{-1}$

(iii) $K = 3.2 \times 10^{-7}\ \text{s}^{-1}$ (iv) $K = 4.0 \times 10^{-8}\ \text{atm}^{-1}\ \text{s}^{-1}$

(v) $K = 1.6 \times 10^{2}\ \text{L}^{2}\ \text{mol}^{-2}\ \text{s}^{-1}$ (vi) $K = 3 \times 10^{-3}\ \text{L}^{3/2}\ \text{mol}^{-3/2}\ \text{s}^{-1}$

7. A substance A reacts according to the first order rate law with $K = 5.0 \times 10^{-5}\ \text{s}^{-1}$
If $[A_0] = 1\ \text{mol L}^{-1}$ what is initial rate?

8. A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

9. The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

10. Two substances A ($t_{1/2}$= 5 mins) and B ($t_{1/2}$ = 15 mins) follow first order kinetics are taken in such a way that initially [A]= 4[B]. Calculate the time after which the concentration of both the substance will be equal.

11. The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+ 11.6	+ 10.2	+9.0	+5.87	−3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

12. In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

13. The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerising into a completely insoluble solid. The polymerisation follows first order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrest the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.

14. In a first order reaction, it takes the reactant 40.5 min to be 25% decomposed. Calculate the rate constant of the reaction.

15. For a first order reaction, the time required for 99.9% completion is x times of $t_{1/2}$. Find x.

16. For a 1st order reaction $t_{1/2} = 8$ min. How long will it take for concentration of reactant to reduced to 1% of the initial value.

17. The rate constant for a 2nd order reaction is 3.33×10^{-2} L mol^{-1} s^{-1}. If $[A_0] = 0.05$ mol L^{-1} calculate its half life.

18. The rate constant for a 2nd order reaction is 8.00×10^{-5} mol^{-1} L min^{-1}. How long will it take for a 1.0 M solution reduced to 0.25M.

19. For a reaction A $\rightarrow$ product $[A_0] = 0.010$ M. After 100 sec $[A] = 0.001$ M. The rate constant has numerical value = 9.0. What is the order of the reaction.

20. The $t_{1/2}$ of a reaction is halved as the initial conc. of the reaction is doubled. What is the order of the reaction.

21. The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. What is the order of the reaction.

22. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1}.

23. The rate constant of a reaction is 1.5×10^{7} sec^{-1} at 50°C and 4.5×10^{7} sec^{-1} at 100°C. Evaluate the Arrhenius parameters. A and E_a.

24. Calculate the activation energy of a reaction whose rate constant doubles by a 10°C rice in temperature in vicinity of 32°C.

25. The rate constant of a reaction is 6×10^{-5} L mol^{-1} s^{-1} at 30°C & 3×10^{-4} L mol^{-1} s^{-1} at 50°C. Calculate Ea.

26. The activation energy of a non-catalysed reaction at 27°C is 108.716 kJ mol^{-1} & the activation energy in presence of catalyst is 80 kJ mol^{-1}. Calculate the factor by which rate of reaction increase.

27. For 1st order reaction the rate constant is k at 27°C. Temperature is increased to 127°C & catalyst is also introduced and the result found is no change in rate. Find activation energy if catalyst change Ea by 100 kJ mol^{-1}.

28. The rate constant for the second order decomposition of N_2O fallows equation:
$K = (5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}) \exp(-29000 \text{ K}/T)$
Calculate the activation energy of the reaction.

29. The rate constant for the first order decomposition of ethylene oxide into CH_4 & CO follows the equation:

$$\log K = 14.34 - \left(\frac{1.25 \times 10^{4} \text{K}}{T}\right) \text{ in s}^{-1}$$

Calculate (a) Activation energy of the reaction
(b) Rate constant at 700 K.
(c) The frequency factor (A).

30. For the given concurrent reactions:

$$A \xrightarrow{k_1} B;\ 2A \xrightarrow{k_2} C;\ 3A \xrightarrow{k_3} D$$

What is the total rate of disappearance of A?

31. Predict the rate of the following reactions as per the given mechanism.

(a) $2O_3 \rightarrow 3O_2$

Mech. $O_3 \xrightarrow{k_1} O_2 + O$

$O + O_3 \xrightarrow{k_2} 2O_2$

(b) $2NO_2 + F_2 \rightarrow 2NO_2F$

Mech. $NO_2 + F_2 \xrightarrow{k_1} NO_2 + F$ (slow)

$F + NO_2 \xrightarrow{k_2} NO_2F$ (fast)

(c) $2NO + O_2 \rightarrow 2NO_2$

Mech. $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (Rapid equilibrium)

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow)

(d) $NH_4^+ + OCN^{\ominus} \longrightarrow \underset{\text{urea}}{OC(NH_2)_2}$

Mech. $NH_4^+ + OCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(complex)}}{NH_4OCN}$ (Rapid equilibrium)

$NH_4OCN \xrightarrow{k_2} OC(NH_2)_2$ (slow)

(e) $H_2 + I_2 \longrightarrow 2HI$

Mech. $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$ (Rapid equilibrium)

$H_2 + 2I \xrightarrow{k_2} 2HI$ (slow)

(f) $OCl^{\ominus} + I^{\ominus} \xrightarrow{OH^{\ominus}} OI^{\ominus} + Cl^{\ominus}$

Mech. $OCl^{\ominus} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-$ (fast)

$I^{\ominus} + HOCl \xrightarrow{k_2} HOI + Cl^{\ominus}$ (slow)

$OH^{\ominus} + HOI \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^{\ominus}$ (fast)

(g) $CO + Cl_2 \longrightarrow COCl_2$

Mech. $Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

$Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow)

(h) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Mech. $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$

$NO_3 + NO \xrightarrow{k_3} 2NO_2$

32. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$; $k_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $k_2 = 3.6 \times 10^{-5}\ sec^{-1}$. Calculate the % distribution of B & C.

33. For the following consequtive reaction $[A_0] = 5\ mol\ L^{-1}$. Find B_{max} and t_{max}.

$A \xrightarrow{k_A} B \xrightarrow{k_B} C$

$k_A = 0.4\ s^{-1}$

$k_B = 0.1\ s^{-1}$.

34. The gas phase decomposition of acetic acid at 1190 K proceeds by way of 2 parallel reactions

1. $CH_3COOH \rightarrow CH_4 + CO_2$ $\quad k_1 = 3.74 s^{-1}$

2. $CH_3COOH \rightarrow H_2C = C = O + H_2O$ $\quad k_2 = 4.65\ s^{-1}$

What is the % yield of ketene, CH_2CO, obtainable at this temperature.

35. At 460 nm a blue filter transmits 72.7% of the light and a yellow filter 40.7% of the light. What is the transmittance at the same wavelength in two filters in combination ?

36. In a given absorption call transmittance of 0.1 mol dm^{-3} of A is 0.75 and that of 0.1 mol dm^{-3} of B is 0.55 at a given wavelength. Calculate the transmittance of a solution that is simultaneous 0.1 mol dm^{-3} in A and 0.1 mol dm^{-3} in B.

37. A certain substance in a cell of length *l* absorbs 10 per cent of the incident light. What fraction of the incident light will be absorbed in a cell five times as long ?

38. In a cell of a certain length and at a pressure of 100 mmHg, gaseous acetone transmits 25.1 per cent of the incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98 per cent of the incident radiation will be absorbed by acetone in the same cell at the same temperature.

39. In the photochemical combination of $H_2(g)$, and $Cl_2(g)$, a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm. What amount of HCl(g) would be produced under these conditions per calories of radiant energy absorbed ?

40. At 360 nm a blue filter transition 37.0 per cent and a yellow filter 19.0 per cent of a radiation what is the transmittance at the same wavelength of the two filters in combination.

41. In a certain cell 10^{-3} mol dm^{-3} solution of a substance absorbs 10% of incident radiation. What concentration of the same solute in the same cell will absorb 90% of incident radiation ?

42. An 0.03 mol dm^{-3} solution of a substance has a absorbance of 2.0 at 660 nm using a 1 cm cell. Calculate (a) the value of absorption coefficient, (b) the value of I/I_0 and (c) the percent absorption for an 0.015 mol dm^{-3} solution in the same cell.

43. Dinitropentaoxide decomposes as follows :

$$N_2O_5(g) \longrightarrow 2NO_2(g) + 1/2O_2(g)$$

Given that $-d[N_2O_5]/dt = k_1[N_2O_5]$

$d[NO_2]/dt = k_2[N_2O_5]$

$d[O_2]/dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

44. Ammonia and oxygen reacts at higher temperatures as

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre^{-1} in 3 seconds. Calculate.

(i) rate of reaction. (ii) rate of disappearance of ammonia

(iii) rate of formation of water

45. At 800° C the rate of reaction

$$2\,NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and H_2 are

	[NO] in M	$[H_2]$ in M	$-\frac{1}{2}\frac{d[NO]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?

(b) What is the rate equation for the reaction?

(c) What is the rate when

$[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.1 \times 10^{-3}$M?

46. In this case we have $A \longrightarrow B + C$

Time	t	∞
Total pressure of A + B+C	P_2	P_3

Find k.

47. A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the

(a) rate constant for the reaction at 27°C & 47°C and

(b) energy of activation for the reaction.

48. A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1}. What will be the effect on the rate of reaction at 25°C, after things being equal.

49. For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

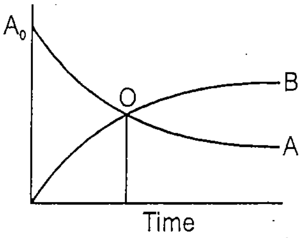
$2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{K_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{K_3} N_2 + H_2O$ (fast)

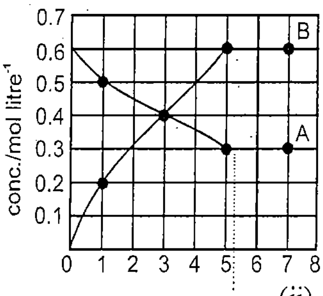
Establish the rate law for given reaction.

50. Figure represents the variation of the concentrations of A and B with time for the reaction : $A \longrightarrow nB$. Calculate the concentration of B at the point of intersection O.



51. Two reactants A and B separately shows two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half lives, compare their rates (a) at the start of reaction (b) after the lapse of one half life.

52. The progress of the reaction, $A \rightleftharpoons nB$ with time is presented in the figure. Determine :



(i) the value of n

(ii) the equilibrium constant K and

(iii) the initial rate of conversion of A.

53. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minute and 73% in 100 minute. (a) What is order of reaction ? (b) Calculate velocity constant. (c) How much will it decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm ?

54. At 100°C, a gaseous reaction, $A \longrightarrow B + 2C$, is observed to be of I order. On starting with pure A, at the end of 14 minute, the total pressure was found to be 264 mm of Hg. After a long time the total pressure of the system was 450 mm of Hg. Calculate (a) initial pressure of A (b) rate constant of reaction (c) half life period of reaction.

55. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(\ell).$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate : (i) time taken for NH_2NO_2 to decomposition 99% (ii) volume of dry N_2O produced at this point measured at STP.

56. For a homogenous gaseous reaction, $A \longrightarrow B + C + D$, the initial pressure was P_0 while pressure after time t was P. Derive an expression for rate constant K in terms of P_0 and t.

57. In a II order reaction, when the concentration of both the reactants are equal, the reaction is completed 20% in 500 sec. How long it would take for the reaction to go to 60% completion ?

58. Half-life period for decomposition of NH_3 over tungsten wire are given below :

Initial Pressure in mm	50	100	200
$t_{1/2}$	3.52	1.82	0.93

Calculate order of reaction.

59. A substance A is mixed with equal quantities of the substance B and C. At the end of 1000 second, half of the amount of A has reacted. What fraction of A will be left unreacted at the end of 2000 second. If the reaction is (a) zero order with respect to A ? (b) II order with respect to A ?

60. The specific rate constant of the decomposition of N_2O_5 is 0.008 min^{-1}. The volume of O_2 collected after 20 minute is 16 mL. Find the volume that would be collected at the end of reaction. NO_2 formed is dissolved in CCl_4.

61. A vessel contains dimethyl ether at a pressure of 0.4 mm. Dimethyl ether decomposes as :

$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is 4.78×10^{-3} min^{-1}. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and gas diffused to be same.

62. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B ?

63. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C ; other things being equal ?

64. The rate constant for the II order neutralization of 2-nitropropane by aqueous alkali obeys the equation

$$\log_{10} K = \frac{3163}{T} + 12$$

T is temperature in Kelvin.

Time and concentration were in minute and mol $litre^{-1}$ respectively. Calculate half life at 43.3°C and for an initial concentration of 0.001 mol $litre^{-1}$ for each of the reactant.

65. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 18 kcal/mol while it decreases to 6 kcal/mol when the decomposition was carried out in the presence of a catalyst at 300 K. How many times is the catalysed reaction faster than uncatalysed one ?

66. A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to ¼ of the initial value after passing through 10 cm length of solution. Calculate molar extinction coefficient

67. A substance when dissolved in water at 10^{-3} M concentration absorbs 10% of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90% of some radiation?

68. In an absorption cell, the transmittance of 0.1 M solution of a substance X is 80% and that of 0.1 M solution of another substance Y is 60% at a given wave length. What is the transmittance of a solution that is simultaneously 0.1 M in X and 0.1 M in %?

69. A sample of gaseous HI was irradiated by light of wave length 253.7 nm when 307 J of energy was found to decompose 1.30×10^{-3} mole of HI. $\phi = ?$

70. For a photochemical form of ethylene from di-n-propylketone using $\lambda = 313$ nm, $\phi = 0.21$. Calculated the no. of moles of ethylene formed when the sample is irradiatied with 50 watt of this radiation.

EXERCISE IV

Previous Year Questions

1. In the Arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as the rate constant at :

(a) $T = 0$ (b) $T = 298$ K (c) $T \rightarrow \infty$ (d) none

2. The rate constant of a first order reaction, $A \rightarrow$ Products, is $60 \times 10^{-4}\ s^{-1}$ its rate at [A] = 0.01 ml l^{-1} would be :

(a) 60×10^{-6} mol l^{-1} min^{-1} (b) 36×10^{-4} mol l^{-1} min^{-1}

(c) 60×10^{-2} mol l^{-1} min^{-1} (d) 36×10^{-1} mol l^{-1} min^{-1}

3. For a first order reaction :

(a) the degree of dissociation is equal to $(1-e^{-kt})$

(b) a plot of reciprocal concentration of the reactant vs time gives a straight line

(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

4. For a first order reaction $A \longrightarrow$ Product, the rate of reaction at [A] = 0.2 mol l^{-1} is 1.0×10^{-2} mol l^{-1} min^{-1}. The half life period for the reaction is :

(a) 832 s (b) 440 s (c) 416 s (d) 14 s

5. The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$

is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is 2.40×10^{-5} mol L^{-1} s^{-1}, then conc. of N_2O_5 (in mol L^{-1}) is

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

6. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photo-chemical process $AB + h\nu \rightarrow AB^*$, rate of formation of AB^* is directly proportional to

(a) C (b) I (c) I^2 (d) C.I.

7. Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions

(a) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$ (b) $\text{Rate} = -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(c) $\text{Rate} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$ (d) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

reaction the conc. of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is

(a) 2×10^4 (b) 3.45×10^{-5} (c) 1.386×10^{-4} (d) 2×10^{-4}

9. The reaction $X \longrightarrow$ Product follow first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M.

(a) 1.73×10^{-4} M min^{-1} (b) 3.47×10^{-5} M min^{-1}

(c) 3.47×10^{-4} M min^{-1} (d) 1.73×10^{-5} M min^{-1}

10. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$; $k_1 = 6.8 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$

then formation constant of $[Ag(NH_3)_2]^+$ is

(a) 6.8×10^{-6} (b) 1.08×10^{-5} (c) 1.08×10^{-6} (d) 6.8×10^{-5}

11. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

12. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reactions is

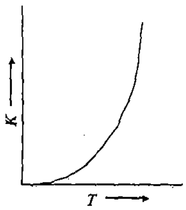
(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol dm^{-3} (c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^3

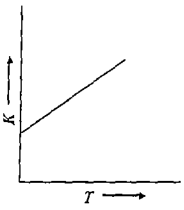
13. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are

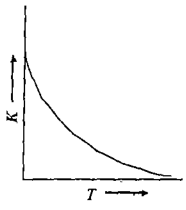
(a) 1.0×10^6 s^{-1} and 9.2 kJmol^{-1} (b) 6.0 s^{-1} and 16.6 kJmol^{-1}

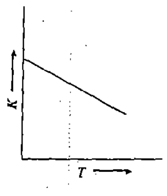
(c) 1.0×10^6 s^{-1} and 16.6 kJmol^{-1} (d) 1.0×10^6 s^{-1} and 38.3 kJmol^{-1}

14. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is

(a) 

(b) 

(c) 

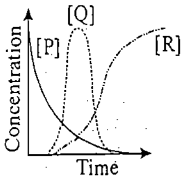
(d) 

15. For a reaction with rate $-dC/dt = kC^2$, C_0 and C are the concentrations of the reactant at time 0 and t respectively. If 10 minutes required for C_0 to become $C_0/2$, the time required for C_0 to become $C_0/4$ is

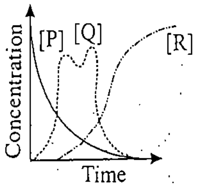
(a) 10 min (b) 20 min (c) 30 min (d) 40 min

16. For the first order consecutive reaction P → Q → R, under steady state approximation to [Q], the variations of [P], [Q] and [R] with time are best represented by

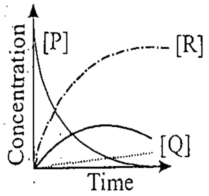
(a)



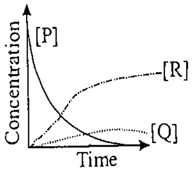
(b)



(c)



(d)



17. For a reaction involving two steps given below

First step $G \rightleftharpoons 2H$

$G + H \rightleftharpoons P$

Assume that the first step attains equilibrium rapidly. The rate of formation of P is proportional to

(a) $[G]^{1/2}$ (b) $[G]$ (c) $[G]^2$ (d) $[G]^{3/2}$

18. In a homogeneous catalytic reaction, 1.0 M of a substrate band 1.0 μM of a catalyst yields 1.0 mM of a product in 10s. The trunover frequency (TOF) of the reaction (s^{-1}) is

(a) 10^{-2} (b) 10^{2} (c) 10^{-3} (d) 10^{3}

19. A reaction follows second order rate law, $\frac{-d[A]}{dt} = k[A]^2$, if

(a) a plot of [A] versus t is the straight line (b) a plot of 1/[A] versus t is a straight line

(c) a plot of ln[A] versus t is a straight line (d) a plot of $e^{[A]}$ versus t is a straight line

20. The specific rate constant of decomposition of a compound is represented by

$$\ln k = 5.0 - \frac{12000}{T}$$

The activation energy of decomposition for this compound at 300 K is

(a) 24 kcal/mol (b) 12 kcal/mol (c) 24 cal/mol (d) 12 cal/mol

21. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half-life of 28.4 min. The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is

(a) 56.8 min (b) 170.4 min (c) 85.2 min (d) 227.2 min

22. The reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ proceeds via the following steps:

$$NO + NO \xrightarrow{k_a} N_2O_2$$
$$N_2O_2 \xrightarrow{k_{a'}} NO + NO$$

Equilibrium step (ere)

$$N_2O_2 + O_2 \xrightarrow[\text{(slow)}]{k_b} NO_2 + NO_2$$

The rate of this reaction is equal to

(a) $2k_b[NO][O_2]$ (b) $(2K_ak_b[NO]^2[O_2]) / (K_a + k_b[O_2])$

(c) $2k_b[NO]^2[O_2]$ (d) $K_a[NO]^2[O_2]$

23. 1 g of ^{90}Sr gets converted to 0.953 g after 2 yr. The half-life of ^{90}Sr, and the amount of ^{90}Sr remaining after 5 yr are

(a) 1.44 yr and 0.916 g (b) 57.6 yr and 0.75 g

(c) 28.8 yr and 0.887 g (d) 100 yr and 0.982 g

24. Consider an exothermic reaction, $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$

As the temperature increases

(a) k_1, k_{-1} increases and k_1/k_{-1} decrease (b) k_1 increases, k_{-1} decreases and k_1/k_{-1} increases

(c) k_1, k_{-1} and k_1/k_{-1} decreases (d) k_1 and k_{-1} decreases and k_1/k_{-1} increases

25. A reaction proceeds through the formation of an intermediate B in a unimolecular reaction

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

The integrated rate law for this reaction is

(a) $[A] = [A]_0 e^{-k_a t}$ (b) $[A] = [A]_0 (e^{-k_a t} - e^{-k_b t})$

(c) $[A] = \dfrac{[A]_0}{2}\left(1 + \dfrac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_a - k_b}\right)$ (d) $[A] = [A]_0 (1 + e^{-k_a t} - e^{-k_b t})$

26. The half-life of a first order reaction varies with temperature according to

(a) $\ln t_{1/2} \propto 1/T$ (b) $\ln t_{1/2} \propto T$ (c) $t_{1/2} \propto 1/T^2$ (d) $t_{1/2} \propto T^2$

27. If the concept of half-life is generalized to quarter-life of a first order chemical reaction, it will be equal to

(a) ln 2/k (b) ln 4/k (c) 4/k (d) 1/4k

28. For a reaction, the rate constant k at 27°C was found to be: $k = 5.4 \times 10^{11} e^{-50}$

The activation energy of the reaction is

(a) 50 J mol^{-1} (b) 415 J mol^{-1} (c) 15,000 J mol^{-1} (d) 125,000 J mol^{-1}

29. The carbon-14 activity of an old wood sample is found to be 14.2 disintegrations min^{-1} g^{-1}. Calculated age of old wood sample, if for a fresh wood sample carbon-14 activity is 15.3 disintegrations min^{-1} g^{-1} ($t_{1/2}$ carbon-14 is 5730 years) is

(a) 5,000 years (b) 4,000 years (c) 877 years (d) 617 years

30. In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained is

$$\frac{v}{[E]_0[S]} = 1.4 \times 10^{12} - \frac{10^4 v}{[E]_v}$$

The values of k_3 (k_{ems} mol L^{-1} s^{-1}) and K (Michaelis constant, mol L^{-1}), respectively, are

(a) 1.4×10^{12}, 10^4 (b) 1.4×10^8, 10^4 (c) 1.4×10^8, 10^{-4} (d) 1.4×10^{12}, 10^{-4}

31. The addition polymerization of M (monomer) involves the following stages:

(I = initiator; R = free radical)

$I \xrightarrow{k_1} R$ (initiation)

$R + M \xrightarrow{k_2} RM$

$RM + M \rightarrow RM_2$ and so on

$RM_n + M_nR \xrightarrow{k_1} R-M_n-M_n-R$

The rate constant for free radical formation is $2 \times 10^{-3}\ s^{-1}$. The initial concentration of initiator is 10^{-3} mol dm^{-3}. The overall rate of the reaction is $4 \times 10^{-3}\ dm^{-3}\ s^{-1}$. Assuming steady state approximation for free radical, the kinetic chain length is

(a) 2000 (b) 8×10^9 (c) 20 (d) 200

32. The half life of a zero order reaction ($A \rightarrow P$) is given by (k = rate constant)

(a) $t_{1/2} = \frac{[A]_0}{2k}$ (b) $t_{1/2} = \frac{2.303}{2k}$ (c) $t_{1/2} = \frac{[A]_0}{k}$ (d) $t_{1/2} = \frac{1}{k[A]_0}$

[illegible] later

33. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25 % completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9\ s^{-1}$, calculate its rate constant at 318 K and also the energy of activation.

34. The rate constant for the first order decomposition of a certain reaction is given by the equation,

$$\ln K(\sec^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

Calculate :

(a) the energy of activation. (b) the rate constant at 500 K.

(c) At what temperature will its half life period be 256 minute ?

35. (a) In a reaction with initially 0.12 M, the concentration of reactant is reduced to 0.06 M in 10 hour and to 0.03 M in 20 hour.

(i) What is order of reaction ? (ii) What is rate constant ?

Simple

(b) The rate of a first order reaction is 0.04 mol $litre^{-1}s^{-1}$ at 10 minute and 0.03 mol $litre^{-1}\ sec^{-1}$ at 20 minute after initiation. Find the half life of the reaction.

use

$K = \frac{1}{10} \ln \frac{0.04}{0.03}$

Good

36. Some $PH_3(g)$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant.

Time (sec)	0	60	120	∞
P(mm Hg)	262.40	272.90	275.51	276.40

37. For the given reaction , $A + B \longrightarrow$ Products

Following data were given

Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [$ml^{-1}s^{-1}$]
[A]	[B]	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) write the rate equations. (b) calculate the rate constant.

[A] ∝ rate as in radioactive (dis. per time) & use time as diff. b/w the two

38. At constant temperature and volume, X decomposes as

$$2X(g) \longrightarrow 3Y(g) + 2Z(g);\ \text{Px is the partial pressure of X.}$$

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

(i) What is the order of reacion with respect to X ?

(ii) Find the rate constant. (iii) Find the time for 75% completion of the reaction

39. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$, the rate constant is terms of initial pressure (p_0) and pressure at time t(p_t) is given by

(a) $\frac{1}{t}\ln\frac{p_0}{p_t - p_0}$ (b) $\frac{1}{t}\ln\frac{2p_0}{3p_0 - p_t}$ (c) $\frac{1}{t}\ln\frac{3p_0}{p_t - p_0}$ (d) $\frac{1}{t}\ln\frac{3p_0}{3p_t - p_0}$

40. For a reaction $2A + B \rightarrow C + D$, if rate of consumption of A is 0.1 mol L^{-1} s^{-1}, the rate of production of C (in mol L^{-1} s^{-1}) is _____

41. For a zero order reaction, the half-life depends on the initial concentration $[C_0]$ of the reactant as

(a) $[C_0]$ (b) $[C_0]^0$ (c) $[C_0]^{-1}$ (d) $[C_0]^{1/2}$

42. The rate constants for a reaction at 300 and 350 K are 8 and 160 L mol^{-1} $s-1$, respectively. The activation energy of the reaction in kJ mol^{-1} is ____.

[Given R = 8.314 J K^{-1} mol^{-1}]

43. An aqueous solution of haemoglobin has a molar absorptivity value of 18,600 L mol^{-1} cm^{-1} for an absorbance value of 0.1 at 540 nm (Guiven: cell thickness = 1 cm). The concentration (in µM) of the haemoglobin solution is

(a) 0.537 (b) 5.37 (c) 53.7 (d) 537.0

44. For the reaction:

$$2NO + 2H_2 \xrightarrow{700°C} N_2 + 2H_2O$$

(i) Write the expression for the rate of the reaction in terms of the change in concentrations of NO and H_2O.

(ii) Given the following data for the above reaction, find the order of the reaction with respect to (a) NO and (b) H_2 and the rate constant of the reaction along with the proper unit,

	$[NO]_{t=0}$ (mol dm^{-3})	$[H_2]_{t=0}$ (mol dm^{-3})	Intial rate (mol $dm^{-3}s^{-1}$)
Experiment 1	0.025	0.01	2.4×10^{-6}
Experiment 2	0.025	0.005	1.2×10^{-6}
Experiment 3	0.0125	0.01	0.6×10^{-6}

45. The kinetics of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ in liquid bromine medium was measured independently for three different initial concentration of N_2O_5 : 0.11, 0.07 and 0.05 mol L^{-1}. The half-life of the reaction was found to be 4.5 hours for all these concentrations. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 0.5

46. A 2.5×10^{-4} M solution of a complex exhibits an absorption maximum at 625 nm with an absorbance of 0.90 when measured in a cuvette with a path length of 1.5 cm. The absorbance of 1.5×10^{-3} M solution of the same complex recorded in a cuvette with a path length of 0.2 cm is _______

47. For a reaction, the rate constant at 25°C is doubled when the temperature is raised to 45°C. The activation energy (in kJ mol^{-1}) of the reaction is _______ [Given: ln2 = 0.693]

1.
8. b
15. a
22. c
29.
36.
43.
50. b
57. c
64. a
71.
78.
85.
92. a
99. c
106.
113
120 b
127. d
134. b
141.
148.
155
162 a
169. a
176. a
183.

1. a, b c,
8. a,c

48. The rate constants for a reaction at 300 and 350 K are 8 and 160 L mol^{-1} ^{s}–1, respectively. The activation energy of the reaction in kJ mol^{-1} is ____.
[Given R = 8.314 J K^{-1} mol^{-1}]

ANSWER KEY

EXERCISE- I

1. b	2. c	3. b	4. d	5. b	6. b	7. b
8. b	9. c	10. a	11. b	12. b	13. d	14. d
15. a	16. b	17. c	18. b	19. b	20. b	21. a
22. c	23. d	24. d	25. b	26. d	27. a	28. d
29. c	30. c	31. a	32. c	33. a	34. a	35. a
36. d	37. a	38. b	39. b	40. a	41. b	42. b
43. d	44. a	45. d	46. c	47. b	48. a	49. a
50. b	51. b	52. a	53. b	54. d	55. b	56. c
57. c	58. b	59. c	60. c	61. a	62. c	63. d
64. a	65. a	66. c	67. a	68. a	69. a	70. a
71. d	72. a	73. d	74. c	75. a	76. c	77. d
78. d	79. a	80. c	81. c	82. b	83. b	84. a
85. c	86. a	87. c	88. c	89. c	90. a	91. a
92. a	93. c	94. d	95. c	96. b	97. c	98. b
99. c	100. b	101. c	102. c	103. c	104. a	105. c
106. c	107. a	108. c	109. b	110. a	111. a	112. d
113. a	114. d	115. d	116. b	117. b	118. a	119. c
120. b	121. c	122. b	123. a	124. c	125. a	126. b
127. d	128. d	129. d	130. c	131. c	132. d	133. a
134. b	135. d	136. a	137. a	138. b	139. b	140. c
141. b	142. a	143. a	144. a	145. c	146. a	147. d
148. c	149. d	150. a	151. c	152. b	153. d	154. c
155. b	156. d	157. b	158. b	159. a	160. a	161. a
162. a	163. a	164. a	165. a	166. c	167. d	168. c
169. a	170. b	171. a	172. c	173. b	174. c	175. d
176. a	177. d	178. a	179. c	180. b	181. b	182. c
183. c	184. d					

EXERCISE - II

1. a,b,c,d	2. b,c,d	3. c,d	4. b,c	5. a,b,c	6. a,b,c	7. b,c
8. a,c	9. a,b,d	10. a,b	11. b,c	12. a,b,c,d	13. a,b	14. a,b,c,d

ad

EXERCISE - III

1. 3.4352×10^{-3} M min^{-1}

2. (a) $\xi = 0.10$; amount of A = 0.18, B = 0.19, Z = 0.33 (b) $\xi = 0.195$

3. Rate of consumption of B = 1.68×10^{-4}; Rate of formation of Z = 5.04×10^{-4};
Rate of reaction = 1.68×10^{-4}

4. $\alpha = 2, \beta = 1$

5. $\alpha = 2, \beta = 1$

6. (i) zero order (ii) second order (iii) first order (iv) second order (v) third order (vi) 2.5th order

7. 5.0×10^{-5}

8. 1.2 hr

9. 166.6 min

10. 15 min

11. 966 min

12. 207.398

13. 1.005×10^{-4} min^{-1}

14. 0.0071 min^{-1}

15. x = 10

16. 53.15 min

17. 600.6 sec

18. 37500 min

19. second order

20. second order

21. zero order

22. 100 kJ mol^{-1}

23. $E_a = 2.2 \times 10^4$ J mol^{-1}; $A = 5.44 \times 10^{10}$ s^{-1}

24. 53.6 KJ mol^{-1}

25. 64.478 KJ mol^{-1}

26. 99707.8 times

27. E_a (at 27°C) = 150, E_a (at 127°C) = 250

28. 241.106 KJ mol^{-1}

29. (i) 239.339 KJ mol^{-1} (ii) $10^{-3.51}$ (iii) $10^{-14.34}$

30. $-\frac{d[A]}{dt} = k_1[A] + 2k_2[A]^2 + 3k_3[A]^3$

31. (a) $-\frac{1}{2}\frac{d[O_3]}{dt} = k_1[O_3]$
(b) $-\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2][F_2]$
(c) $\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$
(d) $\frac{d[urea]}{dt} = k[NH_4^+][OCN^-]$
(e) $\frac{1}{2}\frac{d[HI]}{dt} = k[H_2][I_2]$
(f) $-\frac{d[I^-]}{dt} = \frac{k[OCl^-][I^-]}{[OH^-]}$
(g) $\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$
(h) $\frac{d[O_2]}{dt} = k[N_2O_5]$

32. % distribution of B = 77.77%; % distribution of C = 22.22%

33. $B_{max} = 3.164$ mol L^{-1}; $t_{max} = 4.62$ s

34. 55.42%

35. 0.296

36. 0.4125

37. 40.98

38. 283.0 mm of Hg

39. 33.54 mol

40. 0.07

41. 0.022 mol dm^{-3}

42. (a) 66.7 mol^{-1} dm^3 cm^{-1} (b) 0.01 (c) 90%

43. $2k_1 = k_2 = 4k_3$

44. (i) 9×10^{-4} mol L^{-1} s^{-1} (ii) 36×10^{-4} mol L^{-1} s^{-1} (iii) 54×10^{-4} mol L^{-1} s^{-1}

45. (a) 3; (b) Rate = $k[NO]^2[H_2]$; (c) 8.85×10^{-3} M sec^{-1}.

46. $K = \frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}$

47. (a) 2.31×10^{-2} min^{-1}, 6.93×10^{-2} min^{-1} (b) 43.85 kJ mol^{-1}

48. increases by $e^{20.21}$ times

49. Rate = $K[NO]^2[H_2]$
$K = k_2 \times k_1$

50. $[B] = \frac{nA_0}{1+n}$

51. (a) 0.693 (b) 1.386

52. (i) 2, (ii) 1.2 mol L^{-1}, (iii) 0.1 mol L^{-1} $hour^{-1}$

53. (a) 1, (b) 1.308×10^{-2} (c) 73%

54. (a) 150 mm (b) 3.415×10^{-2} min^{-1} (c) 20.29 min

55. (i) 13.95 hour (ii) 2.217 L

56. $K = \frac{2.303}{t}\log\frac{2P_0}{3P_0 - P}$

57. 3000 sec.

58. 2

59. (a) zero (b) 1/3

60. 108.23 mL

61. 0.261

62. 53 min.

63. 2.35×10^{13}

64. 10^{-19} min.

65. 4.8×10^{8} times

66. 1.204 dm^3 mol^{-1} cm^{-1}

67. 0.0218 M

68. 48%

69. 2

70. 2.74×10^{-5} mol

EXERCISE IV

1. c 2. a 3. ad 4. a 5. d 6. b 7. a
8. c 9. c 10. b 11. d 12. a 13. d 14. a
15. c 16. c 17. d 18. b 19. b 20. a 21. c
22. b 23. c 24. a 25. a 26. a 27. b 28. d
29. d 30. c 31. a 32. a

33. $\Delta E = 18.33$ Kcal mol^{-1}; $k = 9.22 \times 10^{-4}$ sec^{-1}

34. (a) $E_a = 24.83$ kcal mol^{-1} (b) $K = 2.35 \times 10^{-5}$ sec^{-1} (c) T = 513 K

35. (a) (i) O.R. = I order (ii) K = 0.069 hr^{-1} (b) $t_{1/2} = 24.09$ min

36. order = 1 $k = 2.30 \times 10^{-2}$ sec^{-1}

37. (a) $r = k[A][B]^{\circ}$ (b) $k = 5 \times 10^{-1}$ sec^{-1}

38. (i) 1, (ii) 6.93×10^{-3} min^{-1}, (iii) 200 min,

39. b 40. 0.05 41. a 42. 52.3 kJ mol^{-1} 43. b

44. (i) $-\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2}\frac{d}{dt}[H_2] = +\frac{d[N_2]}{dt} = +\frac{1}{2}\frac{d}{dt}[H_2O]$

(ii) rate law is $r = k[NO]^2[H_2]$; $k = 0.3840$ mol^{-2} dm^{-6} sec^{-1}

45. b 46. 0.72 47. 27.99 48. 52.3

CHAPTER 10

LIQUID SOLUTION

Solutions are homogeneous mixtures and they contain particles like ion or small molecule. There are seven possible kinds of solutions. For solutions in which a gas or solid is dissolved in a liquid, the dissolved substance is called the **solute** and the liquid is called the **solvent.**

Terminology

A	B
Solvent	Solute
w_A = Given mass of solvent	w_B = Given mass of solute
M_A = molar mass of solvent	M_B = molar mass of solute
n_A = number of moles of solvent	n_B = number of moles of solute

The concentration of a solution can be expressed in many ways, like molarity, mole fraction, % by mass, and molality etc.

Raoult's Law

This law is applied for a solution of liquid in liquids and can be stated as follows.

"The partial vapour pressure of any component in the solution is directly proportional to its mole fraction".

$P_A \propto X_A$ where, P_A = Partial vapour pressure of A

$P_A = KX_A$ X_A = Mole fraction of A in solution

For pure liquids $X_A = 1$

Then $K = P°_A$ where $P°_A$ is the vapour pressure of component A in pure state

Hence, $P_A = X_AP°_A$, similarly for component B, $P_B = X_BP°_B$

Raoult's law in combination with Dalton's law of partial pressure

Assuming that vapours of a liquid is behaving like an ideal gas, then according to Dalton's law of partial pressure the total pressure P_T is given by

$P_T = P_A + P_B$ or $P_T = X_A P°_A + X_BP°_B$ or $P_T = P°_B + (P°_A - P°_B)X_A$

In vapour phase,

$P_A = P_T y_A$

$P_B = P_T y_B$

where y_A & y_B are the composition of A & B in vapour phase respectively.

Colligative Propeties

The properties of dilute solution which depend only on number of particle of solute present in the solution & not on their identify called.

We shall assume here that the solute is non volatile (B), so it does not contribute to the vapour. The vapour is only due to the volatile solvent (A).

Colligative properties are the properties of only dilute solution which are supposed to behave as ideal solutions. The various colligative properties are :

1. Relative Lowering of Vapour Pressure by a Non-volatile Solute

Let us consider a solution obtained by dissolving n_B moles of a non-volatile solute in n_A moles of a volatile solvent has a pressure P_A, vapour pressure of pure solvent $A = P_A^o$

$\therefore$ Lowering in vapour pressure $= P_A^o - P_A$

Relative lowering in vapour pressure $= \dfrac{P_A^o - P_A}{P_A^o}$

As $\quad P_T = P_A + \underset{\substack{\downarrow\\0}}{P_B}$ (non volatile)

$$P_T = P_A^o \times X_A$$

Since $X_1 + X_2 = 1$, above Equation may be written as

$$P_A = (1 - X_B)P_A^o$$

or $\quad P_A / P_A^o = 1 - X_B \quad$ or $\quad \boxed{\dfrac{P_A^o - P_A}{P_A^o} = X_B}$

Determination of molar mass from lowering of vapour pressure

$$\frac{P_A^o - P_A}{P_A^o} = \frac{n_B}{n_A + n_B} = \frac{W_B / M_B}{W_A / M_A + W_B / M_B}$$

Since in dilute solution, $n_B << n_A$.

$$\frac{P_A^o - P_A}{P_A^o} = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B M_A}{W_A M_B}$$

$$\therefore M_B = \frac{W_B M_A P_A^o}{W_A (P_A^o - P_A)}$$

Alternatively, we can derive the relation without taking any approximations.

$$\frac{P_A^o}{P_A^o - P_A} = \frac{n_A + n_B}{n_B} = 1 + \frac{n_A}{n_B}$$

$$\frac{P_A}{P_A^o - P_A} = \frac{n_A}{n_B}$$

$$\boxed{\frac{P_A^o - P_A}{P_A} = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B M_A}{W_A M_B}}$$

$$M_B = \frac{W_B M_A P_A}{W_A (P_A^o - P_A)}$$

2. **Elevation in Boiling point**

T_b^o = Boiling point of pure solvent A

T_b = boiling point of solution when a non volatile solute B is dissolved in A.

$\because T_b > T_b^o$

Elevation in boiling point $\Delta T_b = T_b - T_b^o \Rightarrow \Delta T_b \propto m$

$$\boxed{\Rightarrow \Delta T_b = k_b m \Rightarrow \Delta T_b = \frac{k_b n_B \times 1000}{w_A} = \frac{k_b w_B \times 1000}{M_B \times w_A}}$$

where k_b = molal elevation constant or efulioscopic constant

m = molality

k_b is a solvent dependent quantity

$$\boxed{k_b = \frac{MRT_b^{o2}}{1000\,\Delta H_{vap,\,m}}}$$

M = molar mass of solvent in grams

R = Gas constant

T_b^o = Boiling point of pure solvent

$\Delta H_{vap,\,m}$ = molar enthalpy of vaporisation of solvent

3. **Depression in Freezing Point**

T_f^o = Freezing point of pure solvent A

T_f = Freezing point of solution when a non volatile solute B is dissolved in A.

$\because T_f < T_f^o$

Depression in freezing point $\Delta T_f = T_f^o - T_f \Rightarrow \Delta T_f \propto m$

$$\boxed{\Rightarrow \Delta T_f = k_f m \Rightarrow \Delta T_f = \frac{k_f n_B \times 1000}{w_A} = \frac{k_f w_B \times 1000}{M_B \times w_A}}$$

where k_f = molal depression constant or cryoscopic constant

m = molality

k_f is a solvent dependent quantity

$$\boxed{k_f = \frac{MRT_f^{o2}}{1000\,\Delta H_{fus,\,m}}}$$

M = molar mass of solvent in grams

R = Gas constant

T_f^o = Freezing point of pure solvent

$\Delta H_{fus,\,m}$ = molar enthalpy of fusion of solvent

4. **Osmotic Pressure**

π = CRT (van't Hoff equation)

where π = Osmotic pressure

C = Concentration (Molarity)

R = Gas constant

T = Temperature in kelvin

$$\pi = \frac{n_B}{V} RT = \frac{w_B RT}{M_B V}$$

For Electrolytic Solute

If the solute undergoes dissociation or association in solution, abnormal results for all the colligative properties are observed.

Van't Hoff factor (i)

$$= \frac{\text{Observed C.P.}}{\text{Theoretical C.P.}}$$

$$= \frac{\text{No. of molecules actually present}}{\text{No. of molecules expected to be present}}$$

$$\because \text{ C.P.} \propto \frac{1}{\text{Molar mass of solute}}$$

$$i = \frac{\text{Abnormal molar mass of solute}}{\text{Normal molar mass of solute}}$$

Two cases possible are :

(1) $\dfrac{\text{Dissociation}}{i > 1}$

$$i = 1 + (n - 1)\,\alpha$$

where α = degree of dissociation

n = no. of particle formed after dissociation

(2) $\dfrac{\text{Association}}{i < 1}$

$$i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

α = degree of association

n = no. of particle undergoing association

* For a strong electrolyte $\alpha = 1$.

$\therefore\ i = n$.

EXERCISE - I

Single Correct Type

Raoult's Law and Vapour Pressure

1. Mole fraction of vapours of A above the solution in mixture of A and B ($X_A = 0.4$) will be

[Given : $P_A^{\circ} = 100$ mm Hg and $P_B^{\circ} = 200$ mm Hg]

(a) 0.4 (b) 0.8 (c) 0.25 (d) none of these

2. For an ideal binary liquid solution with $P_A^{\circ} > P_B^{\circ}$, which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?

(a) $Y_A < Y_B$ (b) $X_A > X_B$ (c) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (d) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

3. The exact mathematical expression of Raoult's law is

(a) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (b) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$ (c) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (d) $\frac{P^0 - P_s}{P^0} = n \times N$

4. A mixture contains 1 mole of volatile liquid A ($P_A^{\circ} = 100$ mm Hg) and 3 moles of volatile liquid B ($P_B^{\circ} = 80$ mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is

(a) 85 mm Hg (b) 85.88 mm Hg (c) 90 mm Hg (d) 92 mm Hg

5. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

$$P_{Total} = 120 - 75\,X_B$$

hence, vapour pressure of pure A and B respectively (in Torr) are

(a) 120, 75 (b) 120, 195 (c) 120, 45 (d) 75, 45

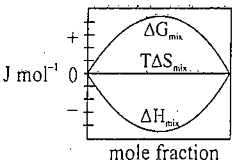
6. Which of the following plots represents an ideal binary mixture?

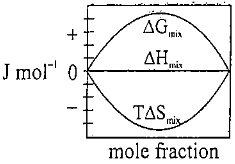
(a) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).

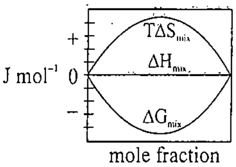
(b) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)

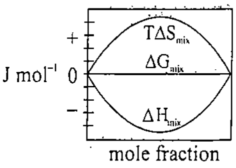
(c) Plot of $\frac{1}{P_{total}}$ v/s Y_A is linear (d) Plot of $\frac{1}{P_{total}}$ v/s Y_B is non linear

7. Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mole of an ideal binary solution.

(a)


(b)


(c)


(d)


8. What is the mole ratio of benzene (P_B = 150 torr) and toluene (P_T = 50 torr) in vapour phase if the given solution has a vapour pressure of 120 torr?

(a) 7 : 1 (b) 7 : 3 (c) 8 : 1 (d) 7 : 8

9. Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temp., if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. What is the the v.p. of A & B respectively in their pure states.

(a) 400, 600 (b) 600, 400 (c) 700, 100 (d) 100, 700

Colligative Properties

Part A: Relative Lowering of Vapour Pressure

10. The Van't Hoff factor for a dilute aqueous solution of glucose is

(a) zero (b) 1.0 (c) 1.5 (d) 2.0

11. The van't Hoff factor (i) for an infinitely dilute solution of $NaHSO_4$ is :

(a) 1/2 (b) 1/3 (c) 3 (d) 2

12. Which of the following aqueous solution will show maximum vapour pressure at 300 K?

(a) 1 M NaCl (b) 1 M $CaCl_2$ (c) 1 M $AlCl_3$ (d) 1 M $C_{12}H_{22}O_{11}$

13. The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

(a) 0.15 (b) 5.7 (c) 0.2 (d) 4.0

14. If P_0 and P are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and non-volatile solute respectively, then correct relation is :

(a) $P = P_0N_2$ (b) $P = P_0N_1$ (c) $P_0 = PN_1$ (d) $P = P_0(N_1/N_2)$

15. The vapour pressure of pure liquid A is 10 torr and at the same temperature when 1 g of B solid is dissolved in 20 g of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is :

(a) 100 amu (b) 90 amu (c) 75 amu (d) 120 amu

16. The vapour pressure of a dilute aqueous solution of glucose is 750 mm of mercury at 373 K. The mole fraction of solute is -

(a) $\frac{1}{10}$ (b) $\frac{1}{7.6}$ (c) $\frac{1}{35}$ (d) $\frac{1}{76}$

Part B: Elevation in Boiling Point

17. In a solute undergoes dimerisation and trimerisation, the minimum values of the van't Hoff factors are

(a) 0.5 and 1.50 (b) 1.5 and 1.33 (c) 0.5 and 0.33 (d) 0.25 and 0.67

18. The correct relationship between the boiling points of very dilute solution of $AlCl_3$ (T_1K) and $CaCl_2$ (T_2K) having the same molar concentration is

(a) $T_1 = T_2$ (b) $T_1 > T_2$ (c) $T_2 > T_1$ (d) $T_2 \leq T_1$

19. A solution containing 28 g of phosphorus in 315 g CS_2 (b.p. 46.3°C) boils at 47.98°C. If K_b for CS_2 is 2.34 K kg mol^{-1}. The formula of phosphorus is (at. mass of P = 31).

(a) P_6 (b) P_4 (c) P_3 (d) P_2

20. A solution of 1.22 g of benzoic acid in 1000 gm of ~~free~~benzene shows a boiling point elevation of 1.4°. Assuming that solute is dimerized to the extent of 80 percent at 80°C). Calculate normal b.p. of benzene (molar enthalpy of vap. of benzene = 7.8 Kcal/mole)

(a) 513.43 K (b) 317.93 K (c) 418.33 K (d) 600.23 K

21. Which of the aq. solution has the highest boiling point

(a) 0.1 M KNO_3 (b) 0.1 M Na_3PO_4 (c) 0.1 M $BaCl_2$ (d) 0.1 M K_2SO_4

22. Consider equimolal aqueous solutions of $NaHSO_4$ and NaCl with ΔT_b and ΔT_b° as their respective boiling point elevations. The value of $\underset{m\to 0}{Lt}\ \frac{\Delta T_b}{\Delta T_b^\circ}$ will be :

(a) 1 (b) 1.5 (c) 3.5 (d) 2 / 3

23. Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is

(a) K_b (b) 1.20 K_b (c) 1.02 K_b (d) 0.98 K_b

24. 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is $(K_{b(H_2O)} = 0.52\ K\,kg\,mol^{-1})$

(a) 274.76 K (b) 377 K (c) 376.4 K (d) 374.76 K

25. Assuming each salt to be 90% dissociated which of the following will have highest boiling point ?

(a) Decimolar $Al_2(SO_4)_3$ (b) Decimolar Na_2SO_4

(c) Decimolar $BaCl_2$

(d) A solution obtained by mixing equal volumes of (b) & (c)

Part C: Depression in Freezing Point

26. The freezing point of equimolal aq. solution will be highest for

(a) $C_6H_5NH_3Cl$ (b) $Ca(NO_3)_2$ (c) $La(NO_3)_4$ (d) $C_6H_{12}O_6$

27. The freezing point of aqueous solution containing 5% by mass urea, 1% by mass KCl and 10% by mass of glucose is

(a) 290.2 K (b) 285.5 K (c) 269.93 K (d) 250 K

28. A complex is represented as $CoCl_3.xNH_3$. Its 0.1 M aq. solution shows $\Delta T_f = 0.558°C$ ($K_f(H_2O) = 1.86\ mol^{-1}\ K$) and assume 100% ionization and coordination no. of Co(III) is six. What is the complex ?

(a) $[Co(NH_3)_4Cl_2]Cl$ (b) $[Co(NH_3)_6]Cl_3$ (c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(NH_3)_5Cl]Cl_2$

29. Which of the following has been arranged in the order of decreasing freezing point ?

(a) 0.05 M KNO_3 > 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$

(b) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3

(c) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3

(d) 0.075 M $CuSO_4$ > 0.05 M KNO_3 > 0.140 M sucrose > 0.04 M $BaCl_2$

30. A solution contains 0.1 M of acetamide in 1 litre of glacial acetic acid. When the solution is cooled, the first crystal that appeared at the freezing point contains the molecule of

(a) acetamide only (b) acetic acid only

(c) both acetamide and acetic acid (d) None

31. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water to –9.3°C is ($K_f = 1.86$ K kg mol^{-1})

(a) 38.71 g (b) 38.71 mg (c) 42 g (d) 42 mg

32. What will be the molecular weight of $CaCl_2$ determined in its aq. solution experimentally from depression of freezing point?

(a) 111 (b) < 111 (c) > 111 (d) data insufficient

33. The freezing point depression of 0.1 M of solution of weak acid (HX) is –0.20°C. What is the value of equilibrium constant for the reaction

$$HX(aq) \longrightarrow H^+(aq) + X^-(aq)$$

Given – K_f for water = 1.8 K kg mol^{-1} & (molality = molarity)

(a) 1.46×10^{-4} (b) 1.35×10^{-3} (c) 1.21×10^{-2} (d) 1.35×10^{-4}

Part D: Osmotic Pressure

34. Osmotic pressure of blood is 7.40 atm at 27°C. Number of moles of glucose to be used per L for an intravenous injection that is to have the same osmotic pressure as blood is :

(a) 0.3 (b) 0.2 (c) 0.1 (d) 0.4

35. Osmotic pressure of 30% solution of glucose is 1.20 atm and that of 3.42% solution of cane sugar is 2.5 atm. The osmotic pressure of the mixture containing equal volumes of the two solutions will be

(a) 2.5 atm (b) 3.7 atm (c) 1.85 atm (d) 1.3 atm.

36. Which has maximum osmotic pressure at temperature T :

(a) 100 mL of 1 M urea solution

(b) 300 mL of 1 M glucose solution

(c) mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution

(d) all are isotonic

37. If 6 g of urea, 18 gm glucose & 34.2 gm sucrose is dissolved to make 500 ml of a solution at 300 K, what is the osmotic pressure ?

(a) 4.92 atm (b) 9.84 atm (c) 14.77 atm (d) 12.96 atm

38. Ba^{2+} ions, CN^- & Co^{2+} ions form a water soluble complex with Ba^{2+} ions as free cations for a 0.01 M sol. of this complex, osmotic pressure = 0.984 atm & degree of dissociation = 75%). Find the coordination no. of Co^{2+} ion in this complex (T = 300 K, R = 0.082 L atm K^{-1} mol^{-1})

(a) 5 (b) 4 (c) 6 (d) 7

39. If 200 ml of 0.2 M $BaCl_2$ solution is mixed with 500 ml of 0.1 M Na_2SO_4 solution. What is the osmotic pressure of resulting solution

(a) 6.685 atm (b) 12.307 atm (c) 3.162 atm (d) 4.927 atm

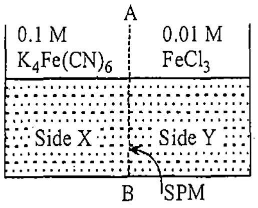
40. The value of observed and calculated mole weight of silver nitrate are 92.64 and 170 respectively. The degree of dissociation is

(a) 60% (b) 83.5% (c) 46.7% (d) 60.23%

41. Among the following the solution which shows the highest osmotic pressure is

(a) 0.5 M NaCl (b) 0.10 M $BaCl_2$ (c) 0.05 M $FeCl_3$ (d) 0.05 M Na_2SO_4

42. $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is



(a) blue colour formation in side X.

(b) blue colour formation in side Y.

(c) blue colour formation in both of the sides X and Y.

(d) no blue colour formation.

EXERCISE II

More Than One Correct Type

1. In which case van't Hoff factor are equal ?

(a) KCl, 50% ionised (b) K_2SO_4, 40% ionised

(c) $FeCl_3$, 30% ionised (d) $SnCl_4$, 20% ionised

2. For the given electrolyte A_xB_y, the degree of dissociation 'α' can be given as

(a) $\alpha = \frac{i-1}{x+y-1}$ (b) $i = (1-\alpha) + x\alpha + y\alpha$

(c) $\alpha = \frac{1-i}{1-x-y}$ (d) None

3. Which has the equal boiling point ?

(a) 0.1 M Na_2SO_4 (b) 0.1 M $C_6H_{12}O_6$ (glucose)

(c) 0.1 M $MgCl_2$ (d) 0.1 M $Al(NO_3)_3$

4. Which of the following is correct for an ideal solution ?

(a) Raoult's law is obeyed for entire concentration range and temperatures

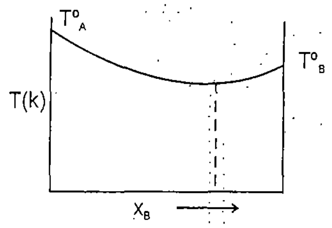
(b) $\Delta H_{mix} = 0$ (c) $\Delta V_{mix} = 0$ (d) $\Delta S_{mix} = 0$

5. Which of the following will form non-ideal solution ?

(a) C_2H_5OH and water (b) HNO_3 and water

(c) $CHCl_3$ and CH_3COCH_3 (d) C_6H_6 and $C_6H_5CH_3$

6. The diagram given below represents boiling point composition diagram of solution of component A and B, which is/are incorrect among the following?



(c) The solution is ideal solution (d) The solution shows positive deviation.

7. Which of the following is/are correct for an ideal binary solution of two volatile liquids (eg. benzene & toluene)?

(a) Its vapour is always richer in the more volatile component (compared to the liquid).

(b) The liquid will gradually become richer in the less volatile component if such a mixture is boiled (distilled).

(c) The P_T (ie. the total pressure) above the solution will be the sum of the vapour pressures of the two pure components.

(d) The boiling point of the solution will be less than the boiling points of the two components.

8. For chloroform and acetone or for a solution of chloroform and acetone if p_s (observed (actual)) is compared with p_s (Theoretical (Raoult)) then which of the following is /are true ?

(a) $p_s(\text{actual}) < p_s(\text{raoult})$ (b) $\overset{\text{Limit}}{X_{\text{chloroform}}} \longrightarrow 0 \ (p^{o}_{\text{acetone}} - p_{s\ \text{actual}}) = 0$

(c) $\overset{\text{Limit}}{X_{\text{acetone}}} \longrightarrow 0 \ (p^{o}_{\text{chloroform}} - p_s\,(\text{actual})) = 0$ (d) $p^{o}_{\text{acetone}} > p^{o}_{\text{chloroform}}$ near room temperature

9. In which of the following pairs of solutions will the values of the vant Hoff factor be the same?

(a) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$

(b) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4\,(NH_4)_2SO_4 \cdot 6H_2O$

(c) 0.20 M NaCl and 0.10 M $BaCl_2$

(d) 0.05 M $FeSO_4\,(NH_4)_2SO_4 \cdot 6H_2O$ and 0.02 M $KCl \cdot MgCl_2 \cdot 6H_2O$

10. When 100 ml of 0.2M $BaCl_2$ (aq) is added to 100ml of 0.2M K_2SO_4 solution, _______of K_2SO_4 solution is lowered. Assume 100% dissociation of soluble salts and 100% precipitation of insoluble ones.

(a) Freezing point (b) Boiling point (c) Vapour pressure (d) Osmotic pressure

11. Which pair will show positive deviation from raoult's law

(a) Methanol and chloroform (b) Methanol and cyclo pentane

(c) Ethanol + cyclohexane (d) Toulene + benzene

12. Select the incorrect statements

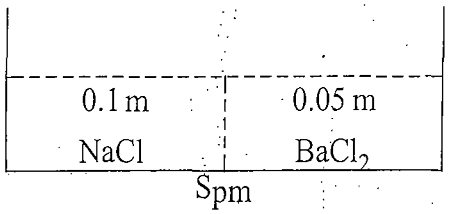
(a) The freezing of water is an endothermic process

(b) Addition of any substance to water lowers it freezing point

(c) At freezing point or below it, the freezing of both solute and solvent occurs

(d) In freezing, $\Delta S_{\text{solvent}} < \Delta S_{\text{solution}}$

13. Study the following figure, and choose the correct option (s)



(a) There will be no movement of any substance across the membrane

(b) $BaCl_2$ will flow towards the NaCl solution.

(c) The osmotic pressure of 0.1 M NaCl is higher than the osmotic pressure of 0.05 M $BaCl_2$ assuming complete dissociation of electrolyte

(d) NaCl will flow towards the $BaCl_2$ solution

EXERCISE III

Numerical Answer Type

1. The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

2. Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?

3. What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?

   $P_b^{\circ}=119$ torr and $P_t^{\circ}=37$ torr

4. Liquid A and B form an ideal solution. The vapour pressure of A and B at 100°C are 300 and 100 mm Hg respectively. Suppose that vapour above solution is composed of 1 mole of A and 1 mole of B is collected and condensed. This condensate is then heated at 100°C and vapour are again condensed to form a liquid L. What is the mole fraction of A in the vapours of L ?

5. The density of a 0.438 M solution of potassium chromate at 298 K is 1.063 g cm^{-3}. Calculate the vapour pressure of water above this solution.

   Given : P^0 (water) = 23.79 mm Hg.

6. The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calcualte molality of the solution.

7. A solution containing 3.24 g of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)

8. The elements X and Y form compounds having molecular formula XY_2 and XY_4. When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3°, whereas 1 gm of XY_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

9. Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. K_f(water) = 1.86kg.mol^{-1}.K.

10. A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877%(w/v) of urea solution. Find molecular weight of urea.

11. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be105.3 mm. Determine extent of dilution.

12. 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

13. Calculate the osmotic pressure of sucrose solution containing 1.75 gms in 150 ml of solution at 17°C.

14. 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol^{-1}. What is the percentage association of the acid?

15. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. (R=8.314 JK^{-1} mol^{-1})

16. Pure benzene freeze at 5.45°C. A solution containing 7.24 g of $C_2H_2Cl_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?

17. The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

18. What is the osmotic pressure of a solution having 0.1 M NaCl & 0.2 M Na_2SO_4 and 0.5 M HA. (Given weak acid is 20% dissociated at 300 K)

19. If 200 ml of 0.2 M $HgCl_2$ sol is added to 800 ml of 0.5 M KI (100% dissociated) solution assuming that the following complex formation taken place to 100% extent

$$Hg^{2+} + 4I^- \rightleftharpoons [HgI_4]^{2-}$$

What is the osmotic pressure of the resulting solution at 300 K.

20. River water is found to contain 11.7% NaCl, 9.5% $MgCl_2$ and 8.4% $NaHCO_3$ by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of $MgCl_2$ and 50% ionization of $NaHCO_3$. (K_b for water = 0.52)

21. A 1.2% solution (W/V) of NaCl is isotonic with 7.2% solution (W/V) of glucose. If degree of ionization is x & van't hoff factor of NaCl is y. Then what is 2x + y ?

EXERCISE IV

Previous Year Questions

IIT-JAM Previous Year Questions

1. For an ideal solution formed by mixing of pure A and B

(a) $\Delta H_{mix} = 0$ (b) $\Delta H_{mix} < 0$ (c) $\Delta H_{mix} > 0$ (d) $\Delta S_{mix} = 0$

2. Additon of 1.0 g of a compound to 10 g of water increases the boiling point by 0.3°C. The amount of compound needed to prepare a 500 ml or 0.1 M solution is (given : assume negligible dissociation or association of the compound, boiling point constant K_b of water = 0.513 K kg mol^{-1})

(a) 0.855 g (b) 17.1 g (c) 8.55 g (d) 85.5 g

3. An aqueous solution containing 1g/L of a polymer exerts osmotic pressure of 4 torr at 300 K. Given R = 0.082 L atm, the molar mass (g/mol) of the polymer is

(a) 4500 (b) 4564 (c) 4674 (d) 4800

4. The amount (in grams) of potassium dichromate (MW = 294) present in 75 mL of 0.16 M aqueous solution is ________.

5. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm^3. Determine the molecular weight of the protein.

6. The vapour pressure of D_2O at 20°C is 745 mm Hg. When 15 g of a non-volatile compound is dissolved in 200 g of D_2O, the pressure changes to 730 mm Hg. Assuming the applicability of Raoult's law, calculate the molecular weight of the compound.

7. One mole of a salt of type MX is dissolved in 1.00 kg of water. The freezing point of the solution is –2.4 °C. Calculate the percent dissociation of the salt in water.

8. At 20°C, the vapour pressure of two pure liquids X and Y which form an ideal solution are 70 torr and 20 torr respectively. If the mole fraction of X in solution is 0.5. Find the mole fractions of X and Y in the vapour phase in equilibrium with the solution.

IIT-JEE Previous Year Questions

8. The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is
(a) 91.3% (b) 87% (c) 100% (d) 74%

9. In the depression of freezing point experiment, it is found that
(I) The vapour pressure of the solution is less than that of pure solvent.
(II) The vapour pressure of the solution is more than that of pure solvent.
(III) Only solute molecules solidify at the freezing point.
(IV) Only solvent molecules solidify at the freezing point.
(a) I, II (b) II, III (c) I, IV (d) I, II, III

10. During depression of freezing point in a solution, the following are in equilibrium
(a) liquid solvent-solid solvent (b) liquid solvent-solid solute
(c) liquid solute-solid solute (d) liquid solute-solid solvent

11. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(a) 25% (b) 50% (c) 75% (d) 85%

12. The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is [Some useful data, K_b (H_2O) = 0.52 kg K mol^{-1}, mol. wt. of $CuCl_2$ = 134.4 gm]
(a) 0.05 (b) 0.1 (c) 0.16 (d) 0.21

13. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (k_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is
(a) 0.5 (b) 1 (c) 2 (d) 3

14. The freezing point (in °C) of solution containing 0.1 g of $K_3[Fe(CN)_6]$ (mol. wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is
(a) –0.02°C (b) –0.13°C (c) –0.05°C (d) –0.14°C

15. For a dilute solution, Raoult's law states that

(a) the lowering of vapour pressure is equal to the mole fraction of solute

(b) the relative lowering of vapour pressure is equal to the mole fraction of solute

(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution

(d) the vapour pressure of the solution is equal to the mole fraction of solvent

16. Which of the following 0.1 M aqueous solution will have the lowest freezing point?

(a) Potassium sulphate (b) Sodium chloride

(c) Urea (d) Glucose

17. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to

(a) ionization of benzoic acid (b) dimerization of benzoic acid

(c) trimerization of benzoic acid (d) solvation of benzoic acid

18. A solution of a nonvolatile solute in water freezes at –0.30°C. The vapour pressure of pure water at 298K is 23.51mmHg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298K.

19. To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively.

20. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii) 100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively.

(a) What are the molecular weights of benzoic acid in both the solutions?

(b) What do you deduce out of it in terms of structure of benzoic acid?

21. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance?

22. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

23. Addition of 0.643 g of a compound to 50 mL of benzene (density: 0.879 g/mL) lowers the freezing point from 5.51°C to 5.03°C. If k_f for benzene is 5.12, calculate the molecular weight of the compound.

24. What weight of the non-volatile solute urea ($NH_2 - CO - NH_2$) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

TIFR Previous Year Questions

25. Vapour pressure of a liquid in a closed container depends upon

(a) volume of the container (b) volume of the liquid

(c) temperature (d) both B & C

26. When 10 ml of each of liquid pairs listed below are mixed and then allowed to stand, which pair is most likely to seperate into two layers ?

(a) carbon tetrachloride and hexane (b) ethanol and methanol

(c) carbon tetrachloride and methanol (d) hexane and pentane

27. What is the molecule mass 1 (M) of a compound that has a concentration W = 1.2 g/L and an osmotic pressure of A = 0.20 atm and at T = 300 K ?

(a) M = 576 g/mol (b) M = 3876 g/mol (c) M = 147 g/mol (d) M = 9818 g/mol

28. Which of the following observations reflect colligative properties?

(i) A 0.5 M NaCl solution has a higher vapor pressure than a 0.5 M $BaCl_2$ solution.

(ii) A 0.5 M NaOH solution freezes at a lower temperature than pure water.

(iii) Pure water freezes at a higher temperature than pure methanol.

(a) (i) and (ii) only (b) (i) and (iii) only (c) (ii) and (iii) only (d) (i), (ii) and (iii)

CHEMACADEMY

ANSWER KEY

EXERCISE I

1. c 2. c 3. a 4. a 5. c 6. c 7. c
8. a 9. a 10. b 11. c 12. d 13. b 14. b
15. b 16. d 17. c 18. b 19. b 20. c 21. b
22. b 23. d 24. d 25. a 26. d 27. c 28. d
29. a 30. b 31. a 32. b 33. b 34. a 35. c
36. d 37. c 38. a 39. a 40. b 41. b 42. d

EXERCISE II

1. b,d 2. a,b,c 3. a,c 4. a,b,c 5. a,b,c 6. a,b,c 7. a,b
8. a,b,c,d 9. b,d 10. b,d 11. b,c 12. a,b,c 13. c

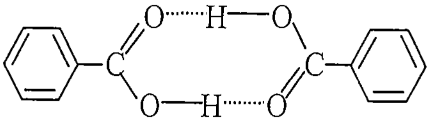
EXERCISE III

1. 0.25
2. $P_A^o = 213.33$ torr, $P_B^o = 960$ torr
3. 0.682, 0.318; 0.829, 0.171
4. 0.9
5. 23.22 mm Hg
6. 0.741 atm
7. 64.0 g/mol
8. x = 25.6, y = 42.6
9. –2.28°C
10. 59.99
11. $V_{final} = 5\ V_{original}$
12. 0.3
13. 0.812 atm
14. 99.2%
15. 7.482×10^5 N m^{-2}
16. 5.08°C / M
17. C_6H_6
18. 34.482 atm
19. 18.69 atm
20. 105.68°C
21. 3.85

EXERCISE IV

1. a 2. c 3. c 4. 3.528 5. 39.885 kg 6. 73
7. 29% 8. b 9. c 10. a 11. c 12. c 13. a
14. a 15. b 16. a 17. b 18. 23.44 mm Hg 19. 0.229°C

20. (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene as

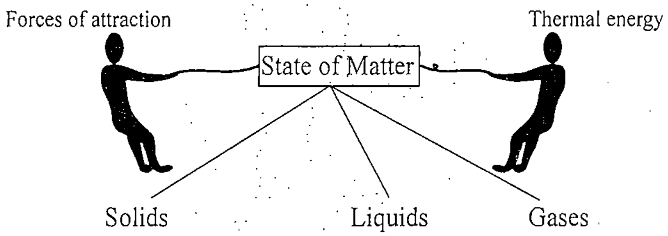


21. 65.25
22. 746.24 mm Hg
23. 156 g/mol
24. 111 g, 18.5
25. c 26. c 27. c 28. a

CHAPTER 11

GASEOUS STATE

KEY CONCEPTS



Parameters:

(i)	Forces of attraction	👍	✋	👎
(ii)	Thermal energy	down	moderate	up
(iii)	Space	down	moderate	up
(iv)	Shape	up	down	down
(v)	Volume	up	up	down
(vi)	Density	up	up	down

Ideal Gas: A gas with no intermolecular attractions & having very negligible volume occupied by molecules when compared with volume of gas is termed as ideal gas. A theoretical concept which for gases present can be obtained only under certain condition.

Real Gas: Considerable forces of attraction & appreciable size of molecules. These under " certain conditions" behave like ideal. (High Temperature Low Pressure)

Parameter associated with the gas : P, V, T, n

where

P represents pressure exerted by the gas molecules on the walls of the container assuming negiligible intermolecular attractions,

V represents free volume available for motion (equal to the volume of the container),

T represents absolute temperature, **n** represents no of moles.

Conversion factors : Pressure → 1 **atm** =1.013 × 10^5 **Pa** = 760 **mm of Hg** = 760 **torr** = 1.013 **bar**

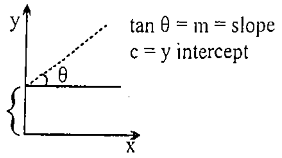
Volume →1 *l* = 1**dm^3** = 10^{-3} **m^3** = 1000 **ml** = 1000 **cm^3**

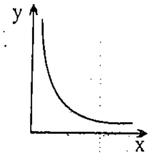
Temperature → $T_K = T_C^{\circ} + 273 = \frac{5}{9} T_F^{\circ} + 255.22$

EQUATION & GRAPHS OF EXTENSIVE UTILITY IN GASEOUS STATE :

Two Parameters 'y' & 'x' if are related as

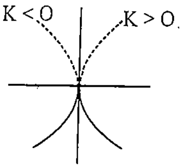
(a) $y = mx + C$ (where m & C are constants) [then there will be a <u>direct relationship</u> between them & graph will be a straight line as shown]
$y = mx + C$ (straight line)



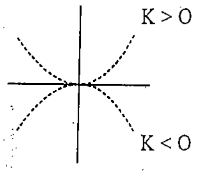


(b) xy = constant (rect hyperbola) / $y = \frac{m}{x} + C$ (where m & C are constant)

(c) $y^2 = Kx$ (K is a constant)



(d) $x^2 = Ky$ (K is a constant)



Experimental Gas laws: Relationship between various parameter of the gas. Gaseous state is the only state that allows a quantitative descriptive between the four parameters, P, V, T & n. The relationship which connects the four variables is known as equation of state, which can be obtained experimentally from the following gas laws.

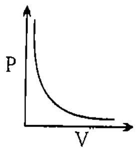
All are based on experimental data.

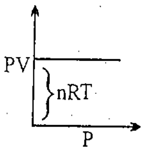
All are applicable for ideal gases only.

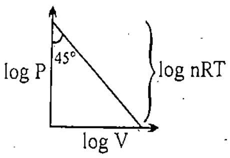
Get yourselves comfortable with all the various types of graphs to get a 'feel' of them.

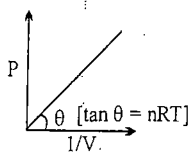
I. **Boyle's law** $V \propto \frac{1}{P}$ $\begin{pmatrix} T, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $P_1V_1 = P_2V_2$

graphs are Isotherms



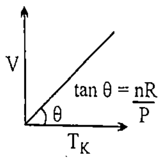


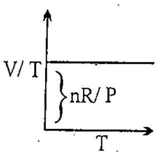


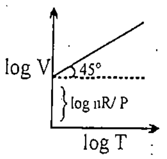


II. **Charle's law** $V \propto T$ $\begin{pmatrix} P, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

graphs are Isobars

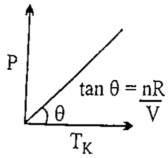


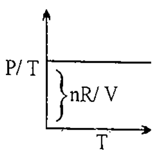


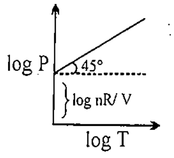


III. **Gay Lussac's law** $P \propto T$ $\begin{pmatrix} V, \text{constant} \\ n \text{ constant} \end{pmatrix}$ $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

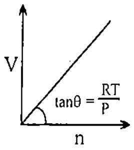
graphs are Isochor

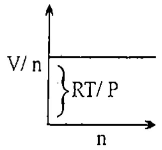


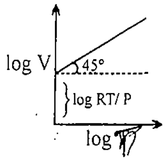




IV. **Avogadro's law** $V \propto n$ (T, P constant) $\frac{V_1}{n_1} = \frac{V_2}{n_2}$







Combined Gas Law : $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

Equation Of State : $PV = nRT$

d = density of gas

$\Rightarrow PV = \frac{w}{M} RT$ R = Universal Gas constant = 0.0821 atm litres /kelvin/mol

$\Rightarrow PM = dRT$ = 8.314 joule/kelvin/mol = 2cal / kelvin/mol

Dalton's law of partial pressure:

$P_{total} = P_A + P_B + ...$; ✓ $\boxed{P_{wet\ gas} = P_{dry\ gas} + P_{H_2O\ vapour} \text{ i.e. aq. tension.}}$

P_A, P_B are partial pressures . ; P_A = mole fraction$_A$ × Total pressure

and % of gas in mixture = $\frac{\text{Partial pressure}}{\text{Total pressure}} \times 100$.

Graham's law of Diffusion & Effusion :

$r \propto \frac{1}{\sqrt{d}}$ or $r \propto \frac{1}{\sqrt{M}}$ $r \propto \frac{P}{\sqrt{M}}$ [For gases effusing at different pressures]

r is rate of diffusion of any gas.

$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$; $\frac{\text{volume / time}}{\text{volume / time}} = \sqrt{\frac{M_2}{M_1}}$ **d** is density at some temperature.

$$r = \frac{\text{moles diffused}}{\text{time taken}} = \frac{\text{distance travelled in a narrow tube}}{\text{time taken}} = \frac{\text{Pressure drop I}}{\text{Pressure drop II}}$$

Kinetic theory of gases :

$$PV = \frac{1}{3} m N u^2_{rms} = \frac{1}{3} M u^2_{rms} \text{ (For 1 mole)}$$

Types of velocities :

1. **root mean square speed,** $U_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + ... + u_N^2}{N}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{m}} = \sqrt{\frac{3P}{d}}$

2. **Average speed** (U_{avg}) $= \frac{u_1 + u_2 + ... + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$

3. **Most probable speed** (U_{mp}) $= \sqrt{\frac{2RT}{M}}$

Note: Take R = 8.314 Pa m^3 k^{-1} mol^{-1} & molar mass is kilograms

most probable : average : r. m. s. = 1 : 1.13 : 1.22
$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$

Relationship between three types of speeds

$$u_{rms} > u_{av} > u_{mp}$$

Average kinetic energy of a single molecule $= \frac{3}{2} \cdot \frac{R}{N_A} \cdot T = \frac{3}{2} kT$

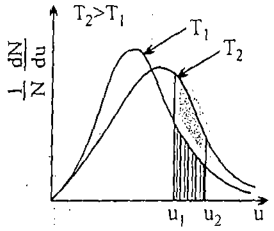
k = Boltzman constant $= 1.3806 \times 10^{-23}\ JK^{-1}$

Total kinetic energy for **one mole** of a gas $= \frac{3}{2} RT$.

kinetic energy of **n moles** of a gas $= n \times \frac{3}{2} RT$

Maxwell distribution Laws: $dN_u = 4\pi N \left(\frac{M}{2\pi RT}\right)^{3/2} \exp(-Mu^2 / 2RT)\, u^2\, du$

$$= 4\pi N \left(\frac{M}{2\pi kT}\right)^{3/2} \exp(-mu^2 / 2kT)\, u^2\, du$$



Collision frequency & Mean Free Path :

Mean free path $\lambda = \frac{d_1 + d_2 + \ldots\ldots + d_n}{n}$

$$\lambda = \frac{\text{Average velocity / RMS velocity}}{\text{collision number or frequency}} = \frac{kT}{\sqrt{2}\,\pi\,\sigma^2\,P}$$

k = Boltzman constant ; σ = collision diameter .

$Z_1 = \sqrt{2}\,\sigma^2 \bar{u} N^*$ [collisions made by one molecule

$$Z_{11} = \frac{1}{\sqrt{2}}\,\sigma^2 \bar{u} N^{*2}$$

THE REAL PATH

Vander Waals equation of state :

$$\left(P + \frac{a}{V^2} \cdot n^2\right)(v - nb) = nRT.$$

a , b are Vander Waals constants ; different for each gas

unit of a ⟶ $atm\ L^2\ mol^{-2}$; S.I. unit ⟶ $P_a\ m^6\ mol^{-2}$

unit of b ⟶ $L\ mol^{-1}$; S.I. unit ⟶ $m^3\ mol^{-1}$

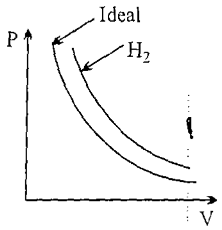
greater the value of 'a' more easily the gas is liquefiable ; $a = \frac{PV^2}{n^2}$

greater the value of 'b' greater the molecular size, $b = 4 \times N_A \times \frac{4}{3}\pi r^3$.

v = volume occupied by all the gas molecules .

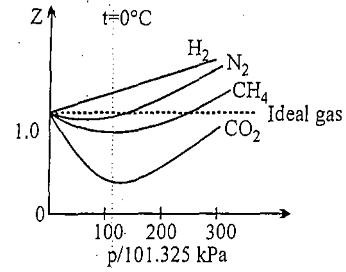
Real gases: Deviation from ideal behaviour

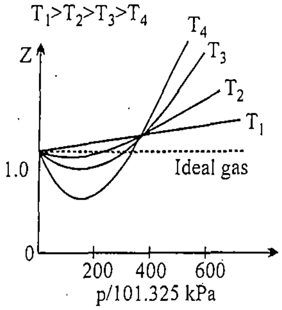
The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume is large. At higher pressures, however deviations are observed.



Compressibility factor:

$$z = \frac{PV}{nRT} = \frac{V_{real}}{V_{ideal}}$$





Boyle Temperature :

$$T_B = \frac{a}{bR}$$

Interpretation Of Deviation From Vander Waals Equation :

(i) At low pressure $z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$

(ii) At high pressure $z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$

(iii) At extremely low pressure $z = \frac{PV}{RT} = 1$; $Pb = \frac{a}{V}$

SOME OTHER EQUATION OF STATE

Dieterici Equation:

$$Pe^{na/VRT} \times (V - nb) = nRT$$

Berthelot Equation :

$\left(P + \frac{n^2 a}{TV^2}\right)(V - nb) = nRT$ (a & b are Berthlot's constant different from vander Waal's constant)

Virial Equation Of State For 1 Mole Of Gas :

$z = \frac{PV}{RT} = 1 + B\frac{1}{V} + C\frac{1}{V^2} + D\frac{1}{V^3} + ...$ (B, C, D... are temp. dependent constant)

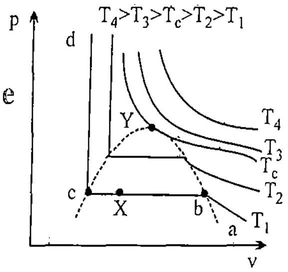
for vander waal's gas B = second virial co–efficient $= b - \frac{a}{RT}$

C = third virial co–efficient $= b^2$.

gas dependent

Critical Phenomenon: Critical Temp, Critical pressure, Critical volume

$$T_c = \frac{8a}{27Rb} \; ; \quad P_c = \frac{a}{27b^2} \; ; \quad V_c = 3b$$



EXERCISE I

Single Correct Type

Ideal Gases

1. A gas occupies 100.0 mL at 50°C and 1 atm pressure. The gas is cooled at constant pressure so that volume is reduced to 50.0 mL. What is the final temperature.

(a) –111.5°C (b) 111.5°C (c) 111.5 K (d) 384 K

2. If the temp. of a particular amount of gas is increased from 27°C to 57°C, find final volume of the gas, if initial volume = 1 lt and assume pressure is constant.

(a) 1.0 L (b) 1.1 L (c) 0.9 L (d) 2 L

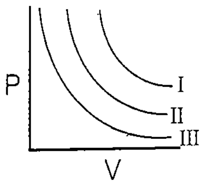
3. If the pressure of a gas contained in a closed vessel is increased by 0.4 % when heated by 1°C its initial temperature must be :

(a) 250 K (b) 250°C (c) 25°C (d) 25 K

4. Four one litre flasks are separately filled with the gases, O_2, F_2, CH_4 and CO_2 under the same conditions. The ratio of number of molecules in these gases :

(a) 2 : 2 : 4 : 3 (b) 1 : 1 : 1 : 1 (c) 1 : 2 : 3 : 4 (d) 2 : 2 : 3 : 4

5. I, II, III are three isotherms respectively at T_1, T_2 and T_3 as shown in graph. Temperature will be in order

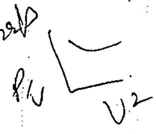


(a) $T_1 = T_2 = T_3$ (b) $T_1 < T_2 < T_3$ (c) $T_1 > T_2 > T_3$ (d) $T_1 > T_2 = T_3$

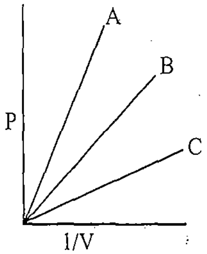
6. Which of the following curve does not shows a linear variation (slope either +ve or –ve)?

(a) P v/s 1/V (b) log P v/s log V (c) P/V v/s $1/V^2$ (d) P/V v/s V^2

Perhaps



7.



Identify the gases A, B, C if the graph is plotted for same amount gas at constant temperature?

(a) A – CH_4, B – N_2, C – He (b) A – CH_4, B – He, C – N_2

(c) A – He, B – CH_4, C – N_2 (d) A – N_2, B – CH_4, C – He

8. The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be

(a) 1 : 6 (b) 7 : 8 (c) 6 : 1 (d) 1 : 4

9. The density of a mixture of O_2 and N_2 at NTP is 1.3 g litre^{-1}. What is the partial pressure of N_2

(a) 1.725 atm (b) 0.725 atm (c) 0.593 atm (d) 1.593 atm

11.
12
13
14
15
Kinet
16.
17.
18.
19.
20.
21.

V => 11 L

10. A 11 litre flask contains 20g of neon and an unknown weight of hydrogen. The gas density is found to be 2g/litre at 0^0C. What is the average molecular weight?

(a) 11 (b) 12 (c) 13 (d) 10

11. A and B are two identical vessels. A contains 15 g ethane at 1atm and 298 K. The vessel B contains 75 g of a gas X_2 at same temperature and pressure. The vapour density of X_2 is :

(a) 75 (b) 150 (c) 37.5 (d) 45

12. A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Partial pressure of hydrogen will be

(a) 0.2 bar (b) 0.4 bar (c) 0.6 bar (d) 0.8 bar

13. 2 moles of NH_3 & 1 mol of HCl are kept in 8.21 L container. The temperature is 300 K. Calculate the final pressure after the reaction. Given NH_4Cl is solid.

(a) 0.5 atm (b) 1 atm (c) 2 atm (d) 4 atm

14. The partial pressure of hydrogen in a flask containing two grams of hydrogen and 32 gm of sulphur dioxide is :

(a) 1/16th of the total pressure (b) 1/9th of the total pressure

(c) 2/3 of the total pressure (d) 1/8th of the total pressure

15. An amount of 1.00 g of a gaseous compound of boron and hydrogen occupies 0.820 liter at 1.00 atm and at 3^0C. The compound is (R = 0.0820 liter atm $mole^{-1}$ $^0K^{-1}$; at. wt: H = 1.0, B = 10.8)

(a) BH_3 (b) B_4H_{10} (c) B_2H_6 (d) B_3H_{12}

Q 10.
$m_2 = 2g$
$n_{Ne} = 1$
$n_{H_2} = 1$
$M_{mix} = \frac{22}{2} = 11$
$M_{mix} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$
11
E M.M

Kinetic Theory of Gases

16. What is the value of total KE of 0.5 mol of an ideal gas at 273 K

(a) 1702 J (b) 1803 J (c) 2053 J (d) 1930 J

17. The ratio between the r. m. s. velocity of H_2 at 50 K and that of O_2 at 800 K is :

(a) 4 (b) 2 (c) 1 (d) 1/4

18. At what temperature K.E. of a gas molecules is half of its value at 327°C?

(a) 13.5°C (b) 150°C (c) 27°C (d) -123°C

19. Which statement is correct?

(a) K.E. of molecules is highest in solid state

(b) P.E. is lowest in solid state

(c) K.E. of molecules is highest in gaseous state ✓

(d) Torr is a unit of temperature

20. Most probable speed, average speed and RMS speed are related as :-

(a) 1:1.28 : 1.224 (b) 1:1.28 : 1.424 (c) 1: 1.128 : 1.224 (d) 1:1.428:1.442

21. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom

(a) two times that of a hydrogen molecule (b) same as that of a hydrogen molecule

(c) four times that of a hydrogen molecule (d) half that of a hydrogen molecule

22. According to the kinetic theory of gases, for a diatomic molecule

(a) the pressure exerted by the gas is proportional to the mean speed of the molecules

(b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules

(c) the root mean square speed of the molecules is inversely proportional to the temperature

(d) the mean translation kinetic energy of the molecules is proportional to the absolute temperature

23. The ratio of average speed of an oxygen molecule to the rms speed of a nitrogen molecule at the same temperature is –

(a) $\left(\frac{3\pi}{7}\right)^{1/2}$ (b) $\left(\frac{7}{3\pi}\right)^{1/2}$ (c) $\left(\frac{3}{7\pi}\right)^{1/2}$ (d) $\left(\frac{7\pi}{3}\right)^{1/2}$

24. At what temperature will be total kinetic energy (KE) of 0.30 mole of He be the same as the total KE of 0.40 mole of Ar at 400 K –

(a) 400 K (b) 373 K (c) 533 K (d) 300 K

25. If for two gases of molecular weights M_A and M_B at temperature T_a and T_B, $T_AM_B = T_BM_A$, then which property has the same magnitude for both the gases-

(a) Density (b) Pressure (c) KE per mol (d) RMS speed

26. The ratio of the average molecule kinetic energy of UF_6 to that of H_2, both at 300 K is –

(a) 1 : 1 (b) 7 : 2 (c) 176 : 1 (d) 2 :7

27. Which of the following statement is not correct about the states of matter?

(a) Molecules of gases possess least energy

(b) Molecules of solids are least energetic

(c) Molecules of liquids have slow molecular motion

(d) Interparticle forces are maximum in solids

28. In a container of capacity 1 litre there are 10^{23} molecules each of mass 10^{-22} gms. If root mean square speed is 10^5 cm/sec and the pressure is $1/3 \times 10^x$ Pascals. What is the value of x?

(a) 6 (b) 7 (c) 8 (d) 9

29. The rates of diffusion of SO_3, CO_2, PCl_3 and SO_2 are in the following order -

(a) $PCl_3 > SO_3 > SO_2 > CO_2$ (b) $CO_2 > SO_2 > PCl_3 > SO_3$

(c) $SO_2 > SO_3 > PCl_3 > CO_2$ (d) $CO_2 > SO_2 > SO_3 > PCl_3$

30. 20 ℓ of SO_2 diffuses through a porous partition in 60 seconds. Volume of O_2 diffuse under similar conditions in 30 seconds will be :

(a) 12.14 ℓ (b) 14.14 ℓ (c) 18.14 ℓ (d) 28.14 ℓ

31. If a gas is allowed to expand at constant temperature then which of the following does hold true:

(a) the kinetic energy of the gas molecules decreases

(b) the kinetic energy of the gas molecules increases

(c) the kinetic energy of the gas molecules remains the same

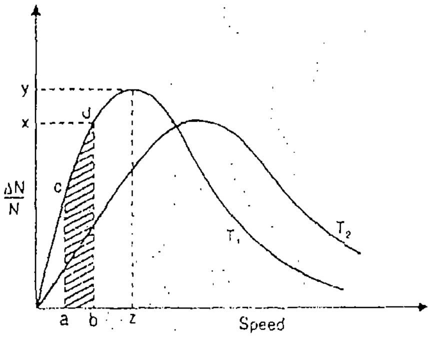
(d) Can not be predicted

32. The mass of molecule A is twice that of molecule B. The root mean square velocity of molecule A is twice that of molecule B. If two containers of equal volume have same number of molecules, the ratio of pressure P_A/P_B will be :

(a) 8 : 1 (b) 1 : 8 (c) 4 : 1 (d) 1 : 4

Maxwell Distribution of Molecular Speeds and Molecular Collisions

33. Consider the given curve



(i) The correct relationship among T_1 & T_2 is

(a) $T_1 < T_2$ (b) $T_2 > T_1$ (c) $T_1 = T_2$ (d) Can't be predicted

(ii) The area abcd represents

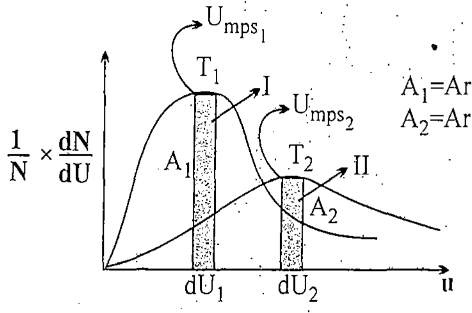
(a) Number of molecules having speed between a and b

(b) Fraction of molecules having speed between a and b

(c) Number of molecules having speed equal to Ump

(d) Fraction of molecules having speed less than Ump

34. Following represents the Maxwell distribution curve for an ideal gas at two temperatures T_1 & T_2. Which of the following option(s) is incorrect?



A_1=Area of small rectangle I
A_2=Area of small rectangle II

(a) Total area under the two curves is independent of moles of gas

(b) If $dU_1 = f\ Umps_1$ & $dU_2 = f\ Umps_2$ then $A_1 = A_2$

(c) $T_1 > T_2$ and hence higher the temperature, sharper the curve.

(d) The fraction of molecules having speed = Umps decreases as temperature increases.

3mps

35. What is the ratio of number of molecules having speeds in the range of 2Ump and 2UMp + du to the number of molecules having speeds in the range of Ump and Ump + du?

(a) $4e^{-3}$ (b) $\frac{1}{4}e^{3}$ (c) $4e^{3}$ (d) $\frac{1}{4}e^{-3}$

36. What is the ratio of speed possessed by maximum number of particular to the speed possessed by miniumum number of particles at a constant temperature?

(a) $\sqrt{2}/\sqrt{3}$ (b) $\sqrt{3}/\sqrt{2}$ (c) $\sqrt{8}/\sqrt{2\pi}$ (d) $1/\sqrt{2}$

37. What is the value of fraction of molecules attaining the most probable speed

(a) 1 (b) < 1 (c) > 1 (d) cannot be predicted

Imp

38. 1.4 g of N_2 is present in a container behaves ideally. If the maxwell distribution curve is drawn between $\frac{dN}{dU}$ and U representing y and x, then the correct option is

(a) $\int_0^\infty ydx = 1$ (b) $\int_0^\infty ydx = 3.011 \times 10^{22}$

(c) $\int_0^\infty ydx = \infty$ (d) $\int_0^\infty ydx =$ cannot be determined

39. For an ideal gas, the number of molecules per unit volume N is directly proportion to

(a) PT (b) P/T (c) T/P (d) P/T^2

40. At constant pressure, for a gas,

If λ_1 is the mean free path at temperature T_1 and λ_2 is the mean free path at temperature T_2. ($T_2 > T_1$). Then

(a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 > \lambda_2$ (c) $\lambda_1 < \lambda_2$ (d) Data insufficient

Check

41. For a gas at constant temperature, what is the ratio of collision frequencies at two different temperature 200 K & 800 K?

Pressure

(a) 2 : 1 (b) 1 : 2 (c) 1 : 4 (d) 4 : 1

Real Gases

42. Real gases behave differently from ideal gases because

(i) the molecules of real gases are in constant motion

(ii) the molecules of real gases collide with the walls of the container.

(iii) molecules of real gases have volume

(iv) molecules of real gases attract each other.

(a) i & ii (b) iii only (c) iii & iv (d) all of the above

43. The compressibility factor $z = \left(\frac{PV}{nRT}\right)$ of a gas above $T = \left(\frac{a}{Rb}\right)$ will be

(a) Less than unity (b) Greater than unity (c) Equal of unity (d) None of these

44. What is the S.I. unit of vander waal constant 'a'?

(a) Pa L mol^{-2} (b) Pa m^3 mol^{-2} (c) Pa m^6 mol^{-2} (d) Pa m^6 mol^{-1}

45. For the following statements about compression factor, Z, which of the option is true

(1) At low pressures, almost all gases (NH_3, CH_4, C_2H_4, H_4) show $Z \approx 1$

(2) At high pressures, all gases (NH_3, CH_4, H_2, C_2H_4) show $Z > 1$, which mean attractive forces are dominant

(3) At intermediate pressure, all gases (NH_3, CH_4, H_2, C_2H_4) show $Z < 1$, which means repulsive forces are dominant.

(4) $\dfrac{1}{Z} = \dfrac{\text{molar volume of a perfect gas}}{\text{molar volume of a gas}}$

Very Imp

(a) 1, 2, 3, 4 (b) 1, 2, 3 (c) Only 1 (d) 1 and 4

46. Equations of state for gas A and B are written as $PV_m = RT$ and $P(V_m - b) = RT$, respectively. Which of these gas can be liquefy. (b = positive constant)

(a) Gas A (b) Gas B

Imp (c) Both gas A and B (d) Neither gas A nor gas B

47. 1 mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If van der waal's constants are $a = 20.39\ L^2\ atm\ mol^{-2}$ and $b = 0.1383\ L\ mol^{-1}$, then the value of compressibility factor, Z, under low pressure region and high pressure region will be respectively.

Good

(a) 1.004 and 0.98 (b) 0.98 and 1.004

(c) 0.98 and 0.98 (d) 1.004 and 1.004

48. For the non-zero values of force of attraction between gas molecules, gas equation will be :

(a) $PV = nRT - \dfrac{n^2a}{V}$ (b) $PV = nRT + nbP$ (c) $PV = nRT$ (d) $P = \dfrac{nRT}{V - b}$

49. Calculate the radius of He atoms if its Vander Waal's constant 'b' is 24 ml mol^{-1}.
(Note ml = cubic centimeter)

(a) 1.355 Å (b) 1.314 Å (c) 1.255 Å (d) 0.355 Å

50. Compressibility factor for H_2 behaving as real gas is :

(a) 1 (b) $\left(1 - \dfrac{a}{RTV}\right)$ (c) $\left(1 + \dfrac{Pb}{RT}\right)$ (d) $\dfrac{RTV}{(1-a)}$

51. At low pressures (For 1 mole), the Vander Waal's equation is written as

$$\left[p + \frac{a}{V^2}\right] V = RT$$

The compressibility factor is then equal to :

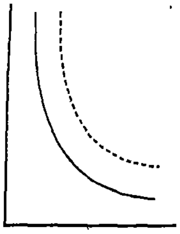
(a) $\left(1 - \dfrac{a}{RTV}\right)$ (b) $\left(1 - \dfrac{RTV}{a}\right)$ (c) $\left(1 + \dfrac{a}{RTV}\right)$ (d) $\left(1 + \dfrac{RTV}{a}\right)$

Imp.

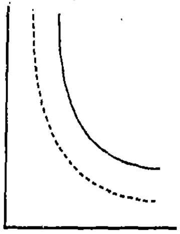
52. Which of the following (P - V) curves represents correctly the deviation of a real gas from an ideal gas?

-------- Real
——— Ideal

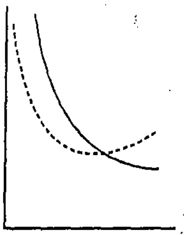
(a)



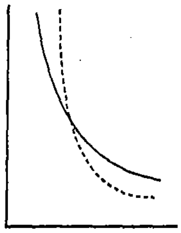
(b)



(c)



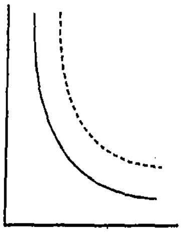
(d)



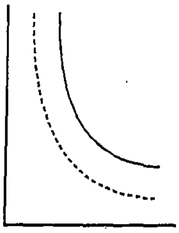
53. Which of the following curves represents the correct variation of H_2 gas w.r.t. an ideal gas at 0°C?

.... H_2
—— ideal gas

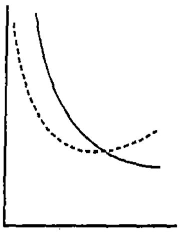
(a)



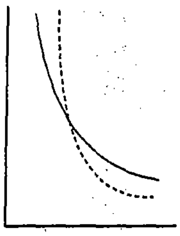
(b)



(c)



(d)



54. Arrange following in decreasing 'a' factor (H_2O, CO_2, Ar)

(1) H_2O, CO_2, Ar (2) He, Ne, Ar, Kr (3) n-pentane, isopentane, neopentane

55. Two vander waals gases have same value of b but different a values ($a_1 > a_2$). Which of these would occupy greater volume under identical conditions ?

56. The value of van der Waal's constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} respectively. The gas which has the most ideal behaviour.

(a) O_2 (b) N_2 (c) NH_3 (d) CH_4

57. Select the correct order of the b values of the gases H_2, N_2, He, Cl_2

(a) $He < H_2 < N_2 < Cl_2$ (b) $He < N_2 < H_2 < Cl_2$

(c) $H_2 < He < N_2 < Cl_2$ (d) $H_2 < He < Cl_2 < N_2$

58. The Vander Waals constants for gases A, B and C are as follows

Gas	a/dm^6 kPa mol^{-2}	b/dm^3 mol^{-1}
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

1 Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 600 K?

59. The vander waals constant for O_2 are a = 1.59 atm L^2 mol^{-2} and b = 0.0318 L mol^{-1}. Calculate the temperature at which O_2 gas behaves, ideally for longer range of pressure.

[Use : R = 0.08 atmL/molK]

(a) 604 K (b) 600 K (c) 60 K (d) 24.5 K

Imp.

60. n moles of Helium gas are placed in a vessel of volume V Litre. at T K. If V_I is ideal volume of Helium then diameter of He atom is

(a) $\left[\frac{3}{2}\frac{V_I}{\pi N_A n}\right]^{\frac{1}{3}}$ (b) $\left[\frac{3(V-V_I)}{2\ \pi N_A n}\right]^{\frac{1}{3}}$ (c) $\left[\frac{6(V-V_I)}{\pi N_A n}\right]^{\frac{1}{3}}$ (d) $\left[\frac{6V_I}{\pi N_A n}\right]^{\frac{1}{3}}$

Hint Excluded volume

⑥① One litre gas at 400 K and 300 atm pressure is compressed to a pressure of 600 atm and 200 K. The compressibility factor is changed from 1.2 to 1.6 respectively. Calculate the final volume of the gas.

(a) $\frac{2}{3}$ L (b) $\frac{1}{3}$L (c) $\frac{1}{4}$L (d) $\frac{3}{4}$L

Liquification of Gases and Critical Constants

62. If two gases A and B have critical temperature 600 K and 500 K respectively, which will liquify first?

63. For a vander waal gas, the value of excluded volume 'b' is

(a) equal to actual volume (b) 2 times of actual volume

(c) 4 times of actual volume (d) 8 times of actual volume

64. For a vander waal gas at critical point, the volume of gas is equal to

(a) 4 times of actual volume (b) 8 times of actual volume

(c) 12 times of actual volume (d) 16 times of actual volume

65. What is the value of Z (compressibility factor) for a vander waal gas at critical state

(a) 0.375 (b) 0.495 (c) 1.375 (d) 1.495

⑥⑥ Find the critical constant (P_c, V_c and T_c) in terms of A and B, also find compressibility factor (z) for the following equation of state.

$$PV = RT - \frac{A}{V} + \frac{2B}{V^2}$$

where A and B are constant, P = pressure and V = molar volume.

67. For the following equation of state $P = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$; B and C are constants the value of critical compression factor (Z_c) will be

(a) 3/8 (b) 1/2 (c) 1/3 (d) 1/6

68. For the gas with equation of state as

$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$ the value of critical volume V_c will be

(a) b (b) 2b (c) 3b (d) 4b

69. The critical temperature and critical pressure of a gas are 31°C and 728 atmospheres respectively. Calculate the constant 'a'. (atm L^2 mol^{-2})

(a) 1.56 (b) 0.36 (c) 1.39 (d) 2.39

EXERCISE II

More Than One Correct Type

1. Which of the following statement(s) is/are correct?

(a) Gas molecules never come to rest except at 0K

(b) At T > 0, some gas molecules are unfortunate not to possess translation kinetic energy

(c) On raising temperature, fraction of molecules processing most probable velocity increases.

(d) At a given temperature the most probable velocity varies inversely with the square root of vapour density of the gas.

2. Which of the following statements is/are correct?

(a) All real gases are less compressible than ideal gas at high pressures?

(b) Hydrogen and helium are more compressible than ideal gas for all values of pressure

(c) Except H_2 and He, the compressibility factor $Z = \left(\frac{PV}{nRT}\right) < 1$ for all gases at low pressures.

(d) The compressibility factor of real gases is independent of temperature

3. For gaseous state which of the following is incorrect ?

(a) Thermal energy = Molecular attraction (b) Thermal energy >> Molecular attraction

(c) Thermal energy << Molecular attraction (d) Molecular force >> attraction in liquid

Check ④ The rate of diffusion of 2 gases 'A' and 'B' are in the ratio 16: 3. If the ratio of their masses present in the mixture is 2 : 3. Then

(a) The ratio of their molar masses is 16 : 1 (b) The ratio of their molar masses is 1 : 4

(c) The ratio of their moles present inside the container is 1 : 24

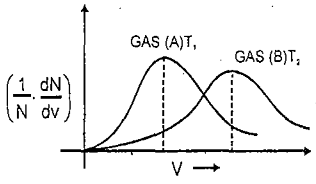
(d) The ratio of their moles present inside the container is 8 : 3

5. The vander waal gas constant 'a' is given by

(a) $\frac{1}{3} V_C$ (b) $3P_C V_C^2$ (c) $\frac{1}{8}\frac{RT_C}{P_C}$ (d) $\frac{27}{64}\frac{R^2 T_C^2}{P_C}$

6. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure guaze of cylinder indicates 12 atmosphere at 27 °C. Due to sudden fire in the building temperature starts rising. The temperature at which cylinder will explode is :

(a) 372.5 K (b) 99.5 °C (c) 199 °C (d) 472.5 k

7. 

For the above graph, drawn for two different samples of gases at two different temperatures. T_1 and T_2, which of the following statements is/are necessarily true.

(a) If $T_2 > T_1$, M_B is necessarily greater than M_A

(b) If $T_1 > T_2$, M_A is necessarily greater than M_B

(c) $\frac{T_2}{M_B} > \frac{T_1}{M_A}$ (d) Nothing can be predicted

Check 8. Which of the following statements are correct ?

(a) Helium diffuses at a rate 8.65 times as much as CO does.

(b) Helium escapes at a rate 2.65 times as fast as CO does.

(c) Helium escapes at a rate 4 times as fast as CO_2 does.

(d) Helium escapes at a rate 4 times as fast as SO_2 does.

9. Which of the following are correct statements ?

(a) vander Waals constant 'a' is a measure of attractive force

(b) van der Waals constant 'b' is also called co-volume or excluded volume

(c) 'b' is expressed in L mol^{-1}

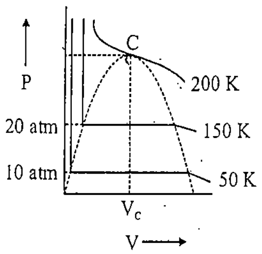
(d) 'a' is expressed in atm L^2 mol^{-2}

10. Select the factor(s) upon which the root mean square speed of an ideal gas depends

(a) temperature (b) pressure (c) volume (d) molar mass

11. Identify the correct statement

Check (C) option



(a) At 70 K and below 20 atm, it has vapour state only

(b) At a temperature > 200 K, the gas behaves as a permanent gas.

(c) If vander waals equation of state is applicable below critical temperature, then it will have three values of volume.

(d) If pressure is between 10 atm - 20 atm and temperature is 100 K, it has both liquid & vapour state.

12. Select correct statement(s):

(a) we can condense vapours simply by applying pressure

(b) to liquify a gas one must lower the temperature below T_C and also apply pressure

(c) at T_c, there is no distinction between liquid and vapour state, hence density of the liquid is nearly equal to density of the vapour

(d) all the statements are incorrect statements

13. Select the **correct** option(s) for an ideal gas

(a) Most probable speed increases with increase in temperature

(b) Fraction of particles moving with most probable speed increases with increase in temperature

(c) Fraction of particles moving with most probable speed are more for Cl_2 than H_2 under similar condition of T, P & V.

(d) Most probable speed is more for Cl_2 than H_2 at same temperature

14. At moderate pressure the compressibility factor for a particular gas is given as

Check later

$$Z = T + 0.35P - \frac{168}{T}P.$$

Where P is in bar & T is in Kelvin. Which of the following statement(s) is/are correct for the gas?

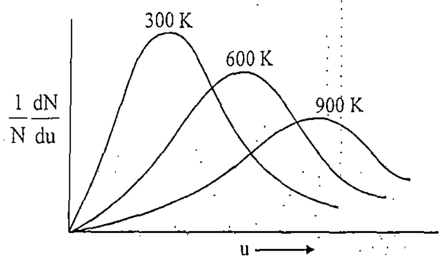
(a) At a temperature 500 K, attractive forces dominates

(b) At a temperature 480 K, repulsive forces dominates

(c) At a temperature 520 K, attractive forces dominates

(d) At a temperature, 520 K, repulsive forces dominates

15. For the given maxwell curve at three different temperatures 300 K, 600 K, 900 K respectively for a particular gas



Select the correct statement

(a) The area under the curve at 900 K is less than that at 600 K.

(b) The area under the three curves is same.

(c) The total fraction occupied by the gas at these three temperature is same.

(d) The maximum fraction occupied by the gas at these three temperature is same

EXERCISE III

Numerical Answer Type

1. 12 g N_2, 4 gm H_2 and 9 gm O_2 are put into a one litre container at 27°C. What is the total pressure.

2. A flask of 1.5 L capacity contains 400 mg of O_2 and 60 mg of H_2 at 100°C. Calculate the total pressure of the gaseous mixture. If the mixture is permitted to react to form water vapours at 100°C, what materials will be left and what will be their partial pressures.

3. An open vessel at 27°C is heated until (3/5)th of the air in it has been expelled. Assuming that the volume of the vessel remains constant. Find out.

(a) The temperature at which vessel was heated.

(b) The air escaped out if vessel is heated to 900 K

(c) The temperature at which half of the air escapes out.

4. At what temperature in °C, the U_{rms} of SO_2 is equal to the average velocity of O_2 at 27°C.

5. The density of CO at 273 K and 1 atm is 1.2504 kg m^{-3}. Calculate (a) root mean square speed (b) the average speed and (c) most probable speed.

6. At what temperature would the most probable speed of CO_2 molecules be twice that at 127°C

7. Calculate the average kinetic energy in joule per molecule in 8g of methane at 27°C.

8. At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of O_2 is 0.927. Calculate the mass of O_2 necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

9. A gas mixture contains equal number of molecules of N_2 and SF_6, some of it is passed through a gaseous effusion apparatus. Calculate how many molecules of N_2 are present in the product gas for every 100 molecules of SF_6.

10. Two gases NO and O_2 were introduced at the two ends of a one metre long tube simultaneously (tube of uniform cross-section). At what distance from NO gas end, Brown fumes will be seen.

11. Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm^3 at 300 K using:
(a) the ideal gas law and (b) Vander Waals equation. Given:
[a = 363.76 kPa dm^6 mol^{-2} and b = 42.67 cm^3 mol^{-1}]
[Use : R = 0.08 atmL/mol K, 1 atm = 10^5 Pascal]

check

12. The compressibility factor for N_2 at –50°C and 800 atm pressure is 1.95 and at 100°C and 200 atm, it is 1.10. A certain mass of nitrogen occupied one litre at – 50°C and 800 atm. Calculate the volume occupied by the same quantity of N_2 at 100°C and 200 atm.

13. At what temperature will hydrogen molecules have the same root mean square speed as nitrogen molecules have at 35°C ?

14. Check A container contains the mixture of water vapour and oxygen gas with total pressure 1.1 atm at certain temperature. If volume is made one third then find the total pressure (assume aqueous tension of water at this temperature is 0.1 atm.) ?

15. Density of dry air (only N_2 and O_2) is 1.146 g $litre^{-1}$ at 740 mm and 300 K. The percentage composition of N_2 in air is ____________.

16. Impo N_2 molecule is spherical of radius 100 pm.
(a) What is the volume of molecules of one mole gas?
(b) What is the value of vander waal's constant b?
(c) What is free volume of gas at STP
[Use : $\frac{4}{3}\pi = 4.2$, $N_A = 6 \times 10^{23}$]

17. The critical constants for water are 647 K, 22.09 MPa and 0.0566 dm^3 mol^{-1}. Calculate the values of a, b and R

18. Calculate the mean free path in CO_2 at 27°C and a pressure of 10^{-9} bar.
(molecular diameter = 500 pm)
(Given $R = \frac{25}{3}$ J $mol^{-1}K^{-1}$, $\sqrt{2} = 1.4$, $\pi = \frac{22}{7}$, $N_A = 6 \times 10^{23}$)

19. Calculate the values of σ, λ, z_1 and z_{11} for oxygen at 298.15 K at the pressure of 101.325 kPa, given vander waals constant b = 3.183 × 10^{-2} dm^3 mol^{-1}

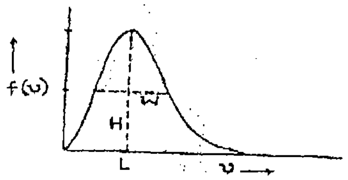
20. The vander waals constant for HCl are a = 371.843 KPa.dm^6 mol^{-2} and b = 40.8 cm^3 mol^{-1} find the critical constant of this substance.

EXERCISE IV

Previous Year Questions

IIT-JAM Previous Year Questions

1. The Maxwell-Boltzmann distribution for molecular speeds is shown in the following figure.



In the figure, H is the height of the peak, L is the location of the maximum and W is the width at half height. As the temperature is decreased

(a) H increases, L decreases and W increases

(b) H increases, L decreases and W decreases

(c) H decreases, L increases and W increases

(d) H decreases, L decreases and W decreases

2. The average speed of H_2, N_2 and O_2 gas molecules is in the order

(a) $H_2 > N_2 > O_2$ (b) $O_2 > N_2 > H_2$ (c) $H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2$

3. For an ideal gas, the plot that is Nonlinear is

(a) PV v/s T (b) Pv v/s P, at constant T

(c) P v/s V at constant T (d) ln P v/s ln V at constant T

4. Consider two identical containers one with 1 mole of H_2 and the other with 1 mole of He. If the root mean square (RMS) velocities of the two gases are the same, the ratio of the temperatures. $T(H_2)$ / T(He) is

(a) 1/2 (b) 2 (c) $1\sqrt{2}$ (d) $\sqrt{2}$

5. Given that the most probable speed of oxygen gas is 1000 ms^{-1}, the mean/average speed (ms^{-1}) under the same conditions is

(a) 1224 (b) 1128 (c) 886 (d) 816

6. For the distribution of molecular velocities of gases, identify the correct order from the following (where v_{mp}, v_{av} and v_{rms} are the most probable velocity, average velocity and root mean square velocity, respectively):

good

(a) $v_{rms} > v_{av} > v_{mp}$ (b) $v_{mp} > v_{rms} > v_{av}$ (c) $v_{av} > v_{rms} > v_{mp}$ (d) $v_{mp} > v_{av} > v_{rms}$

7. The relationship between the van der Waals 'b' coefficient of N_2 and O_2 is

(a) $b(N_2) = b(O_2) = 0$ (b) $b(N_2) = b(O_2) \neq 0$ (c) $b(N_2) > b(O_2)$ (d) $b(N_2) < b(O_2)$

8. From the kinetic theory of gases, the ratio of most probable speed (C_{mp}) to root mean square speed (C_{rms}) is

(a) $\sqrt{3}$ (b) $\sqrt{2}/\sqrt{3}$ (c) $\sqrt{3}/\sqrt{2}$ (d) $3/\sqrt{2}$

9. In an ideal monoatomic gas, the speed of sound is given by $\sqrt{\frac{5RT}{3M}}$. If the speed of sound in argon at 25°C is 1245 km h^{-1}, the root mean square velocity in m s^{-1} is _____

Check

10. In gas phase the ratio of excluded volume to molecular volume for a spherical molecule is ____

11. A mixture of C_3H_8 and oxygen in 1L closed vessel has an internal pressure of 4 atm at 100°C. When the mixture is ignited, the reaction produces $CO_2(g)$ and $H_2O(g)$ until all the oxygen is consumed. After the reaction, pressure of the vessel is 4.2 atm at the same temperature. Calculate the weight of oxygen present before the reaction. [Gas constant, R = 0.082 L atm mol^{-1} K^{-1}].

But check once

12. Calculate U_{mp} for $CH_4(g)$ at 127°C. Use R = 8 J K^{-1} mol^{-1}

13. $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(l)$

In the above reaction at 1 atm and 298 K, if 6.36 g of copper is used. Assuming ideal gas behavior, the volume of NO_2 produced in litres is_____.

[Given: atomic mass of Cu is 63.6; R = 0.0821 L atm K^{-1} mol^{-1}]

IIT-JEE Previous Year Questions

14. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is:

Imp

(a) 1.086 : 1 (b) 1 : 1.086 (c) 2 : 1.086 (d) 1.086 : 2

15. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is

(a) critical temperature [✓ (b)] Boyle temperature

(c) inversion temperature (d) reduced temperature

16. Equal weight of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is

Imp.

(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3} \times \frac{273}{298}$

17. A liquid is in equilibrium with its vapour at it's boiling point. On the average, the molecules in the two phases have equal:

(a) inter-molecular forces (b) potential energy

(c) kinetic energy (d) total energy

18. Rate of diffusion of a gas is

(a) directly proportional to its density (b) directly proportional to its molecular weight

(c) directly proportional to the square root of its molecular weight

(d) inversely proportional to the square root of its molecular weight

19. The average velocity of an ideal gas molecule at 27°C is 0.3 m/s. The average velocity at 927°C will be :

(a) 0.6 m/s (b) 0.3 m/s (c) 0.9 m/s (d) 3.0 m/s

20. In van der Waal's equation of state for a non-ideal gas, the term that accounts for intermolecular forces is

(a) $(V-b)$ (b) RT (c) $\left(p+\frac{a}{V^2}\right)$ (d) $(RT)^{-1}$

Good

21. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be:

(a) at the centre of the tube (b) near the hydrogen chloride bottle

(c) near the ammonia bottle (d) throughout the length of the tube

22. The value of van der Waal's constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} respectively. The gas which can most easily be liqiefied is

(a) O_2 (b) N_2 (c) NH_3 (d) CH_4

23. The density of neon will be highest at

(a) STP (b) 0°C, 2 atm (c) 273°C, 1 atm (d) 273°C 2 atm

24. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecule weight of X is

(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0

25. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with rise of temperature due to :

(a) increase in average molecular speed (b) increase rate of collisions amongst molecules

(c) increase in molecular attraction (d) decrease in mean free path

26. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is

(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

27. The compressibility factor for an ideal gas is

(a) 1.5 (b) 1.0 (c) 2.0 (d) ∞

28. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

(a) fewer electrons than O_2 (b) two covalent bonds

(c) V-shape (d) dipole moment

29. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B is given by (where, p and M are pressures and molecular weights of gases A and B respectively)

Check once all options

(a) $\left(\frac{p_A}{p_B}\right)\left(\frac{M_A}{M_B}\right)^{1/2}$ (b) $\left(\frac{M_A}{M_B}\right)\left(\frac{p_A}{p_B}\right)^{1/2}$ (c) $\left(\frac{p_A}{p_B}\right)\left(\frac{M_B}{M_A}\right)^{1/2}$ (d) $\left(\frac{M_A}{M_B}\right)\left(\frac{p_B}{p_A}\right)^{1/2}$

30. A gas will approach ideal behaviour at

(a) low temperature and low pressure (b) low temperature and high pressure

(c) high temperature and low pressure (d) high temperature and high pressure

31. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$ (c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\,T(N_2)$

32. The compressibility of a gas is less than unity at STP. Therefore,

(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L (c) $V_m = 22.4$ L (d) $V_m = 44.8$ L

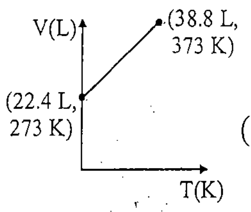
33. At 100°C and 1 atm if the density of the liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 L of steam at this temperature is :

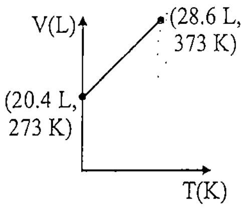
(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3

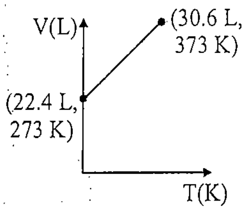
34. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as :

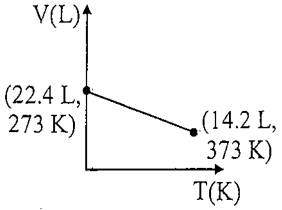
(a) d^2 (b) d (c) $\sqrt{d}$ (d) $1/\sqrt{d}$

35. Which of the following volume (V) temperature (T) plots represents the behaviour of one mole of an ideal gas at the atmospheric pressure?

(a)


(b)


(c)


(d)


36. According to the Kinetic Theory of gases, the root mean square velocity is :

(a) proportional to the temperature (b) proportional to the square of the temperature

(c) proportional to the square root of the temperature

(d) inversely proportional to the square root of the temperature

37. Positive deviation from ideal behaviour takes place because of :

(a) molecular interaction between atom and $pV/nRT > 1$

(b) molecular interaction between atom and $pV/nRT < 1$

(c) finite size of atoms and $pV/nRT > 1$ (d) finite size of atoms and $pV/nRT < 1$

38. For a monoatomic gas kinetic energy = E. The relation with rms velocity is :

(a) $u = \left(\frac{2E}{m}\right)^{1/2}$ (b) $u = \left(\frac{2E}{2m}\right)^{1/2}$ (c) $u = \left(\frac{E}{2m}\right)^{1/2}$ (d) $u = \left(\frac{E}{3m}\right)^{1/2}$

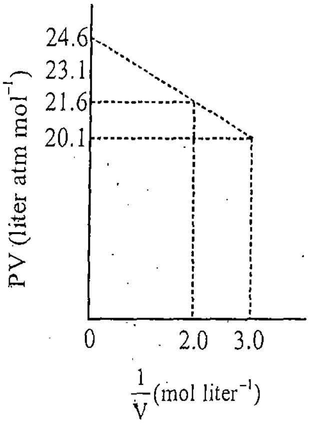
39. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of the diffusion of helium to methane is :

(a) 2.0 (b) 1.0 ~~(c) 0.5~~ (d) 4.0

40. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is

(a) nb (b) n^2a / V^2 (c) $-(n^2 a / V)$ (d) – nb

41. For one mole of a van der Waals gas when b = 0 and T = 300 K, the PV vs. 1/V plot is shown below. The value of the van der Waals constant a (atm.litre^{2}mol^{-2}) is



(a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

ANSWER KEY

EXERCISE I

1. a 2. b 3. a 4. b 5. c 6. d 7. c
8. c 9. b 10. a 11. a 12. d 13. b 14. c
15. c 16. a 17. c 18. c 19. c 20. c 21. b
22. d 23. b 24. c 25. d 26. a 27. a 28. b
29. d 30. b 31. c 32. a 33. (i) b (ii) b 34. c 35. a
36. a 37. b 38. b 39. b 40. c 41. a 42. c
43. b 44. c 45. d 46. d 47. b 48. a 49. a
50. c 51. a 52. d 53. a
54. $H_2O > CO_2 >$ Ar; Kr > Ar > Ne > He, n-pentane > isopentane > neopentane
55. Gas 2 56. a 57. a 58. (i) B (ii) C (iii) A 59. d 60. b
61. b 62. Gas A 63. c 64. c 65. a

66. $V_C = \frac{6B}{A}$, $T_C = \frac{A^2}{6RB}$, $P_C = \frac{A^3}{108B^2}$, $Z_C = \frac{1}{3}$ 67. c 68. c 69. b

EXERCISE II

1. a,d 2. a,c 3. a,c,d 4. b,d 5. b,d 6. a,b 7. b,c
8. b,d 9. a,b,c,d 10. a,d 11. b,c,d 12. a,b,c 13. a,c 14. a,d
15. b,c

EXERCISE III

1. 66.73 atm 2. $P_{initial} = 0.867$ atm, $P_{H_2} = 0.102$ atm, $P_{H_2O} = 0.509$ atm
3. (a) 477°C (b) 2/3 (c) 327 °C 4. 236.3°C
5. $U_{RMS} = 493$ m/s, $U_{mp} = 402.62$ m/s, $U_{av} = 454.4$ m/s
6. 1600 K 7. 6.21×10^{-21} J/molecule

8. 15.40 kg

9. 228

10. 50.8 cm

11. 2.479×10^3 kPa, 2.225×10^3 kPa

12. 3.77 L

13. 22 K

14. 3.1 atm

15. 75.27

16 (a) 2.52×10^{-3} l mol^{-1}, (b) 10.08×10^{-3} dm^3 mol^{-1}, (c) 22.389 L

17. 212.3 kPa dm^6 mol^{-2}, 0.0189 dm^3 mol^{-1}, 5.153 JK^{-1} mol^{-1}

18. 3.788×10^3 cm

19. 2.934×10^{-10} m, 1.06×10^{-7} m, 4.18×10^{-9} s^{-1}, 5.144×10^{34} m^{-3} s^{-1}

20. 4.18×10^{-9} s^{-1}, 5.144×10^{34} m^{-3} s^{-1}

EXERCISE IV

1. b	2. a	3. c	4. a	5. b	6. a	7. c
8. b	9. 462 to 465	10. 8	11. 1.04 g	12. 632.4 m/s	13. 4.89	14. a
15. b	16. a	17. c	18. d	19. a	20. c	21. b
22. c	23. b	24. a	25. a	26. d	27. b	28. d
29. c	30. c	31. c	32. b	33. c	34. d	35. c
36. c	37. c	38. a	39. a	40. b	41. c	

CHAPTER 12

ADSORPTION

INTRODUCTION

The term adsorption implies the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to that present in the bulk of the material. This phenomenon of adsorption is basically due to the presence of residual forces at the surface of the body. These residual forces, in case of liquids, arise from the non-uniform distribution of molecules around the molecules at the surface. In solids, these residual forces are due to the presence of unsatisfied valence forces of atom at the surface.

PHYSICAL ADSORPTION AND CHEMISORPTION

On the basis of forces of attraction between adsorbent and adsorbate, adsorption has been classified into two categories, namely, van der Waals adsorption (or physical adsorption) and chemisorption (or activated adsorption).

	Physical Adsorption	Chemisorption
1.	The forces of attraction between adsorbent and adsorbate are of van der Waals type (weak forces)	The forces of attraction between adsorbent and adsorbate are of chemical nature (strong forces).
2.	This predominates at low temperature.	This usually occurs at high temperature.
3.	Almost all gases show this type of adsorption at low temperatures.	It is highly specific in nature.
4.	The enthalpy of adsorption is low and has has a value of about 20 kJ mol^{-1} or less.	The enthalpy of adsorption is high and has a value of the order of 80 to 420 kJ mol^{-1}.
5.	This type of adsorption attains equilibrium very rapidly on changing the temperature and pressure of the system.	This type of adsorption is relatively slower.
6.	This is reversible in nature.	This is usually irreversible in nature. For example, O_2 adsorbed on charcoal, when desorbed also contains CO and CO_2.

7.	The activation energy involved in this adsorption is small and is often less than 5 kJ mol^{-1}. It is for this reason, this is even attained at low temperatures.	The activation energy involved in this adsorption is high. It is for this reason this is attained only at high temperatures.
8.	Adsorption in this case is often multiplayer.	Adsorption in this case is monolayer and thus Langmuir adsorption isotherm is applicable.

Desorption Activation Energy

$$k_{desorption} = Ae^{-E_a/RT}$$

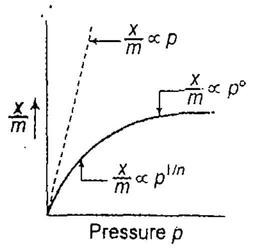
$\frac{1}{k_{desorption}}$ is called life time, τ of the adsorbate molecule on the surface, therefore, $\tau = \tau_0 e^{E_a/RT}$

where, $\tau_0 = \frac{1}{A}$ is known as the pre-exponential factors and E_a = desorption activation energy or adsorbate.

Freundlich equation

$$\log\left(\frac{x}{m}\right) = \log k' + \left(\frac{1}{n}\right)\log\left(\frac{p}{p^\circ}\right)$$

where p° is the unit pressure. A plot of log (x/m) versus log (p/p°) would be a straight line with slope equal to (1/n) and intercept equal to log k′. From these, the values of k and n can be determined.



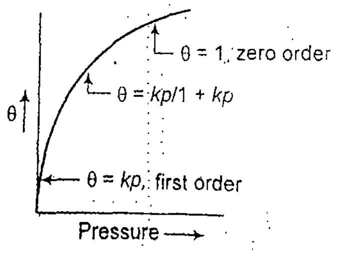
The Freundlich plot.

Langmuir equation

It is based on four assumptions :

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1-\theta)P} \quad \text{or} \quad \theta = \frac{KP}{1+KP}$$



The Langmuir plot.

$$\frac{1}{v}=\frac{1}{Kv_{mono}}\frac{1}{P}+\frac{1}{v_{mono}}$$

BET adsorption isotherm:

The derivation of the formula is more complicated than Langmuir's. We obtain:

$$\frac{x}{v(1-x)}=\frac{1}{v_{mono}c}+\frac{x(c-1)}{v_{mono}c}.$$

x is the pressure divided by the vapour pressure for the adsorbate at that temperature (usually denoted P/P_0), v is the STP volume of adsorbate, v_{mono} is the STP volume of the amount of adsorbate required to form a monolayer and c is the equilibrium constant K we used in Langmuir isotherm multiplied by the vapour pressure of the adsorbate. The key assumption used in deriving the BET equation is that the successive heats of adsorption for all layers except the first are equal to the heat of condensation of the adsorbate.

Derivation of Langmuir Equaiton from BET Equation

$$\frac{p\,p_0}{v_{total}\,(p_0-p)}=\frac{1}{v_{mono}}\frac{p_0}{C}+\frac{1}{v_{mono}}\frac{C-1}{C}p \qquad \ldots(1)$$

Now $\quad C=\frac{K_1}{K_L}$ and $K_L=\frac{1}{p_0}$

Thus $\quad C=\frac{K_1}{K_L}=\frac{K_1}{(1/p_0)=p_0K_1}$

or $\quad K_1=\frac{C}{p_0}$

Substituting the above relation in eq. (1), we get

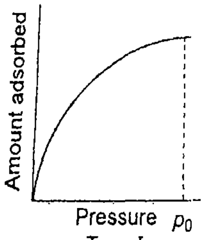
$$\frac{p\,p_0}{v_{total}\,(p_0-p)}=\frac{1}{v_{mono}}+\frac{1}{v_{mono}}\frac{C-1}{C}p \quad \ldots(2)$$

Now if we assume that C is much grater than one and that p_0 is much greater than p, then eq. (2) is modified to

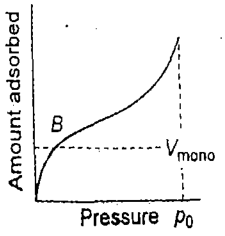
$$\frac{p}{v_{total}}=\frac{1}{v_{mono}}\frac{1}{K_1}+\frac{p}{v_{mono}}$$

which is, in fact, the Langmuir equation.

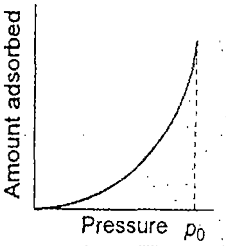
Types of Adsorption Isotherms



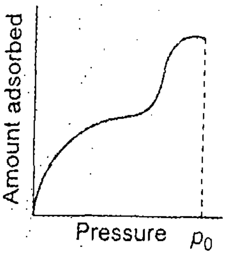
Type I



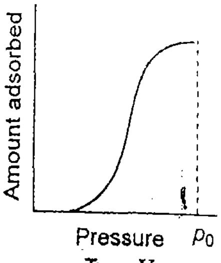
Type II



Type III



Type IV



Type V

The relationship at a given temperature between the amount of the gas adsorbed and equilibrium pressure is known as an adsorption isotherm.

- Type I isotherms show a fairly rapid rise in the amount of adsorption with increasing pressure upto a limiting value (Langmuir-type isotherm). **Example** adsorption of H_2 and N_2 on charcoal at – 180°C.
- Type II isotherms represent multilayer physical adsorption on non-porous solids. Point B represents the formation of an adsorbed monolayer. **Example** adsorption of N_2 on silica gel.
- Type III isotherms show amount of adsorption keeps on rising in each case with increase in pressure. **Example** adsorption of Br_2 on silica or alumina gel at 80°C.
- Type IV and type V are observed in those cases where there is capillary condensation in porous solids. **Example** of type IV: adsorption of benzene on silica gel at 50°C and **example** of type V: adsorption of water vapour on activated carbon at 100°C.

Determination of Surface Area of the Adsorbent

Since the molar volume of an ideal gas at STP is 22.414 dm^3, the number of molecules N adsorbed corresponding to the volume v_{mono} is

$$N = \left(\frac{v_{mono}}{22.414\ dm^3\ mol^{-1}}\right)(6.023 \times 10^{23}\ mol^{-1})$$

where $6.023 \times 10^{23}\ mol^{-1}$ is Avogadro constant. Now if the area of cross-section of a single molecule is known, it can be multiplied by the above number to give the total surface area of the adsorbent.

If ρ is the density, then the volume *v* occupied by a single molecule (assuming the adsorbate to be highy packed with no void volume) is given by

$$\rho = \frac{M}{V_m} = \frac{M}{vN_A} \text{ or } v = \frac{M}{N_A\rho}$$

Assuming the molecule to be spherical, its cross-sectional area can be computed as follows.

If *r* is the radius of the molecule, it follows that

$$v = \frac{4}{3}\pi r^3 = \frac{M}{N_A\rho} \text{ or } r = \left(\frac{3}{4\pi}\frac{M}{N_A\rho}\right)^{1/3}$$

$$\text{Hence, } A = \pi r^2 = \pi\left(\frac{3}{4\pi}\frac{M}{N_A\rho}\right)^{2/3}$$

The obtained value of r (or πr^2) is only an approximate value since it lacks the information regarding the exact nature of packing at the surface of the adsorbent.

Gibbs Adsorption Equation

$\Gamma_2 = - d\gamma/d\mu_2$

Γ = Surface excess

γ = Surface Tension

μ = Chemical potential

Gibbs adsorption equation.

$$\Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d\ln a_2} = -\frac{a_2}{RT}\frac{d\gamma}{da_2}$$

From a dilute solution, we have

$$\Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d\ln(c_2/c^\circ)} = -\frac{c_2}{RT}\frac{d\gamma}{dc_2}$$ (where c^0 is saturated unit concentration.)

Surface-Active Substances

Γ_2 is positive if $(d\gamma/dc_2)$ is negative. In other words, if the surface tension of a solvent is decreased as a result of adding a solute, then the latter has relatively more concentration at the surface than in the bulk of the solutions. Substances which produce a marked reduction in surface tension are known as surface-active substances or surfactants. The limiting value of the decrease of surface tension with concentration, i.e., the quantity $-(d\gamma/dc_2)_{c_2\to 0}$ is called the *surface activity*.

Surface-Inactive Substances

For surface-inactive substances $d\gamma/dc$ is positive, i.e., an increase in the concentration of a surface-inactive substance in a solution causes an increase in the surface tension of the solution. From Gibbs equation, it follows that the value of Γ_2 in such cases is negative indicating that the substance has larger concentration in the bulk in comparison to that present at the surface. This type of behaviour is known as negative adsorption. Examples include most of inorganic salts, sugar, etc.

EXERCISE - I

Single Answer Correct Type

1. According to Langmuir adsorption isotherm, the amount of gas adsorbed at very high pressures

(a) Reaches a constant limiting value (b) Goes on increasing with pressure

(c) Goes on decreasing with pressure θ/Q (d) Increase first and decreases later with pressure

2. For small coverages a plot of ln (Q/P) versus Q gives a straight line. The slope equal to :

(a) K (b) 1 (c) –1 (d) $1/v_{mono}$

3. Adsorption is multilayer in the case of

(a) Physical adsorption (b) Chemisorption

(c) Both (d) None of these

4. When temperature is lowered and pressure is raised, the adsorption of a gas on a solid

(a) Decreases (b) Increases

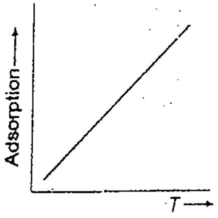
(c) Remains unaffected (d) Decreases first then increases

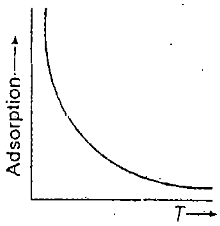
5. Which of the following affects the adsorption of gas on the surface of solid?

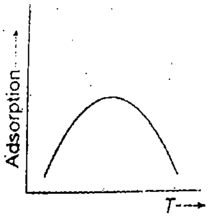
(a) Critical temperature (b) Pressure of gas

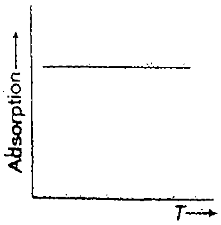
(c) Temperature (d) All of these

6. Following is the variation of physical adsorption with temperature

(a)


(b)


(c)


(d)


7. A plot of log x/m versus log p for the adsorption of a gas on a solid gives a straight line with slope equal to

(a) n (b) $\frac{1}{n}$ (c) log k (d) – log k

8. In Freundlich Adsorption isotherm, the value of $\frac{1}{n}$ is

(a) 1 in case of physical adsorption (b) 1 in case of chemisorption

(c) between 0 and 1 in all cases (d) between 2 and 4 in all cases

9. The volume of gases NH_3, CO_2 and H_2 adsorbed by 1 gram charcoal at 300 K lie in the order:

(a) $CO_2 > NH_3 > H_2$ (b) $NH_3 > CO_2 > H_2$ (c) $NH_3 > H_2 > CO_2$ (d) $H_2 > CO_2 > NH_3$

10. Select correct statement(s)

(a) Residual force-field on a surface a responsible for adsorption.

(b) Rate of adsorption is very rapid in the beginning but decreases until equilibrium is attained.

(c) Desorption and adsorption are two opposite terms.

(d) All of the above

11. Which gas is adsorbed to maximum extent on the given surface?

(a) NH_3 (b) H_2 (c) N_2 (d) O_2

12. The Langmuir adsorption isotherm is deduced using the assumption

(a) The adsorbed molecules interact with each other

(b) The adsorption takes place in multilayers

(c) The adsorption sites are equivalent in their ability the particles.

(d) The heat of adsorption varies with coverage.

13. Adsorption is

(a) an exothermic process hence increase in temperature decreases adsorption in case where van der Waals' forces exist between adsorbate and adsorbent

(b) an endothermic process hence increase in temperature increases adsorption

(c) an exothermic process hence increase in temperature increases adsorption

(d) None of the above

14. Adsorption is the phenomenon in which a substance

(a) accumulates on the surface of the other substance

(b) goes into the body of the other substances

(c) remains close to the other substance

(d) None of the above

15. Sorption is the term used when

(a) Adsorption takes place (b) absorption takes place

(c) Both (a) and (b) (d) desorption takes place

16. The physical adsorption of gases on the solid surface is due to

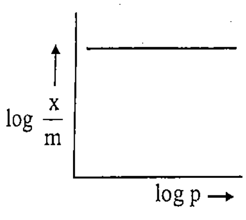
(a) covalent bond (b) hydrogen bond (c) ionic bond (d) van der Waals' forces

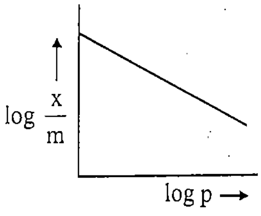
17. If $\left(\frac{x}{m}\right)$ is the mass of adsorbate adsorbed per unit mass of adsorbent. p is the pressure of the adsorbate gas and a and b are constants, which of the following represents "Langmuir adsorption isotherm"?

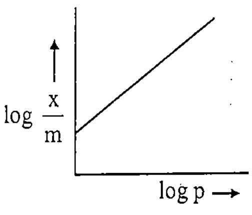
(a) $\log\left(\frac{x}{m}\right) = \log\left(\frac{a}{b}\right) + \frac{1}{a}\log p$ (b) $\frac{x}{m} = \frac{b}{a} + \frac{1}{ap}$

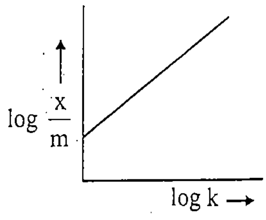
(c) $\frac{x}{m} = \frac{1+bp}{ap}$ (d) $\frac{1}{(x/m)} = \frac{b}{a} + \frac{1}{ap}$

18. Which one of the following graphs represents Freundlich adsorption isotherm?

(a)


(b)


(c)


(d)


19. Plot of $\log \frac{x}{m}$ against log p is straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be (log s = 0.6990)

(a) 1g (b) 2g (c) 3g (d) 5g

20. Calculate how long a hydrogen atom will remain on the surface of a solid at 1000 K if its desorption activation energy is 15 kJ mol^{-1}. Assume that $\tau_0 = 10^{-13}$s.

(a) 1.5×10^{-10} s (b) 4.2×10^{-11} s (c) 5.7×10^{-12} s (d) 6.1×10^{-13} s

21. 1g of charcoal adsorbs 100 mL of 0.5 M acetic acid to form a monolayer and there by the molarity of acetic acid reduces to 0.49. Calculate the surface area of the charcoal adsorb by each molecule of acetic acid. Surface area of charcoal is 3.01×10^2 m^2 g^{-1}.

(a) 5.0×10^{-19} m^2 (b) 5.0×10^{20} m^2 (c) 6.0×10^{-19} m^2 (d) 6.0×10^{20} m^2

22. At 0°C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 cm^3 g^{-1} of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0.162 nm^2.

(a) 5658 m^2 g^{-1} (b) 565.38 m^2 g^{-1} (c) 56.58 m^2 g^{-1} (d) 5.658 m^2 g^{-1}

23. For a 1.0×10^{-4} M aqueous solution of n-butanoic acid $\frac{d\gamma}{dC} = -0.080$ Nm^2 mol^{-1} at 25°C. Using the Gibbs adsorption equation, determine the average surface area available to each molecule.

(a) 2.4×10^{-19} m^2 (b) 3.5×10^{-19} m^2 (c) 4.7×10^{-19} m^2 (d) 5.2×10^{-19} m^2

24. The adsorption of a gas on a solid surface was found to follow a Langmuir isotherm with K = 3.75 kPa^{-1} at a temperature of 25°C. Determine the pressure of gas required to achieve a fractional surface coverage of 10%.

(a) 27 Pa (b) 30 Pa (c) 38 Pa (d) 270 Pa

25. Rate of physisorption increases with:

(a) decrease in temperature (b) increase in temperature

(c) decrease in pressure (d) decreae in surface area

26. Spontaneous adsorption of a gas in solid surface in an exothermic process because:

(a) ΔH increases for system (b) ΔS increases for gas

(c) ΔS decrease for gas (d) ΔG increase for gas

27. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C, for this process, the correct statement is

(a) The adsorption requires activation at 25°C

(b) The adsorption is accompanied by a decrease in enthalpy

(c) The adsorption increases with increase in temperature

(d) The adsorption is irreversible

28. Which of the following characteristics is not correct for physical adsorption?

(a) Adsorption is spontaneous (b) ΔH and ΔS are negative

(c) It is reversible in nature (d) Degree of adsorption increases with temperature

29. Freundlich adsorption isotherm gives a straight line on plotting:

(a) $\frac{x}{m}$ vs P (b) $\log\left(\frac{x}{m}\right)$ vs P (c) $\log\left(\frac{x}{m}\right)$ vs log P (d) $\frac{x}{m}$ vs $\frac{1}{P}$

30. Chemical adsorption

(a) decreases with increase in temperature (b) increase with increase in temperature

(c) first increases then decreases with increase in temperatue

(d) first decreases then increases with increase in temperature

31. The curve showing the variation of pressure with temperature for a given amount of adsorption is called:

(a) adsorption isobar (b) adsorption isotherm (c) adsorption isostere (d) adsorption isochore

32. In Langmuir's model of adsorption of a gas on a solid surface:

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

(b) the adsorption at a single site on the surface may involve multiple molecules at the same time

(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas

(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

33. Which one of the following gases will be adsorbed most easily?

(a) N_2 (b) H_2 (c) O_2 (d) CO_2

34. The most adsorbed gas on activated charcoal is:

(a) N_2 (b) H_2 (c) CO_2 (d) CH_4

35. For chemisorption, which of the following is wrong?

(a) irreversible (b) it requires activation energy

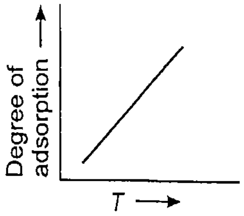
(c) it forms multimolecular layer on adsorbate (d) surface compounds are formed

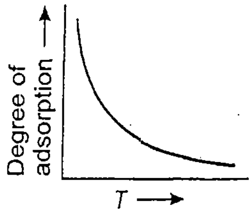
36. According to Freundlich adsorption isotherm, which of the following is correct?

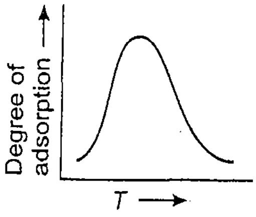
(a) $\frac{x}{m} \propto P^0$ (b) $\frac{x}{m} \propto P^1$ (c) $\frac{x}{m} \propto P^{1/n}$

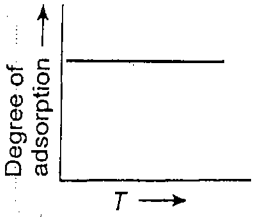
(d) All the above are correct for different range of pressure

37. Which of the following represents correctly, the variation of degree of adsorption against temperature, for physical adsorption?

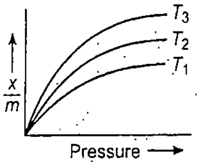
(a)


(b)


(c)


(d)


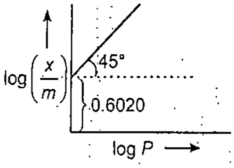
38. The variation of extent of adsorption with pressure at a given constant temperature is given in following figure



Which of the following relation between temperature of isotherms is correct?

(a) $T_1 = T_2 = T_3$ (b) $T_1 < T_2 < T_3$ (c) $T_3 < T_2 < T_1$ (d) $T_1 < T_2 < T_3$

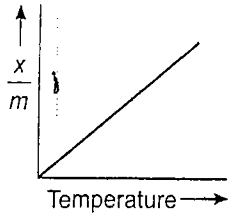
39. Graph between $\log\left(\frac{x}{m}\right)$ and log P is stright line at angle of 45° with the intercept of 0.6020.

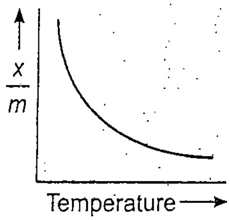


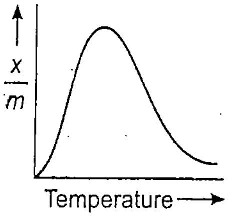
The extent of adsorption $\left(\frac{x}{m}\right)$ at a pressure of 1 atm is:

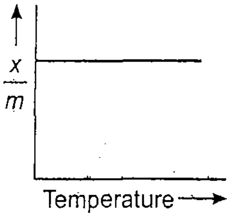
(a) 2 (b) 4 (c) 6 (d) 8

40. Which of the following curves represents the isobar for chemical adsorption?

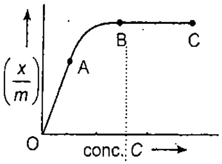
(a)


(b)


(c)


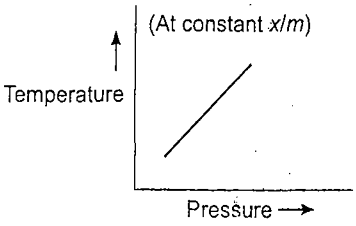
(d)


41. Adsorption also takes place in the solution. When solid surface is saturated by adsorption, then variation of $\left(\frac{x}{m}\right)$ and concentration (C) is given by which of the following portion?



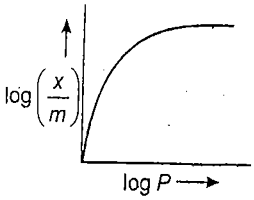
(a) OA (b) AB (c) OB (d) BC

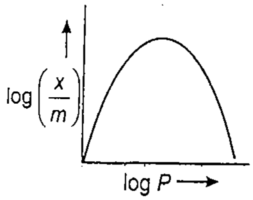
42. Following plot represents the variation of temperature with pressure for a definite extent of adsorption (x/m) is called:

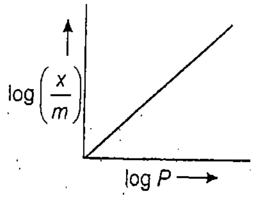


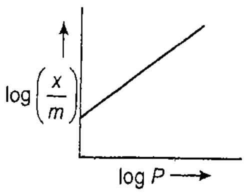
(a) adsorption isotherm (b) adsorption isobar
(c) adsorption isotherm (d) adsorption isostere

43. By plotting $\log\left(\frac{x}{m}\right)$ on Y-axis and log P on X-axis, we get:

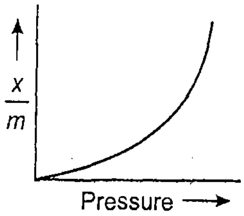
(a)


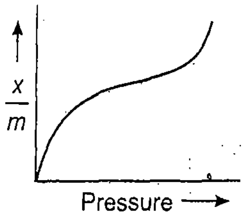
(b)


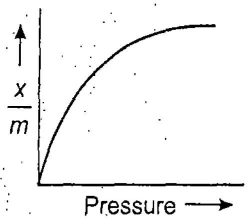
(c)


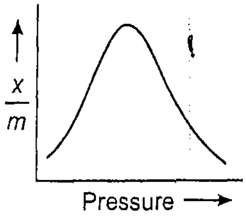
(d)


44. Which of the following plots does not correspond to the adsorption isotherm?

(a)


(b)


(c)


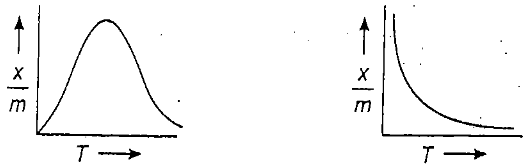
(d)


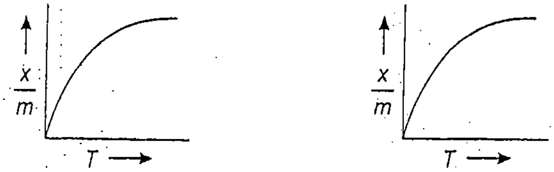
45. Select the correct adsorption isobars for chemisorption and physisorption respectively:

(Here, $\frac{x}{m}$ = degree of adsorption)

(a)


(b)


(c)


(d)


46. The adsorption of a gas is described by the Langmuir isotherm with the equilibrium constant $K = 0.9\ \text{kPa}^{-1}$ at 25°C. The pressure (in kPa) at which the fractional surface coverage is 0.95, is

(a) 1/11.1 (b) 21.1 (c) 11.1 (d) 42.2

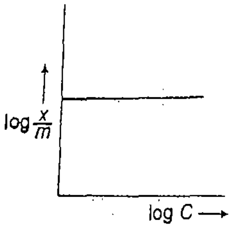
47. Amount of gas adsorbed per gram of adsorbent increases with pressure, but after certain limit is reached, adsorption becomes constant. It is where

(a) multilayers are formed (b) desorption takes place

(c) temperature is increased (d) absorption also starts

48. For the adsorption of solution on a solid surface $\frac{x}{m} = kC^{1/n}$.

Adsorption isotherm of $\log\left(\frac{x}{m}\right)$ and log C was found of the type

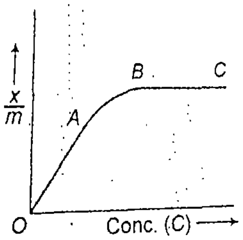


This is when

(a) C = 0 (b) $\frac{1}{n} = 0$

(c) C = constant (d) C = 2M

49. When saturation is attained in terms of adsorption, variation of $\left(\frac{x}{m}\right)$ and C (concentration) is given by the portion of the isotherm



(a) OA (b) OB (c) AB (d) BC

50. With increase in temperature, the Gibbs free energy for the adsorption of a gas on to a solid surface
(a) becomes more positive from a positive value
(b) becomes more negative from a positive value
(c) becomes more positive from a negative value
(d) becomes more negative from a negative value

51. The langmuir adsorption isotherm is given by $\theta = \frac{Kp}{1+Kp}$, where p is the pressure of the adsorbate gas. The Langmuir adsorption isotherm for a diatomic gas A_2 undergoing dissociative adsorption is

(a) $\theta = \frac{Kp}{1+Kp}$ (b) $\theta = \frac{2Kp}{1+2Kp}$ (c) $\theta = \frac{(Kp)^2}{1+(Kp)^2}$ (d) $\theta = \frac{(Kp)^{1/2}}{1+(Kp)^{1/2}}$

52. Isotherm which has fractional coverage, linearly dependent on pressure at low pressures but almost independent at high pressure is called
(a) BET isotherm (b) Langmuir isotherm
(c) Freundlich isotherm (d) Temkin isotherm

53. Charcoal (1 gram) of surface are 100 m^2 per gram, absorbs 60 mg of acetic acid from an aqueous solution at 25°C and 1 atmosphere pressure. The number of moles of acetic acid adsorbed per cm^2 of charcoal surface is
(a) 10^{-2} (b) 10^{-6} (c) 10^{-5} (d) 10^{-9}

54. For a physisorption process, which one of the following statements is NOT correct?
(a) There are van der Waals interactions between the adsorbate and the adsorbent.
(b) The process predominates at low temperature
(c) The process cannot proceed beyond a monolayer
(d) The process is reversible

EXERCISE - II

One or More Than One Correct Answer Type

1. Select the incorrect statement about chemisorption i.e.
(a) Chemisorption involves the weak attractive interactions between adsorbent and adsorbate.

(b) Chemisorption is irreversible in nature

(c) Chemisorption decrease with increase of temperature

(d) Chemisorption involves multilayer formation of adsorbent on adsorbate

Imp 2. Which of the following is not correct

(a) Physical adsorption is due to van der Waal's forces

(b) Chemical adsorption decreases at high temperature and low pressure

(c) Physical adsorption is reversible

(d) Adsorption energy for a chemical adsorption is generally greater than that of physical adsorption

3. Which one of the following statements is correct about adsorption?

(a) It is a selective and specific process (b) it is a reversible process

(c) An increase in the gaseous adsorbate causes increase in adsorption. However, at high pressure, the adsorption becomes constant

(d) It is an endothermic process

4. Which of the following statement(s) is/are incorrect about Langmuir's model of adsorption of a gas on a solid surface

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

(b) the adsorption at a single site on the surface may involve multiple molecules at the same time

(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas

(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

5. Which among the following statements are correct with respect to adsorption of gases on a solid?

(a) The extent of adsorption is equal to kp^n according to Freundlich isotherm.

(b) The extent of adsorption is equal to $kp^{1/n}$ according to Freundlich isotherm.

(c) The extent of adsorption is equal to $(1 + bp)/ap$ according to Langmuir isotherm.

(d) The extent of adsorption is equal to $ap/(1 + bp)$ according to Langmuir isotherm.

6. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are):

(a) Adsorption is always exothermic

(b) Physisorption may transform into chemisorption at high temperature

(c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature

(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation.

7. Which of the following are related to physical adsorption?

(a) It is reversible in nature (b) It involves the formation of unimolecular layer

(c) It has low heat of adsorption

(d) It takes place at low temperature and decreases with increase in temperature

8. Which of the following is/are correct about Freundlich's adsorption isotherm for gases and solutions?

(a) $\frac{x}{m} = K\,C^{1/n}$ (b) $\frac{x}{m} = \frac{1+bP}{a}$

(c) $\log\frac{x}{m} = \log K + n\log P$ (d) $\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log C$

9. Which of the following statements are correct?

(a) Physical adsorption is of multimolecular layer

(b) Degree of chemical adsorption increases with increase in temperature

(c) Adsorption increases the surface energy

(d) Sometimes solvent is adsorbed in preference to solute

10. Select the correct statements among following:

(a) At 83 K, N_2 is physisorped on the surface of iron

(b) At 773 K and above N_2 is chemisorped on the iron surface

(c) Activation energy is +ve in case of physisorption and zero in case of chemisorption

(d) Activation energy is zero in case of physisorption and +ve in case of chemisorption

11. True Statement(s) about Langmuir isotherm is(are)

(a) valid for monolayer coverage (b) all adsorption sites are equivalent

(c) there is dynamic equilibrium between free gas and adsorbed gas

(d) adsorption probability is independent of occupancy at the neighboring sites

EXERCISE - III

Numerical Answer Type and Subjective Questions

1. The dissociative adsorption of oxygen on tungsten is described by the langmuir isotherm with K = 0.36 KPa^{-1}. Calculate the fractional surface coverage at a pressure of 1 KPa.

2. If v is the volume of a gas adsorbed on the surface of a solid, the plot of p/v versus p where p is the gas pressure in the langmuir adsorption isotherm, gives a straight line. What will be the slope of this line?

3. Draw the plot in accordance with BET equation.

4. Calculate how long a hydrogen atom will remain on the surface of a solid at 298 K if its desorption activation energy is : (a) 15 kJ mol^{-1} (b) 150 kJ mol^{-1}. Assume that $\tau_0 = 10^{-13}$ s.

5. At 0°C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 $cm^3\,g^{-1}$ of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0.162 $(nm)^2$.

6. An organic fatty acid forms a surface film on water that obeys the two-dimensional ideal gas law. If the surface tension lowering is 10 mN m^{-1} at 25°C, calculate the surface excess concentration and the surface area per adsorbed molecule.

7. According to Szyszkowski, the surface tension of an aqueous solution of an acid is is related at 291 K to the bulk concentration c by the empirical relation

$$\lambda^* - \lambda = (0.0308\ \text{Nm}^{-1}) \log \{1 + ((0.01864\ \text{mol}^{-1}\ \text{dm}^3)c\}$$

where λ^* is the surface tension of pure water. Apply the Gibbs adsorptio equation to calculate the excess concentration Γ of solute of solute per square metre of surface when $c = 0.01$ mol dm^{-3}. What would be the value of G when c become infinite ?

8. The surface tension of ethanol-water mixtures follows the equation

$$\gamma(10^{-3}\ \text{Nm}^{-1}) = 72.0 - 0.5\ (c/\text{mol dm}^{-3}) + 0.2\ (c/\text{mol dm}^{-3})^2$$

where c is the molar concentration of ethanol. The temperature is 298 K. Calculate the surface excess of ethanol for a 0.5 mol dm^{-3} solution.

9. An insoluble compound X spreads on water to give a gaseous type film at low concentrations. When 10^{-7} g of X is added to 200 cm^2 surface, the surface tension at 298 K is lowered by 0.20 dyne cm^{-1}. Calculate the molar mass of X.

10. A protein with a molar mass of 60,000 g mol^{-1} forms an ideal gaseous film on water. What area of film per milligram of protein will produce a pressure of 0.005 N m^{-1} at 298 K ?

11. Calculate the surface area of a catalyst that adsorbs 10^3 cm^3 nitrogen reduced to STP per gram in order to form a monolayer. The effective area occupied by nitrogen molecule on the surface is 0.162 nm^2, i.e. 0.162×10^{-14} cm^2.

12. The surface excess concentration of surface active reagent if found to be 3×10^{-10} mol dm^{-2} at 25°C. Using the two-dimensional ideal gas law $\pi\sigma = RT$, calculate the surface tension of the solution. The surface tension of pure solvent is 0.072 Nm^{-1}.

13. A certain substance form a surface film that obeys the ideal two-dimensional gas low. Calculate the excess surface concentration required to cause a surface tension lowering of 0.01 Nm^{-1} at 25°C.

14. An organic acid of molar mass 242 g mol^{-1} forms a linearly ideal gaseous monolayer on water at 25°C. Calculate the mass of acid per 100 cm^2 required to produce a film pressure of 1 Nm^{-1}.

15. The adsorption of a gas follows the Langmuir isotherm with K = 1.25 kPa^{-1} at 25°C. The pressure (in Pa) in which surface coverage is 0.2 is ______

16. When a perfect monolayer of stearic acid is formed at the air-water interface, each molecule of stearic acid (MW = 284, density = 0.94 g cm^{-3}) occupies an area of 20 Å^2. The length (in Å) of the molecule is _______

1. a
8. c
15.
22.
29.
36.
43. d
50. c

1. a,c,d
8. a,

1.
2.

3.

5.
7.
9.
11.
13.
15.

ANSWER KEY

EXERCISE - I

1. a   2. c   3. a   4. b   5. d   6. b   7. b
8. c   9. b   10. d   11. a   12. c   13. a   14. a
15. c   16. d   17. d   18. c   19. d   20. d   21. a
22. b   23. d   24. b   25. a   26. c   27. b   28. d
29. c   30. c   31. c   32. c   33. d   34. c   35. c
36. d   37. b   38. c   39. b   40. c   41. d   42. d
43. d   44. d   45. c   46. b   47. a   48. b   49. d
50. c   51. d   52. b   53. d   54. c

EXERCISE - II

1. a,c,d   2. b   3. a,b,c   4. a,b,d   5. b,d   6. b,d   7. a,c,d
8. a,d   9. a,b,d   10. a,b,d   11. a,b,c,d

EXERCISE - III

1. 0.265

2. $1/v_{mono}$

A/C to langmuir isotherm

$$Q=\frac{KP}{(1+KP)},\ \frac{1}{Q}=1+\frac{1}{KP},\ Q=\frac{v}{v_{mono}},\ \frac{v_{mono}}{v}=1+\frac{1}{KP}$$

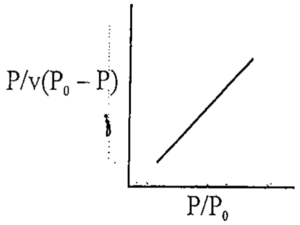
Multiplying throughout by $\frac{1}{v_{mono}}$

$$\frac{1}{v}=\frac{1}{v_{mono}}+\frac{1}{K_p v_{mono}}$$

y = mx + C

Slope = $1/v_{mono}$

3.



4. (a) 4.2×10^{-11} s (b) 600,000 years

5. $565.8\ m^2\ g^{-1}$

6. $0.411\ (nm)^2$

7. $8.68 \times 10^{-7}\ mol\ m^{-2}$

8. $6.05 \times 10^{-12}\ mol\ cm^{-2}$

9. $61.94\ g\ mol^{-1}$

10. $826 \times 10^{-4}\ m^2$

11. $449\ m^2$

12. $0.0645\ Nm^{-1}$

13. $4.04 \times 10^{-6}\ mol\ m^{-2}$

14. $9.77 \times 10^{-7}\ g$

15. 200

16. 25

CHAPTER 13

ATOMIC STRUCTURE & QUANTUM CHEMISTRY

Constants	Symbol	SI Value
Speed of light in vaccum	c	3×10^8 m/s
Proton & electron charge	e	1.60×10^{-19} C
Permittivity of vaccum	ε_0	8.85×10^{-12} C^2/N-m^2
Avogadro constant	N_A	6.02×10^{23} mol^{-1}
Electron rest mass	m_e	9.10×10^{-31} kg
Proton rest mass	m_P	1.67×10^{-27} kg
Neutron rest mass	m_n	1.67×10^{-27} kg
Planck constant	h	6.626×10^{-34} J s
Bohr magneton (BM)	β_e	9.27×10^{-24} J/T
Gas constant	R	8.3145 J/mol-K
Boltzmann constant	k	1.38×10^{-23} J/K

ENERGY CONVERSION FACTORS

1 erg = 10^{-7} J

1 cal = 4.184 J

1 eV = 1.602177×10^{-19} J = 1.602177×10^{-12} erg = 23.0605 kcal/mol

1. Light

(a) Photon is considered massless bundle of energy.

(b) $E = mc^2$

(c) $E_{photon} = h\nu = hc/\lambda = hc\bar{\nu}$

(d) Quantum efficiency or Quantum Yield $= \dfrac{\text{no. of molecules reacting}}{\text{no. of quanta absorbed}}$

2. Bohr's Model

(a) Electrostatic force $= \dfrac{Kq_1q_2}{r^2}$ where $K = \dfrac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N-m^2 / C^2

(b) Potential energy due to electrostatic force $= \dfrac{Kq_1q_2}{r}$

(c) Bohr quantization rule $mvr = n \cdot \frac{h}{2\pi} = n.\hbar$

(d) According to newtons second law in a uniform circular motion resultant of all the forces towards centre must be equal to $\frac{mv^2}{r}$.

(e) $\frac{Kq_1q_2}{r^2} = \frac{mv^2}{r}$

(f) $E_n = \frac{E_1}{n^2}Z^2 = -\frac{2\pi^2 me^4K^2}{n^2h^2}Z^2 = \left(-\frac{13.6Z^2}{n^2}\text{e.v.}\right)$; $E_1 = \frac{-2\pi^2 me^4K^2Z^2}{h^2}$ (energy)

(g) $r_n = \frac{h^2}{4\pi^2e^2mK} \times \frac{n^2}{Z} = \frac{a_0n^2}{Z}$ where $a_0 = 52.9$ pm or 0.529 Å (radius)

(h) $v_n = \frac{2\pi e^2K}{h} \times \frac{Z}{n}$ (velocity)

(i) Revolutions per sec = $v/2\pi r$

(j) Time for one revolution = $2\pi r/v$

(k) Ionisation energy = $E_{n=\infty} - E_{\text{electron}} = -E_{\text{electron}}$

3. **Spectral lines**

(a) Rydberg's Equation $\frac{1}{\lambda} = \bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$; $R_H \cong 109677\ \text{cm}^{-1}$

(b) For First line of a series $n_2 = n_1 + 1$ (H_a line), also known as line of longest λ, shortest ν, least E

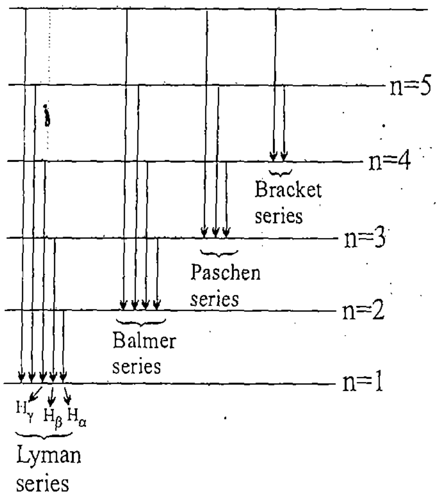
(c) Similarly H_β line means $n_2 = n_1 + 2$

(d) Limiting spectral line (series limit) means $n_2 = \infty$

(e) Number of spectral line observed in the spectrum = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

when e^- de-excites to n_1 from n_2 (number of higher orbit)

(f)



4. Photoelectric effect

(a) Kinetic energy = = $h\nu - w = h\nu - h\nu_0$

where w = work function

ν_0 = Threshhold frequency

(b) Accelerating potential = $eV = KE = \frac{1}{2}mv^2$

5. De-broglie & Heisenberg

(a) Number of waves = n = principal quantum number

(b) $\lambda = h/mv = h/p$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

for thermal energy $\lambda = \frac{h}{\sqrt{2mkT}}$

for potential energy $\lambda = \frac{h}{\sqrt{2meV}}$

on substituting the value of m, e, h for electron $\lambda = \sqrt{\frac{150}{V\,in\,volts}}$ Å

(c) $\Delta x.\Delta p \geq h/4\pi \quad \Rightarrow \quad \Delta x.\Delta v \geq \frac{h}{4\pi m}$

6. Quantum Numbers

Table The four main quantum numbers

	Symbol	Values
Principal quantum number	n	1, 2, 3
Azimuthal or Subsidiary quantum number	l	$0, 1, \ldots (n-1)$
Magnetic quantum number	m	$-l, \ldots 0, \ldots +l$
Spin quantum number	m_s	$\pm\frac{1}{2}$

(a) Orbital angular momentum = $\frac{h}{2\pi}\sqrt{l(l+1)}$

(b) Spin angular momentum = $S = \frac{h}{2\pi}\sqrt{S(S+1)}$

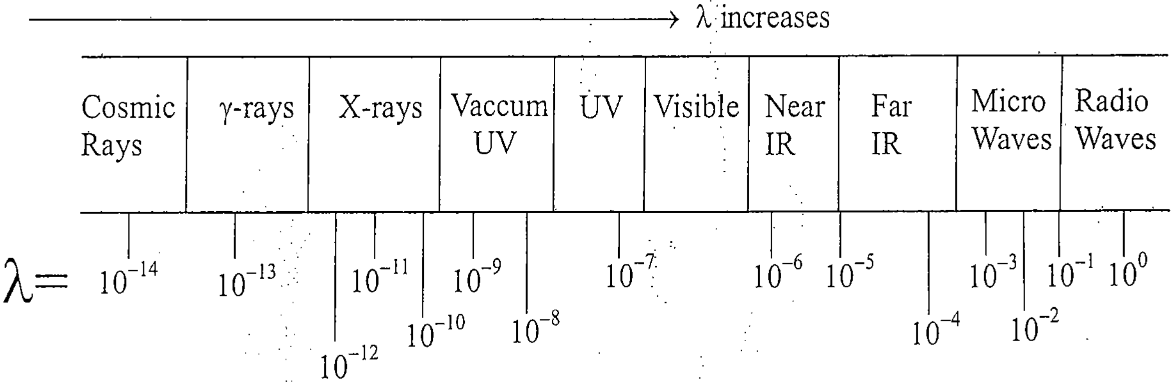
(c) Magnetic momentum $(\mu) = \sqrt{n(n+2)}$ B.M. ; n = number of unpaired electron

(d) Radial Nodes = $(n - l - 1)$

(e) Angular nodes = l

(f) Total nodes = $(n-1)$

7. Electromagnetic Spectrum



8. The Schrodinger equation:

For one dimensional systems.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi = E\psi$$

where V(x) is the potential energy of the particle and E is its total energy. For three dimensional systems.

$$-\frac{\hbar^2}{2m}\nabla\psi + V\psi = E\psi$$

where V may depend on position and ∇^2 (del square) is

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

In the general case the Schrodinger equation is written

$$\hat{H}\psi = E\psi$$

Where $\hat{H}$ is the hamiltonian operator for the system:

ψ = wavefunction

$|\psi|^2$ = probability density

$|\psi|^2\,dx$ = probability of finding the electron within the range from x to x + dx.

9. Operators in Quantum Mechanics:

An operator is identified by (^) this symbol.

	Observable Name	Operator Symbol	Operation
Position	x	$\hat{x}$	Multiply by x
	r	$\hat{R}$	Multiply by r

Momentum	p_x	$\hat{P}_x$	$-i\hbar\frac{\partial}{\partial x}$
	p	$\hat{P}$	$-\hbar\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$U(x)$	$\hat{U}(x)$	Multiply by $U(x)$
	$U(x,y,z)$	$\hat{U}(x,y,z)$	Multiply by $U(x,y,z)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $+U(x,y,z)$
Angular momentum	$L_x = yp_z - zp_y$	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$L_y = zp_x - xp_z$	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$L_z = xp_y - yp_x$	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

10. Commutation property of operators

If $[\hat{A},\hat{B}] = \hat{A}\hat{B}-\hat{B}\hat{A} = 0$

Then the two operators $\hat{A}$ and $\hat{B}$ commuters and for two wavefunctions ψ_1 & ψ_2

$$\int \psi_1^* \hat{A}\psi_2 d\tau = \int \psi_2 \hat{A}^* \psi_1^* d\tau$$

11. Hermitian Operator

$$\int \psi^* \hat{A}\psi d\tau = \int \psi \hat{A}^* \psi^* d\tau$$

If any operator A satisfy above condition it is hermitian operator.

12. Angular Momentum

The classical definition of angular momentum $\vec{L} = \vec{r}\times\vec{p}$ depends on six numbers r_x, r_y, r_z, p_x, p_y and p_z.

Angular momentum (L_x, L_y, L_z):

Mathematically, angular momentum is quantum mechanics is defined like momentum not as a quantity but as an operator on the wave function.

$\vec{L} = \vec{r} \times \vec{p}$ where $\vec{r}$ and $\vec{p}$ are the position and momentum operators respectively.

$$L = L_x\hat{i} + L_y\hat{j} + L_z\hat{k}$$

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$$

$$\vec{L} = \begin{bmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{bmatrix}$$

$$L = \hat{i}(yp_z - p_y z) + \hat{j}(zp_x - xp_z) + \hat{k}(xp_y - yp_x)$$

$L_x = yp_z - zp_y$ $\quad$ $L_y = zp_x - xp_z$ $\quad$ $L_z = xp_y - yp_x$

$= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ $\quad$ $= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ $\quad$ $= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

Relation:

$[L_x, L_y] = i\hbar L_z$ $\quad$ $[L_x, y] = i\hbar z$ $\quad$ $[L_x, x] = 0$

$[L_y, L_z] = i\hbar L_x$ $\quad$ $[L_y, z] = i\hbar x$ $\quad$ $[L_y, y] = 0$

$[L_z, L_x] = i\hbar L_y$ $\quad$ $[L_z, x] = i\hbar y$ $\quad$ $[L_z, z] = 0$

Normalisation

Normalisation means to bring a function in normal state. If a wave function satisfy this equation.

$\int_{-\infty}^{+\infty} \psi^* \psi d\tau = 1$, then it is said to be normalised.

The limits $+\infty$ and $-\infty$ are conventionally used to represent "all space".

If ψ is not a normalized wavefunction, then

$$\int_{-\infty}^{+\infty} (A\psi)^*(A\psi)d\tau = 1 \quad \Rightarrow \quad A^2 \int_{-\infty}^{+\infty} \psi^*\psi d\tau = 1$$

$\therefore$ $\boxed{A = \sqrt{\frac{1}{\int_{-\infty}^{+\infty} \psi^*\psi d\tau}}}$ where A is normalisation.

Orthogonality

If two wave function ψ_m and ψ_n are such that $\int \psi_m^* \psi_n d\tau = 0$ or $\int \psi_n^* \psi_m d\tau = 0$

Then ψ_m and ψ_n are said to be orthogonal.

A set of function that are both normalised and orthogonal to each other is called an orthonormal set.

Probability

Probability of finding a particle within a limit from lower limit to upper limit may be calculated as:

$\boxed{\int_{L,L}^{U,L} \psi\psi^* \partial\tau}$ (ψ must be normalised)

Average value or expectation value

If function ψ is normalised than $\boxed{\langle x \rangle = \int_{L\,L}^{U\,L} \psi^* \hat{x} \psi d\tau}$, $\langle p_x \rangle = \int_{L,L}^{U,L} \psi^* \hat{p}_x \psi d\tau$

Heisenberg uncertainty principal, $\Delta x.\Delta p_x \geq \frac{\hbar}{2}$

$$\boxed{(\Delta p_x)^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2}$$

$$\boxed{(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2}$$

PARTICLE IN 1-D BOX

$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$; $E = \frac{n^2 h^2}{8ml^2}$; l = length of 1-D box

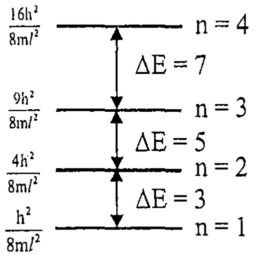
In this case, n represents the quantum number.

So energy difference between the two sucessive energy levels.

$$\Delta E = E_{n+1} - E_n$$

$$\Delta E = \frac{(n+1)^2 h^2}{8ml^2} - \frac{n^2 h^2}{8ml^2} \Rightarrow \frac{[(n+1)^2 - n^2]h^2}{8ml^2} = \frac{(2n+1)h^2}{8ml^2}$$

Energy Order Diagram in 1-D box:

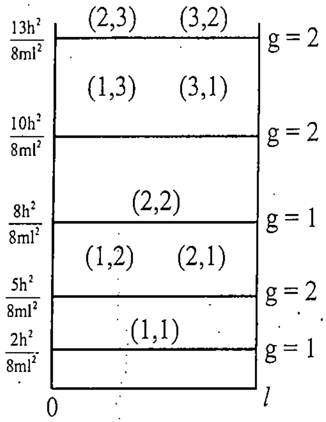


PARTICLE IN TWO DIMENSIONAL BOX

$$\psi = \sqrt{\frac{2}{l_x}}\sin\frac{n_x\pi x}{l_x}\sqrt{\frac{2}{l_y}}\sin\frac{n_y\pi y}{l_y}$$

$$E = \frac{n_x^2h^2}{8ml_x^2} + \frac{n_y^2h^2}{8ml_y^2} = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right)$$

$$\text{If } l_x = l_y,\ E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2)$$



PARTICLE IN THREE DIMENSIONAL BOX

$$\psi = \left(\sqrt{\frac{2}{l_x}}\sin\frac{n_x\pi}{l_x}x\right)\left(\sqrt{\frac{2}{l_y}}\sin\frac{n_y\pi}{l_y}y\right)\left(\sqrt{\frac{2}{l_z}}\sin\frac{n_z\pi}{l_z}z\right)$$

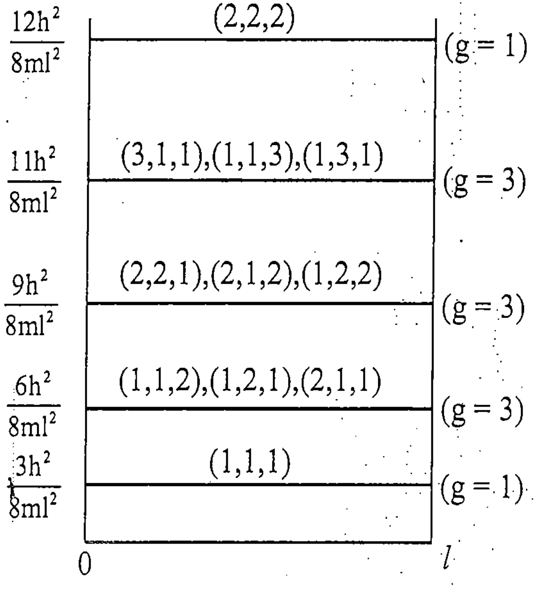
$$\Rightarrow \quad \psi = \sqrt{\frac{8}{l_xl_yl_z}}\sin\left(\frac{n_x\pi}{l_x}x\right)\sin\left(\frac{n_y\pi}{l_y}y\right)\sin\left(\frac{n_z\pi}{l_z}z\right)$$

and total energy is $E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$

If $l_x = l_y = l_z = l$

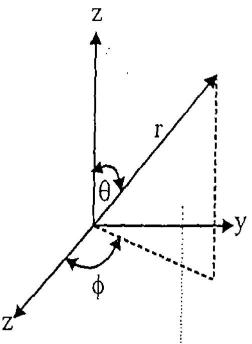
$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

Degeneracy of 3-D box:



HYDROGEN ATOM

Schrodinger Equation in Terms of Spherical Polar Coordinates:



$x = r \sin\theta \cos\varphi$; $y = r\sin\theta \sin\varphi$; $z = r\cos\theta$.

the transformed expression is given below:

$$\left[-\frac{h^2}{8\pi^2\mu r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi = E\psi$$

where ψ is a function of r, θ and φ.

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial Part}}\ \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$$

Three Split Expressions of the Schrodinger Equation:

Thus, the Schrodinger equation for the hydrogen like species can be separated into three equations. These are:

Equation involving only r

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=l(l+1)$$

Equation involving only θ

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\sin^2\theta = m^2$$

Equation involving only φ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi} = -m^2$$

Solution of Φ-dependent equation

$$\Phi_m = \frac{1}{\sqrt{2\pi}}\exp(im\varphi); \qquad m = 0, \pm 1, \pm 2, \ldots\ldots$$

Wave function of hydrogen atom:

$$\psi_{n,l,m} = R_{n,l}\theta_{l,m}, \phi_m$$

The function $R_{n,l}$, $\theta_{l,m}$ and ϕ_m describe the R, θ, ϕ dependence of the function R depends on two quantum number n and l. θ depends on two quantum number l, m and ϕ depends on the quantum number m.

Table

Orbitals	**Wave Functions**
$n = 1, l = 0, m = 0;$	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$
$n = 2, l = 0, m = 0;$	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\frac{Zr}{a_0})e^{-\frac{Zr}{2a_0}}$
$l = 1, m = 0$	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \cos\theta$
$l = 1, m = \pm 1$	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta\cos\phi$
	$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta\sin\phi$

for H-atom

$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$ (for p, d, f orbitals)

$d\tau = 4\pi r^2 dr$ (for s orbital)

Most probable distance

If $P(r)dr = \psi\psi^* d\tau$

$$P(r)dr = \psi\psi^* 4\pi r^2 dr \qquad [d\tau = 4\pi r^2 dr] \text{ (for s orbital)}$$

$$P(r) = \psi\psi^* 4\pi r^2$$

For maximum probable distance $\frac{dP(r)}{dr} = 0$

Average value of radius

$$\langle r \rangle = \int \psi_n r \psi_n d\tau$$

Its general formula is

$$\langle r_{n,l} \rangle = \frac{a_0}{2}(3n^2 - l(l+1))$$

Relation between average value of K.E, P.E. & T.E.

$$\langle V \rangle = -2\langle T \rangle$$

$$\langle E \rangle = -\langle V \rangle$$

$$\langle E \rangle = 2\langle T \rangle$$

Where T = K.E., E = T.E., V = P.E.

for H atom for 1s orbital

$$\langle V \rangle = -\frac{e^2}{4\pi \in_0} \frac{1}{r}$$

$$\langle T \rangle = \frac{e^2}{8\pi \in_0} \frac{1}{r} \qquad \text{(Here } r = a_0 \text{ for 1s orbital)}$$

$$\langle E \rangle = -\frac{e^2}{8\pi \in_0} \frac{1}{r} = -13.6 \text{ eV (on substituting all the values)}$$

EXERCISE I

Single Answer Type

1. Bohr's Model of Atom

1. Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom?

(a) n = 2, Li^{2+} (b) n = 2, Be^{3+} (c) n = 2, He^+ (d) n = 3, Li^{2+}

2. A doubly ionized lithium atom in an excited state (n = 6) emits a photon of energy 4.25 eV. What are the quantum number (n) and the energy (E) of the final state?

(a) n = 2, E = –30.6 eV (b) n = 3, E = –13.6 eV

(c) n = 4, E = –7.65 eV (d) n = 5, E = –4.90 eV

3. The velocity of the electron in the hydrogen atom

(a) increases with increasing principal quantum number

(b) decreases with increasing principal quantum number

(c) is uniform for any value of the principal quantum number

(d) first increases and then decreases with principal quantum number

4. The energies of the 1s orbital in H, He^+ and Li^{2+} are in the ratio

(a) H : He^+ : Li^{2+} = 1 : 1 : 1 (b) H : He^+ : Li^{2+} = 1 : 2 : 3

(c) H : He^+ : Li^{2+} = 1 : 4 : 9 (d) H : He^+ : Li^{2+} = 1 : 1/4 : 1/9

5. If the ionization energy of hydrogen atom is 13.6 eV, the expected third ionization energy of the lithium atom is

(a) 13.6 × 3 eV (b) 13.6 × 2 eV (c) 13.6 × 6 eV (d) 13.6 × 9 eV

6. If the binding energy of 2nd excited state of a hydrogen like sample is 24 eV approximately, then the ionisation energy of the sample is approximately

(a) 54.4 eV (b) 24 eV (c) 122.4 eV (d) 216 eV

7. The de Brogile wavelength of an electron moving in a circular orbit is λ. The minimum radius of orbit is

(a) $\frac{\lambda}{\pi}$ (b) $\frac{\lambda}{2\pi}$ (c) $\frac{\lambda}{4\pi}$ (d) $\frac{\lambda}{3\pi}$

8. What is the ratio of velocities of electron & proton when the De-Broglie wavelength associated with an electron would be equal to that associated with a proton if a proton is 1836 times heavier than an electron.

(a) 1836 (b) 1/1836 (c) 1 (d) 2

2. Quantum Model of Atom

9. The value of the magnetic quantum number of a p_x orbital is

(a) –1 (b) 0 (c) +1 (d) undefined

10. Any p-orbital can accommodate up to

(a) four electrons (b) six electrons

(c) two electrons with parallel spins

11. The principal quantum number of an atom is related to the
(a) size of the orbital (b) spin angular momentum
(c) orientation of the orbital in space (d) orbital angular momentum

orbital angular = $\sqrt{l(l+1)}$ × h

12. The orbital angular momentum of an electron in 2s orbital is
(a) $+\frac{1}{2}\cdot\frac{h}{2\pi}$ (b) zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\cdot\frac{h}{2\pi}$

13. The number of radial nodes in 3s and 2p respectively are
(a) 2 and 0 (b) 0 and 2 (c) 1 and 2 (d) 2 and 1

14. An electron, a proton and an alpha particle have kinetic energies of 16E, 4E and E respectively. What is the qualitative order of their de Broglie wavelengths?
(a) $\lambda_e > \lambda_p = \lambda_\alpha$ (b) $\lambda_p = \lambda_\alpha > \lambda_e$ (c) $\lambda_p > \lambda_e > \lambda_\alpha$ (d) $\lambda_\alpha < \lambda_e \gg \lambda_p$

15. The number of nodal planes in a p_x orbital is:
(a) one (b) two (c) three (d) zero

16. Wave function in quantum mechanics represents
(a) a state of the system (b) shape of the system
(c) probability of the system (d) energy of the system

17. A 3p atomic orbital has
(a) one radial node and one angular node (b) two angular nodes
(c) one angular node (d) one radial node

18. The orbital with two radial and two angular nodes is
(a) 3p (b) 5d (c) 5f (d) 8d

19. Which quantum number is not related with Schrodinger equation
(a) Principal (b) Azimuthal (c) Magnetic (d) Spin

3. Postulates of Quantum Mechanics & Operators

20. When the operator $-\frac{\hbar^2 d^2}{dx^2}$, operates on the function e^{-ikx}, the result is
(a) $k^2\hbar^2 e^{-ikx}$ (b) $ik^2\hbar^2 e^{-ikx}$ (c) $i\hbar^2 e^{-ikx}$ (d) $\hbar^2 e^{-ikx}$

21. The eigenvalue of the eigenfunction $\psi = e^{2ax^2}$ for an operator $\frac{d}{dx}$ is
(a) 4ax (b) 2ax (c) cannot be calculated (d) e^{2ax^2}

22. The angular momentum operator $\hat{L}_y$ is
(a) $-\frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ (b) $\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ $-i\hbar$

(c) $-\frac{i\hbar}{2m}\frac{\partial}{\partial x}$ (d) $\frac{\hbar}{i}\left(z\frac{\partial}{\partial x}-y\frac{\partial}{\partial y}\right)$

23. The value of commutator of p_x with L_y is

(a) $i\hbar p_z$ (b) $-i\hbar p_y$ (c) $+i\hbar p_y$ (d) 0

24. The commutator of the kinetic energy operator, $\hat{T}_x$ and the momentum operator, $\hat{p}_x$ for the one dimensional case is

(a) $i\hbar$ (b) $i\hbar\frac{d}{dx}$ (c) 0 (d) $i\hbar x$

4. Particle in 1-D, 2-D, 3-D

25. The probability of finding the particle in a one dimensional box of length L in the region between L/4 and 3L/4 for quantum number n = 1 is

(a) $\frac{1}{2}$ (b) $\frac{1}{2}+\frac{1}{\pi}$ (c) $\frac{1}{2}-\frac{1}{\pi}$ (d) $\frac{2}{3}$

26. Degeneracy of level $\frac{27h^2}{8ml^2}$ for a 3-D box is

(a) g = 3 (b) g = 2 (c) g = 4 ~~(d)~~ g = 1

27. In units of $\frac{h^2}{8ml^2}$, the energy difference between levels corresponding to 3 and 2 node eigen functions for a particle of mass m in a one-dimensional box of length l is

(a) 1 (b) 3 (c) 5 (d) 7

28. The second lower state of particle in a cubic box is

(a) non degenerate (b) doubly degenerate (c) triply degenerate (d) six-fold degenerate

29. A particle in three dimensional cubic box of a L has energy of $\frac{14h^2}{8mL^2}$. The degeneracy of the state is

(a) 2 (b) 3 (c) 6 (d) 9

30. For the particle-in-a-box problem in (0, L), the value of $\langle x^3 \rangle$ in the n → ∞ limit would be

(a) $\frac{L^3}{6}$ (b) $\frac{L^3}{3}$ (c) $\frac{L^3}{4}$ (d) $\frac{L^4}{4}$

5. H-atom

31. The ionisation potential of hydrogen atom is 13.6 eV. The first ionisation potential of a sodium atom, assuming that the energy of its outer electron can be represented by a H-atom like model with an effective nuclear charge of 1.84 is

(a) 46.0 eV (b) 11.5 eV (c) 5.1 eV (d) 2.9 eV

32. What is the degeneracy of the energy level with n = 6 (n being the principal quantum number) in a hydrogenic atom or ion?

NE 20 Dec (sorry)

(a) 16 (b) 9 (c) 36 (d) 25

33. The energy of a hydrogen atom in a state is $\frac{-hcR_h}{64}$. The degeneracy of state will be

(a) 5 (b) 64 (c) 75 (d) 125

34. The wave function,

$$\psi(r,\theta,\phi) = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}\sin\theta\cos\theta e^{-\left(\frac{r}{3a_0}+i\phi\right)}$$

$e^{i\,m\,\phi}$

The value of n, l, m corresponding to this wavefunction respectively are

(a) 3, 2, 1 (b) 3, 2, –1 (c) 3, 1, 1 (d) 2, 2, 1

35. Ions with a single electron such as He^+, Li^{2+} and Be^{3+} are described by the H-atom wave function with $\frac{z}{a_0}$ substituted for $\frac{1}{a_0}$, where 'z' is nuclear charge. This is wavefunction becomes $\psi(r) = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$. The mean value $\langle r\rangle$ for Be^{3+} is

(a) $\frac{3}{2}a_0$ (b) $\frac{3}{4}a_0$ (c) $\frac{1}{2}a_0$ (d) $\frac{3}{8}a_0$

36. A function has $\sin\theta\cos\phi$ in its angular part of the function it may be

(a) p_x (b) $d_{x^2-y^2}$ (b) d_{z^2} (d) s

37. The angular part of the wavefunction for the electron in a hydrogen atom is proportional to $\sin^2\theta\cos\theta e^{2i\phi}$. The values of the azimuthal quantum number l and the magnetic quantum number (m) are respectively

(a) 2 and 2 (b) 2 and –2 (c) 3 and 2 (d) 3 and –2

38. The average value of the radius <r> in the 1s state of the hydrogen atom ions (a_0 is Bohr radius)

(a) a_0 (b) 1.5 a_0 (c) 0.75 a_0 (d) 0.5 a_0

39. The energy of 2s and 2p orbitals is the same for

(a) Li (b) Li^{+2} (c) Be_2^+ (d) H^-

40. For a hydrogen atom in an n = 4 state, the maximum possible z-component of orbital angular momentum is

(a) $2\hbar$ (b) $3\hbar$ (c) $\sqrt{12}\hbar$ (d) $\sqrt{6}\hbar$

41. The angular part of the wavefunction for the electron in hydrogen atom is proportional to $\sin^2\theta\cos\theta e^{2i\phi}$. Then the eigenvalue corresponding to operator L^2 is :

n'' l=3 ②

(a) $12\hbar^2$ (b) $6\hbar^2$ (c) $\sqrt{6}\hbar^2$ (d) $\sqrt{2}\hbar$

poly

42. A hydrogenic 3p orbital has the following form of the radial wavefunction (α_1 = constant): n−l−1

check (a) $r(\alpha_1 - r)e^{-\alpha_2 r}$ (b) $r^2e^{-\alpha_3 r}$ (c) $r(\alpha_4 - r)(\alpha_5 - r)e^{-\alpha 6r}$ (d) $r^3e^{-\alpha 7r}$

n 3

EXERCISE II

One or More Than One Correct Type

$n-l-1 = ①$ ①

1. Which of the following is iso-electronic with neon?

(a) O^{2-} (b) F^- (c) Mg (d) Na

2. Choose the correct relations on the basis of Bohr's theory.

(a) Velocity of electron $\propto \frac{1}{n}$ (b) Frequency of revolution $\propto \frac{1}{n^3}$

(c) Raidus of orbit $\propto n^2 Z$ (d) Force on electron $\propto \frac{1}{n^4}$

3. The spectrum of He^+ is expected to be similar to that of :

(a) Li^{2+} (b) He (c) H (d) Na

4. Which of the following statement(s) is (are) correct?

(a) The electronic configuration of Cr is [Ar] $(3d)^5 (4s)^1$. (Atomic number of Cr = 24)

(b) The magnetic quantum number may have negative values.

(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)

(d) None of these

5. Which of the following statements is/are correct for an electron of quantum numbers n = 4 and m = 2?

(a) The value of ℓ may be 2. (b) The value of ℓ may be 3.

(c) The value of s may be +1/2. (d) The value of ℓ may be 0, 1, 2, 3.

6. check Choose the incorrect statement(s):

(a) Increasing order of wavelength is

Micro waves > Radio waves > IR waves > visible waves > UV waves

(b) The order of Bohr radius is (r_n : where n is orbit number for a given atom)

$r_1 < r_2 < r_3 < r_4$

(c) The order of total energy is (E_n : where n is orbit number for a given atom)

$E_1 > E_2 > E_3 > E_4$

(d) The order of velocity of electron in H, He^+, Li^+, Be^{3+} species in second Bohr orbit is

$Be^{3+} > Li^{+2} > He^+ > H$

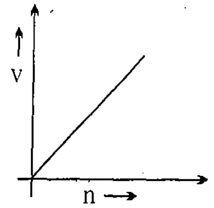
7. Select the correct curve(s):

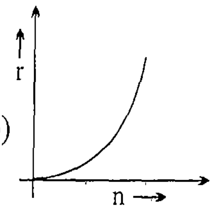
If **v** = velocity of electron in Bohr's orbit

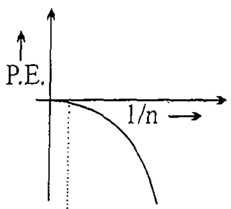
r = Radius of electron in Bohr's orbit

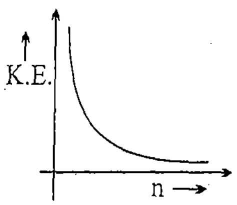
P.E. = Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit.

(a)


(b)


(c)


(d)


8. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are :

(a) -3.4 eV (b) -4.2 eV (c) -6.8 eV (d) $+6.8$ eV

9. Gaseous state electronic configuration of nitrogen atom can be represented as:

(a) ↑↓ ↑↓ ↑ ↑ ↑ (b) ↑↓ ↑↓ ↑ ↓ ↑

(c) ↑↓ ↑↓ ↑ ↓ ↓ (d) ↑↓ ↑↓ ↓ ↓ ↓

EXERCISE III

Numerical Answer Type

1. State the orbital degeneracy of the levels in a hydrogen atom that have energy (a) $-hcR_H$; (b) $-\frac{1}{9}hcR_H$.

2. Consider Bohr's theory for hydrogen atom. The magnitude of angular momentum, orbit radius and velocity of the electron in nth energy state in a hydrogen atom are ℓ, r & v respectively. Find out the value of 'x', if product of v, r and ℓ ($vr\ell$) is directly proportional to n^x.

3. A hydrogen sample is prepared in a particular excited state. Photons of energy 2.55 eV get absorbed into the sample to take some of the electrons to a further excited state B. Find orbit numbers of the states A and B. Given the allowed energies of hydrogen atom :

$$E_1 = -13.6 \text{ eV}, E_2 = -3.4 \text{ eV}, E_3 = -1.5 \text{ eV}, E_4 = -0.85 \text{ eV}, E_5 = -0.54 \text{ eV}$$

4. Calculate radius ratio for 2nd orbit of He^+ ion & 3rd orbit of Be^{+++} ion.

5. A single electron system has ionization energy 11180 kJ mol^{-1}. Find the number of protons in the nucleus of the system.

6. Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n = 2 to n = 1

7. Calculate wavelength for 2nd line of Balmer series of He^+ ion

8. If electron make transition from 7th excited state to 2nd state in H atom sample find the max. number of spectral lines observed.

EXERCISE IV

Previous Years Questions

IIT-JAM Previous Year Questions

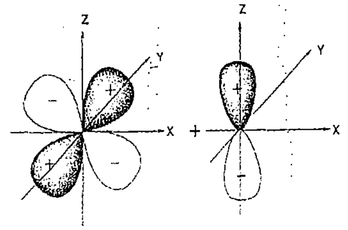
1. For a particle in a cubic box, the total number of quantum numbers needed to specifiy its state are

(a) 1 (b) 2 (c) 3 (d) 9

2. The normalisation constnat 'A' for the wavefunction $\psi(\phi) = Ae^{(im\phi)}$ where $0 \le \phi \le 2\pi$ is

(a) $1/2\pi$ (c) $\sqrt{2\pi}$ (c) 2π (d) $1/\sqrt{2\pi}$

3. The overlap between the atomic orbitals sketched below is



(a) positive (b) negative (c) zero (d) no overlap

4. An atomic orbital is described by the wavefunction $\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\left(\frac{r}{a_0}\right)}$, where a_0 is the Bohr radius.

Given : $d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$ and $\int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$ (n is a positive integer)

(a) Identify the atomic orbital and calculate the mean or the average radius of this orbital in terms of a_0.

(b) Calculate the most probable radius (in terms of a_0) at which an electron wil be found when it occupies this orbital.

5. In the Bohr model of a hydrogen-like atom with atomic number Z.

the angular momentum of an electron (of mass m_e and charge e) is a non-zero integral (n) multiple of $h/2\pi$, where h is the Planck's constant, and

the electrostatic attraction exerted by the nucleus on the electron is balanced by the centrifugal force experienced by the electron.

(i) Write mathematical expressions for the above statements.

(ii) Hence obtain the expression for the radius r of the Bohr orbit of the electron in terms of e, n and Z.

6. (A) The electronic wavefunction (ψ) for hydrogen atom in the 2s state is given as

$$\psi \propto \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$

$$\frac{(3 - \sqrt{5})a_0}{Z}$$

4725

Determine the most probable radial distance for the electron in this state and also the position of the node (in terms of a_0).

(B) Calculate the wavelength corresponding to the lowest energy excitation of an electron confined to a one-dimensional box of length 1 nm. (Energy level for a particle-in-a-one-dimensional box are given by $E_n = n^2h^2/8ma^2$).

7. Use the time-independent Schrodinger equation to calculate the energy of a particle of Mass "m" with V = 0 in the state $\psi = \sqrt{\frac{8}{a^3}}\sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{a}$ in a cubical box of length "a".

8. The $3p_z$ orbital has

(a) one radial node (b) two radial nodes (c) one angular node (d) two angular nodes

9. If $\hat{x} = x$ and $\hat{P}_x = \frac{h}{2\pi i}\frac{d}{dx}$, then the value(s) of $\hat{p}_x\hat{x} - \hat{x}\hat{p}_x$ is/are

(a) $\frac{\hbar}{i}$ (b) $-i\hbar$ (c) 0 (d) $\frac{i}{\hbar}$

10. The energy of an electron in a hydrogenic atom with nuclear charge Z varies as:

(a) Z (b) Z^2 (c) 1/Z (d) $1/Z^2$

11. $\left[\frac{-h^2}{(8\pi^2 m)}\frac{d^2}{dx^2}+\frac{h^2\alpha^2x^2}{(2\pi^2 m)}\right]\exp(-\alpha x^2) = C\frac{h^2}{(4\pi^2)}\exp(-\alpha x^2)$, where h, π, m and α are constants. Then C is

(a) $2\alpha/m$ (b) $\alpha/2m$ (c) α/m (d) α^2/m

12. For unnormalized wave-function, $\psi(r,\theta,\phi) = \sin\theta\cos\phi\left(\frac{2r}{a_0}-\left(\frac{r}{a_0}\right)^2\right)\exp\left(-\frac{r}{a_0}\right)$, the number of radial node(s) is ....

13. Identify the correct statement regarding Einstein's photoelectric effect

(a) The number of electrons ejected depends on the wavelength of incident radiation.

(b) Electron ejection can occur at any wavelength of incident radiation.

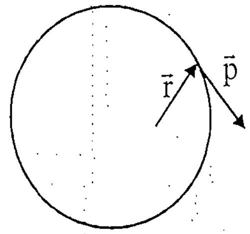
(c) The number of electrons ejected at a given incident wavelength depends on the intensity of the radiation.

(d) The kinetic energy of the ejected electrons is independent of the wavelength of incident radiation.

14. If a particle has linear momentum $\vec{p} = 2\vec{i} + \vec{j} + \vec{k}$ at position $\vec{r} = 3\vec{i} - \vec{j} + \vec{k}$, then its angular momentum is

(a) $\vec{i} + 2\vec{k}$ (b) $-2\hat{i} - \hat{j} + 5\hat{k}$ (c) $5\vec{i} - 2\vec{j}$ (d) $2\vec{i} + 5\vec{j} - \vec{k}$

15. An electron moves around the nucleus in a circular orbit, according to the Bohr model. The radial vector $\vec{r}$ and the instantaneous linear momentum vector $\vec{p}$ are shown in the diagram below.



The direction of the angular momentum vector is

(a) along $\vec{r}$ (b) along $\vec{p}$

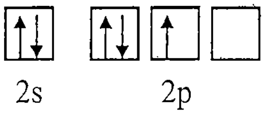
(c) opposite to $\vec{p}$ (d) perpendicular to both $\vec{r}$ and $\vec{p}$

16. An electron is found in an orbital with one radial node and two angular nodes. Which orbital the electron is in?

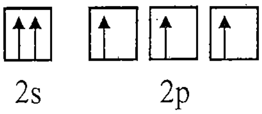
(a) 1s (b) 2p (c) 3d (d) 4d

17. The acceptable valence shell electronic arrangement is

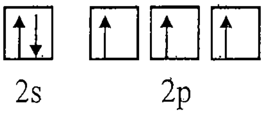
(a)



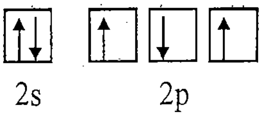
(b)



(c)



(d)



Gate Previous Year Questions

18. An electron of mass m is confined to a one-dimensional box of length b. If it makes a radiative transition from second excited state to the ground state, the frequency of the photon emitted is

(a) $\frac{9h}{8mb^2}$ (b) $\frac{3h}{8mb^2}$ (c) $\frac{h}{mb^2}$ (d) $\frac{2h}{8mb^2}$

19. The wave function for a quantum mechanical particle in a one-dimensional box of length a is given by $\psi = A\sin\frac{\pi x}{a}$. The value of A for a box of length 200 nm is

(a) $4 \times 10^4\ (nm)^2$ (b) $10\sqrt{2}(nm)^{1/2}$ (c) $\sqrt{2}/(10)(nm)^{-1/2}$ (d) $0.1\ (nm)^{-1/2}$

20. The 2s-orbital of H-atom has a radical node at $2a_0$ because ψ_{2s} is proportional to

(a) $\left(\frac{1}{2}+\frac{r}{a_0}\right)$ (b) $\left(2+\frac{r}{a_0}\right)$ (c) $\left(2-\frac{r}{a_0}\right)$ (d) $\left(2-\frac{r}{2a_0}\right)$

21. Which of the following pairs of operators commute?

(a) x and $\frac{d}{dx}$ (b) $\frac{d}{dx}$ and $\frac{d^2}{dx^2}+\frac{2d}{dx}$ (c) $x^2\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ (d) x^3 and $\frac{d}{dx}$

22. The set of eigen functions $\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$ $(0 \le x \le a, n = 1, 2, 3, ...)$ is

(a) orthogonal
(b) normalized
(c) Both orthogonal and normalized
(d) unnormalized

23. The operation of the commutator [x, d/dx] on a function f(x) is equal to

(a) 0
(b) f(x)
(c) –f(x)
(d) x df/dx

24. The degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy is

(a) 3
(b) 6
(c) 1
(d) 4

25. e^{-2x^2} is an eigen function of the operator $\left(\frac{d^2}{dx^2} - 16x^2\right)$. The corresponding eigen value is

(a) +4
(b) –4
(c) +2
(d) –2

26. The value of the magnetic quantum number of a p_x orbital is

(a) –1
(b) 0
(c) +1
(d) undefined

IIT-JEE Previous Years Questions

27. The electrons, identified by n & l ; (i) $n = 4$, $l = 1$ (ii) $n = 4$, $l = 0$ (iii) $n = 3$, $l = 2$ (iv) $n = 3$, $l = 1$ can be placed in order of increasing energy, from the lowest to highest as :

(a) (iv) < (ii) < (iii) < (i)
(b) (ii) < (iv) < (i)
(c) (i) < (iii) < (ii) < (iv)
(d) (iii) < (i) < (iv) < (ii)

28. The number of nodal planes in a p_x orbital is:

(a) one
(b) two
(c) three
(d) zero

29. The principal quantum number of an atom is related to the

(a) size of the orbital
(b) spin angular momentum
(c) orientation of the orbital in space
(d) orbital angular momentum

30. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon ?

(a) 3s
(b) 2p
(c) 2s
(d) 1s

ANSWER KEY

EXERCISE I

1. b 2. c 3. b 4. c 5. d 6. d 7. b
8. a 9. d 10. d 11. a 12. b 13. a 14. a
15. a 16. a 17. a 18. b 19. d 20. a 21. c
22. b 23. a 24. c 25. b 26. d b 27. d 28. c
29. c 30. c 31. c 32. c 33. b 34. b 35. d
36. a 37. c 38. b 39. b 40. b 41. a 42. a

EXERCISE - II

1. a,b 2. a,b,d 3. a,c 4. a,b,c 5. a,b,c 6. a,c 7. b,c,d
8. a 9. a,d

EXERCISE III

1. $g = 1, g = 9$ 2. $x = 2$
3. $A = 2, B = 4$ 4. 8/9
5. 3 6. 4/3 R
7. 4/3 R 8. 21

EXERCISE IV

1. c 2. d 3. a

4. (a) 3/2 a_0 (b) a_0 5. (i) $mvr = \frac{nh}{2\pi}$ (ii) $r = \frac{n^2h^2}{4\pi^2 ZMe^2} \times 4\pi \epsilon_0$

6. (a) $(3 \pm \sqrt{5})a_0$ (b) 2×10^{-9} m 7. $E = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8ma^2}$

8. a,c 9. a,b 10. b 11. c 12. 1 13. c,d 14. b
15. d 16. d 17. c 18. c (b) 19. d 20. c 21. b
22. c 23. c 24. c 25. b 26. d 27. a 28. a
29. a 30. d

perhaps..

CHAPTER 14

RADIOACTIVITY

RADIOACTIVITY

The phenomenon of spontaneous emission of particles, electromagnetic radiation or both by unstable nuclei, is known as radoactivity.

PROPERTIES OF α, β-PARTICLES AND γ-RAYS

	Properties	*Alpha*	*Beta*	*Gamma*
1.	Nature	Fast moving He	Fast moving	High energy
	nuclei	electorns	radiations	
2.	Representation	$_2He^4$ or α	$_{-1}e^0$ or $_{-1}\beta^0$	γ or $_0{}^0\gamma$
3.	Charge	2 unit (+ve)	1 unit (–ve)	No charge
4.	Velocity	1/10 of light	33% to 90% of light	Same as light waves
5.	Relative penetrating power	1 or (0.01 mm of Al foil)	100 or (0.1 cm of Al foil)	10000 or (8 cm lead or 25 cm steel)
6.	Travel distance in air	2 – 4 cm	200 – 300 cm	500 m
7.	Kinetic energy	high	low	–
8.	Effect on ZnS plate	Luminosity	Little effect	–
9.	Mass g/particle	6.65×10^{-24}	9.11×10^{-28}	–
10.	Relative ionising power	10000	100	1

Kinetics of nuclear distintegration

☞ Radioactive decay is a first order process. Hence $-\frac{dN}{dt} = \lambda N$ or $N = N_0\, e^{-\lambda t}$

where N = number of radioactive nuclei at any time t;

N_0 = number of radioactive nuclei at t = 0;

λ = decay constant

☞ **Activity :** Activity (A) = $-dN/dt = \lambda N$

S.I. units :

Disintegration per second (symbol s^{-1} or dps).

1 dps = 1 Bq (Becquerel)

Other units

1 Ci (Curie) = 3.7×10^{10} dps.

1 Rd (Rutherford) = 10^6 dps

Specific activity = dps / gm

☞ **Half life ($t_{1/2}$) :** The time taken by half the nuclei (originally present) to decay:

$$t_{1/2} = \frac{0.693}{\lambda}$$

Note : After *n* half--lives have passed, activity is reduced to $\frac{1}{2^n}$ of its initial value.

☞ **Average life (t_{avg})**

$$t_{avg} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44\ t_{1/2}$$

Uses of Radioisotopes

(i) **Oxygen-18:** Used in studying reaction mechanism. In photosynthesis O^{18} isotope is used in CO_2^{18}.

(ii) **Cobalt-60:** Used to sterilize surgical instruments and to improve the safety and realiability of inductrial fuel oil burners. Used in cancer treatment, food irradiation, gauges, and radiography.

(iii) **Iodine-131:** Used to treat thyroid disorders, (Graves's disease)

(iv) **Cadmium-109:** Used to analyze metal alloys for checking stock, scrap sorting

(v) **Calcium-47:** Important aid to biomedical researchers studying the cellular functions and bone formation in mammals.

(vi) **Carbon-14:** Major research tool. Helps in research to ensure that potential new drugs are metabolized without forming harmful by-products. Used in biological research, agriculture, pollution control and archeology.

(vii) **Caesuim-137:** Used to treat cancerous tumors to measure correct patient dosages of radioactive pharmaceuticals to measure and control the liquid flow in oil pipelines to tell researchers whether oil wells are plugged by sand and to ensure the right fill level for packages of food, drugs and other products. (The products in these packages do not become radioactive).

(viii) **Chromium-51:** Used in research in red blood cell survival studies.

(ix) **Copper-67:** When injected with monoclonal antibodies into a cancer patient, helps the antibodies bind to and destroy the tumor.

(x) **Iodine-123:** Widely used to diagnose thyroid disorders and other metabolic disorders including brain function.

(xi) **Iodine-125:** Major diagnostic tool used in clinical tests and to diagnose thyroid disorders. Also used in biomedical research.

(xii) **Iodine-129:** Used to check some radioactivity counters in in-vitro diagnostic testing laboratories.

(xiii) **Iridium-192:** Used to test the integrity of pipeline welds, boilers and aircraft parts and in brachytherapy/tumor irradiation.

(xiv) **Iron-55:** Used to analyze electroplating solutions and to detect the presence of sulphur in the air. Used in metabolism research.

(xv) **Nickel-63:** Used to detect explosives, and in voltage regulators and current surge protectors in electronic devices, and in electron capture detectors for gas chromatographs.

(xvi) **Phosphorus-32:** Used in molecular biology and genetics research.

(xvii) **Phosphorus-33:** Used in molecular biology and genetics research.

(xviii) **Promethium-147:** Used in electric blanket thermostats and to gauge the thickness of thin plastics, thin sheet metal, rubber, textile and paper.

(xix) **Radium-226:** Makes lighting rods more effective.

(xx) **Sodium-24:** Used to locate leaks in industrial pipe lines and in oil well studies.

(xxi) **Strontium-90:** Used in survey meters by schools, the military and emergency management authorities. Also used in cigarette manufacturing sensors and medical treatment.

(xxii) **Sulphur-35:** Used in genetics and molecular biology research.

(xxiii) **Thorium-229:** Helps fluorescent lights last longer.

(xxiv) **Thorium-230:** Provides coloring and fluorescence in colored glazes and glassware.

(xxv) **Tritium:** Major tool for biomedical research. Used for life science and drug metabolism studies to ensure the safety of potential new drugs for self-luminous aircraft and commercial exist signs for luminous dials, gauges and wrist watches to produce luminous paint, and for geological prospecting and hydrology.

(xxvi) **Uranium-234:** Used in dental fixtures like crowns and dentures to provide a natural colour and brightness.

(xxvii) **Uranium-235:** Fuel for nuclear power plants and naval nuclear propulsion systems and used to produce fluorescent glassware, a variety of coloured glazes and wall tiles.

Application of radioisotopes

(i) **Determination of the age of the rock by rock dating method :** Let us consider a rock containing U-238 isotope formed many years ago. The age of this rock can be determined by considering its radioactive disintegration which, as we have already seen, is governed by the relation $N = N_0 e^{-\lambda t}$

where, N_0 = amount of U-238 isotope originally present in a small quantity of the rock or mineral at the time the rock was formed, N = amount of U-238 still left undecayed after the lapse of time, t which represents the age of the rock, and λ = disintegration constant of U-238.

$$\lambda t = 2.303 \log_{10}\left(1 + \frac{Pb^{206}}{U^{238}}\right) \quad \text{and} \quad e^{\lambda t} = 1 + \frac{Pb^{206}}{U^{238}}$$

(ii) Determination of the age of recent objects by radio-carbon dating method :

$$_6C^{14} \longrightarrow {}_7N^{14} + \beta\text{-particle}$$

$$t = \frac{2.303\, t_{1/2}}{0.693} \log_{10} \frac{N_0}{N} = \frac{2.303\, t_{1/2}}{0.693} \log \left[\frac{\text{Amount of } C^{14} \text{ in fresh wood}}{\text{Amount of } C^{14} \text{ in dead wood}}\right]$$

THEORIES REGARDING NUCLEAR STABILITY

(A) Even odd theory of nuclear stability

The number of stable nuclides is maximum when both p and n are even number.

p	*n*	*No. of stable nucleus*
even	even	165
even	odd	55
odd	even	50
odd	odd	5

(B) Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 50, 82 or 126 protons or neutrons are exceptionally stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

e.g., $_{50}Sn$ having 10 stable isotopes while $_{51}Sb$ has only two stable isotopes.

☞ Nuclei with magic number of protons as well as neutrons have notably high stabilities.

$\left[\text{e.g. } {}^{4}_{2}He,\ {}^{16}_{8}O,\ {}^{40}_{20}Ca \text{ and } {}^{208}_{82}Pb\right]$. 165 such stable nuclei are known.

(C) Packing Fraction

'Aston' expressed relation between atomic mass & mass number in terms of packing fraction.

$$\textbf{Packing Fraction} = \left(\frac{\text{Atomic mass} - \text{Mass number}}{\text{Mass number}}\right) \times 10^4$$

Packing fraction of C-12 is exactly zero.

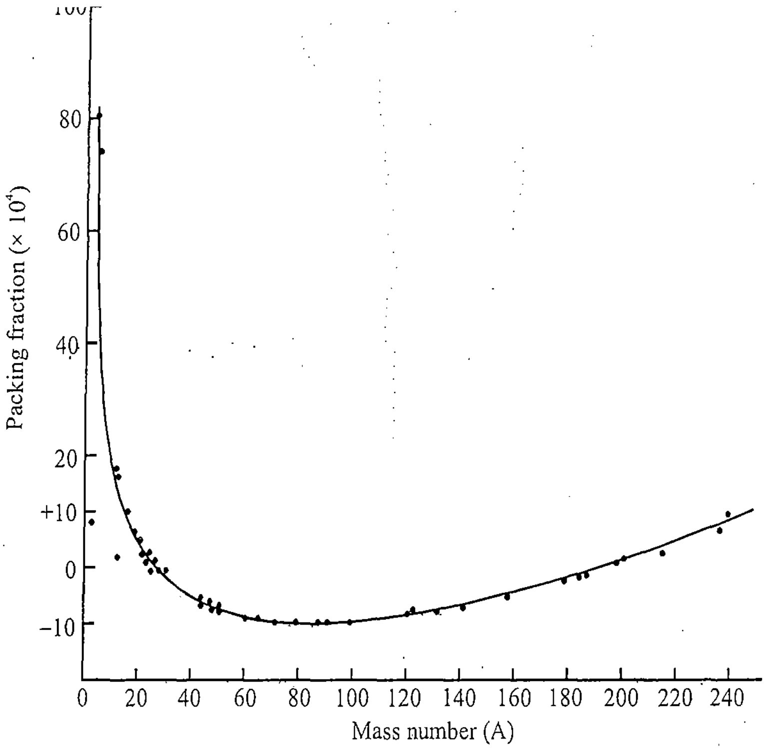
Packing fraction may be positive or negative

Negative packing fraction implies that nuclei is stable

Positive packing fraction implies that nuclei is unstbale

Some lighter nuclei have positive packing fraction although nucleus is stable

Mo, Ru, Rh, Pd have lowest packing fraction



(D) Binding Energy

It is defined as energy required to break the nucleus into its component viz protons & neutrons. Binding energy per nucleon gives a quantitiative measure of nuclear stability.

Mass defect (Δm) = mass of neutron + mass of proton – mass of nucleus

Binding energy of nucleus = Δmc^2

The binding energy for a nucleus containing Z protons and N neutrons can be calculated as

Binding energy = $(ZM_H + Nm_n - {}^{A}_{Z}M)c^2$

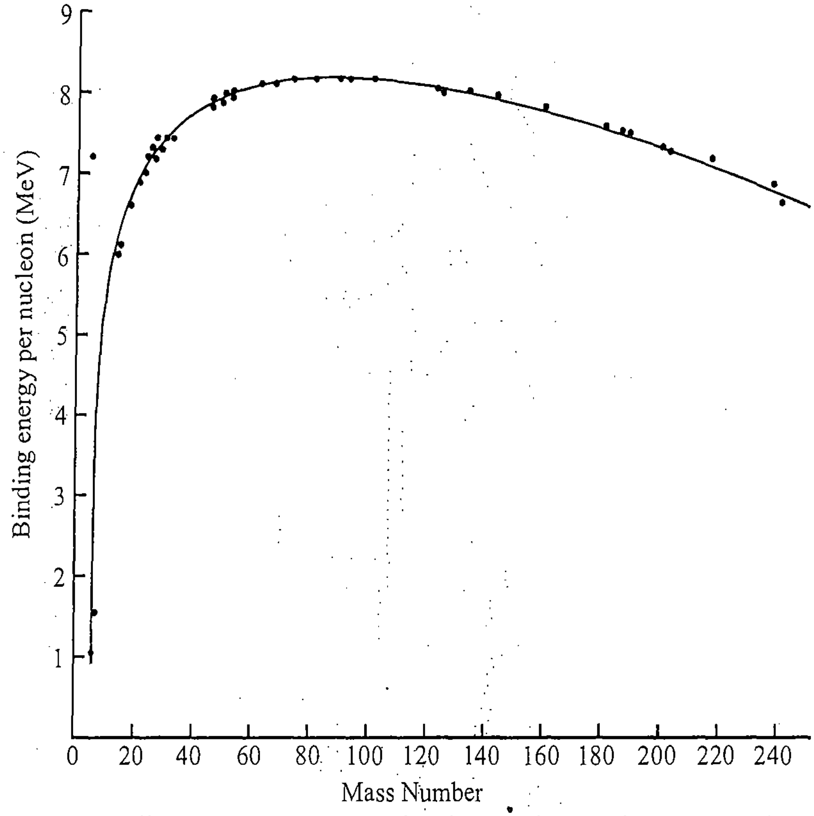
Note that above equation does not include Zm_p (the mass of Z protons). Rather, it contains ZM_H, the mass of Z protons and Z electrons combined as Z neutral ${}^{1}_{1}H$ atoms, to balance the Z electrons include in ${}^{A}_{Z}M$, the mass of the neutral atom is taken.

If $\Delta m = 1$ a.m.u. then B.E. = 931.5 MeV

B.E. = Δm (amu) × 931.5 MeV

$$\text{B.E. per nucleon} = \frac{\text{B.E.}}{\text{No. of nucleons}}$$

A very heavy nucleus, say A = 240, has lower binding energy per nucleon compared to that of a nucleus with A = 120, thus if a nucleus A = 240 brakes into two A = 120 nuclei, energy would be released in the process. This implies nucleons get more tightly bound. It has a very important application for energy production through fission.

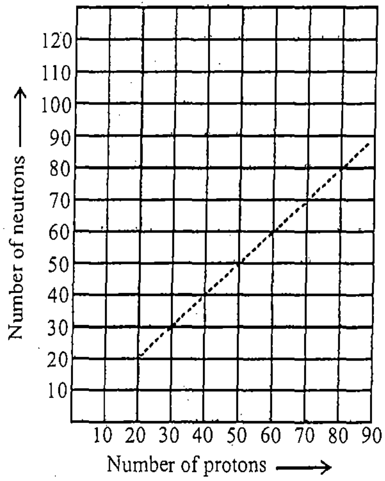


Consider two very light nuclei (A ≤ 10) joining to form a heavier nucleus. the binding energy per nucleon of the heavier nuclei is more than the binding energy per nucleon of the lighter nuclei, again energy would be released in such a process of fusion.

Nuclear binding energy is maximum for mass number 50 – 60.

Fe, Co, Ni have very high nuclear binding energy. Fe has the highest value of nuclear binding energy.

(E) Neutron / Proton Ratio and Stability Belt



☞ For atomic number < 20, most stable nuclei have n : p ratio nearly 1 : 1 (except H & Ar).

☞ For n/p ratio > 1.52, nucleus is unstable. Largest stable nucleus is $^{209}_{83}\text{Bi}$ for which n/p ratio is 1.52.

☞ For atomic number > 83, there are no stable nuclei.

Expected emission from unstable nucleus

1. **n/p ratio above stability belt :** Those nucleus which have high value of n/p ratio (lie above the stability belt) undergoes $^{0}_{-1}\beta$ decay.

$$n \longrightarrow p + {}_{-1}^{0}\beta$$

$${}_{15}^{32}P \longrightarrow {}_{16}^{32}S + {}_{-1}^{0}\beta$$

Beta decay is possible whenever the mass of the original neutral atom is greater than the final atom.

The difference between the rest mass energy of the initial constituents and that of the final products is called the Q-value of the process. Thus, if U_i is the rest mass energy of the intial constituents and U_f is that of the final products,

$$Q = U_i - U_f$$

Q value is positive i.e. isolated neutron may decay into proton.

The energy of ${}_{-1}^{0}\beta$ particle can be any thing between zero & Q.

Such transformation takes place because of weak forces operating within the nucleus.

2. **n/p ratio below stability belt :**

(a) **α-decay**

$${}_{83}^{212}Bi \longrightarrow {}_{81}^{208}Tl + {}_{2}^{4}He$$

Observed in nuclei with A > 210

Mass number & the atomic number of the daughter nucleus decreases by 4 & 2 respectively compared to parent nucleus.

Alpha decay may takes place spontaneously or it can be initiated.

Alpha decay is possible whenever the mass of the original neutral atom is greater than the sum of the masses of the final neutral atom and the neutral helium-4 atom.

All the alpha particles coming from a particular decay reaction have the same kinetic energy.

$\left({}_{+1}^{0}\beta\right)$ **Positron decay**

$$p \longrightarrow n + {}_{+1}^{0}\beta$$

Those nucleus which have low value of n/p ratio (lie below the stability belt) undergoes ${}_{+1}^{0}\beta$ decay.

Q value is negative i.e. isolated proton will not decay into neutron.

Positron decay is possible whenever the mass of the original neutral atom is greater than at least two electron masses larger than the final atom.

K electron capture

$${}_{Z}^{A}X + {}_{-1}^{0}e \longrightarrow {}_{Z-1}^{A}Y$$

$${}_{47}^{106}Ag + {}_{-1}^{0}e \xrightarrow{0} {}_{46}^{106}Pd$$

$$p + e \longrightarrow n$$

Electron capture can occur whenever the mass of origianl neutral atom is larger than that of final atom.

Those nucleus having low n/p ratio can capture K shell electron.

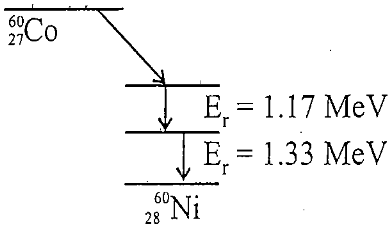
X-rays are emitted during the process.

γ-decay

When an α or β decay takes place, the daughter nucleus generally formed is in excited state & comes to ground state by a single or successive transition by emitting electromagnetic radiations i.e. γ rays.

$${}^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\text{B}$$

$${}^{60}_{28}\text{Ni} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{0}\gamma$$



Life time of metastable nucleus thus form is less than 10^{-9} sec.

No. of neutron and proton remains unchanged while **quantum state** of nucleon changes.

RADIOACTIVITY DISINTEGRATION SERIES

May radioactive necleus (Z > 82) are obtained in nature as a member of natural decay series.

The series of nuclear reaction is known as radioactive disintegration series.

Series	*Parent Nucleus*	*Last Nucleus*	*No. of α*	*No. of β*	*Total Steps involved (α+β)*
4n Thorium series	$_{90}Th^{232}$	$_{82}Pb^{208}$	6	4	10
(4n + 1) Neptunium series	$_{94}Pu^{241}$	$_{83}Bi^{209}$	8	5	13
4n + 2 or Uranium sereis	$_{92}U^{238}$	$_{82}Pb^{206}$	8	6	14
4n + 3 or Actinium sereis	$_{92}U^{235}$	$_{82}Pb^{207}$	7	4	11

4n, 4n + 3 and 4n + 3 series are **Natural** while (4n + 1) is **Artificial**

NUCLEAR REACTIONS

The reaction in which nuclei of atoms interact with other nuclei or elementary particles such as α-particle, proton, neutron, deutron, etc., resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles resulting nuclear reactions are also called projectiles. In all the nuclear reactions, the total number of protons and neutrons are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like

$${}_{7}N^{14} + {}_{2}He^{4} \longrightarrow {}_{8}O^{17} + {}_{1}H^{1}$$

Here, the nucleus of nitrogen atom is converted into the nucleus of oxygen atom by a particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as :

$${}_{7}N^{14} (\alpha, p)\, {}_{8}O^{17}$$

Some difference between nuclear and chemical reactions

No.	Chemical reaction	Nuclear reaction
1.	No new element is formed	New element is formed
2.	Valence electrons of atoms participates in reaction	Only the nucleus of atoms participates in reaction
3.	Balanced by the conservation of atoms	Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons)
4.	Mass conservation is obeyed	Disobey mass conservation
5.	May be exothermic or endothermic, liberating or absorbing relatively small amount of energy	May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy
6.	May be reversible	Only Irrversible
7.	May obey kinetics of any order	Obeys only first order kinetics
8.	Rate depends on external factors like temperature and the catalytic conditions	Rate is independent from any external condition

TYPES OF NUCLEAR REACTIONS

1. **Projectile Capture reactions :**

$${}_{92}U^{239} + {}_{0}n^{1} \rightarrow {}_{92}U^{240} + \gamma$$
$${}_{13}Al^{27} + {}_{0}n^{1} \rightarrow {}_{13}Al^{28} + \gamma$$

2. **Particle - particle reactions**

$${}_{11}Na^{23} + {}_{1}H^{1} \rightarrow {}_{11}Mg^{23} + {}_{1}n^{1}$$
$${}_{11}Na^{23} + {}_{1}H^{2} \rightarrow {}_{11}Na^{24} + {}_{1}H^{1}$$

3. **Spallation reactions:** High speed projectiles with 400 MeV bombarded on heavy nucleus giving smaller nucleus.

$${}_{29}C^{63} + {}_{2}He^{4} \rightarrow {}_{17}Cl^{37} + 14\,{}_{1}H^{1} + 16\,{}_{0}n^{1}$$

4. **Fission reactions:** It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nucleus with the emission of two or more neutrons and large amount of energy. For example,

the reaction of atom bomb : ${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3\,{}_{0}n^{1} + 200\text{ MeV}$

It is also found that the products of nuclear fission reactions are not unique. Some more product are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission

$$_{92}U^{235} + {}_0n^1 \rightarrow {}_{54}Xe^{139} + {}_{38}Sr^{95} + 2\,{}_0n^1$$
$$\rightarrow {}_{53}I^{137} + {}_{39}Y^{97} + 2\,{}_0n^1, \text{ etc.}$$

The distructive action of atom bomb is due to the following reasons :

(i) As some neutrons are produced in each fission, they may collide efficiently with the other U^{235} nuclei to produce more neutrons and thus the reactions occurs in chain like fashion. It results the emission of a large amount of energy in very small time.

(ii) Each product of fission is radioactive and hence increases the intensity of radiation in that region, resulting the problem due to radiations.

5. **Fusion reactions:** It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such a reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is way, very high temperature of the order 10^6 K is needed for the occurrence of such reactions. However, the overall reaction is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are :

Probable reaction of hydrogen bomb :

$$_1H^2 + {}_1H^2 \longrightarrow {}_2He^4 + 24.9 \text{ MeV}$$

Probable reaction occurring at the surface of sun :

$$4\,{}_1H^2 \longrightarrow {}_2He^4 + 2\,{}_{+1}e^0 + 24.7 \text{ MeV}$$

NUCLEAR REACTOR

A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of a nuclear reactor are :

1. **Fuel :** Nuclear fuels are of two types :

(i) **Fissile materials:** These are the nuclides which directly results into chain reaction on bombardment with slow neutrons. Such nuclides are U^{235}, Pu^{239}, U^{233}, etc.

(ii) **Fertile material:** These are the nuclides which are non-fissile but they may be converted into a fissile material by the action of neutrons. Such nuclides are U^{238} and Th^{232}.

$$_{92}U^{238} + {}_0n^1 \longrightarrow {}_{92}U^{239*} \xrightarrow{-\beta} {}_{93}Np^{239} \xrightarrow{-\beta} {}_{94}Pu^{239}$$

$$_{90}Th^{232} + {}_0n^1 \longrightarrow {}_{90}U^{233*} \xrightarrow{-\beta} {}_{91}Pa^{233} \xrightarrow{-\beta} {}_{92}U^{233}$$

Such conversion are performed in a special type of nuclear reactor called Breeder Reactor.

2. **Moderator:** It is used to slow down the fast moving neutrons without absorbing them. Example : water, graphite, helium, D_2O etc.

3. **Control rods:** These are the rods of material wich can absorb neutrons and hence control the fission reaction. Example: Cadmium, boron, etc.

4. **Coolant:** These are the material which transforms the energy produced in the fission reaction into heat energy. Example: Liquid alloy of sodium and potassium, heavy water (D_2O), polyphenyls, etc.

ARTIFICIAL TRANSMUTATION

It is the method of conversion of atom of one element into the atom of other element with the help of some particles like alpha particle, proton, deutron, neutron, etc. (called projectiles). The first such transmutation was performed by Rutherford. When N^{14} atoms were bombarded by very fast moving α-particles, the nitrogen atom has changd into oxygen atom and proton is produced simultaneously.

$$_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1$$

Later on, Rutherford and Chadwick shown that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations become more easier.

ARTIFICAL RADIOACTIVITY

When Irene Curie and F. Juliot bombarded the atoms of Al^{27}, B^{10} or Mg^{24} with fast moving α-particles then protons, neutrons and positrons were produced. They observed that the emission of protons and neutrons stops on stopping the bombardment but the emission of positron continues. they also observed that the rate of emission of positron decreases exponentially in the manner similar to natural radioactivity. They named the isotope emitting positron as **artifical radioisotope** and the phenomenon as **artificial radioactivity.**

$$_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{14}Si^{30} + {}_1H^1$$

$$\longrightarrow {}_{15}P^{30} + {}_0n^1 \longrightarrow {}_{14}Si^{30} + {}_{+1}n^0$$

NUCLEAR TRANSMUTATION

An experiment performed by Rutehrford in 1919, however, suggested the possibility of producing radioactive element artifically. When he bombarded a sample of nitrogen with α particles, the following reaction took place :

$$^{14}_{7}N + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}O + {}^{1}_{1}p \qquad \text{represented as } {}^{14}_{7}N(\alpha, p)\,{}^{17}_{8}O$$

An oxygen-17 isotope was producd with the emission of a proton. This reaction demonstrated for the first time the feasibility of converting one element into another, by the process of nuclear transmutation. Nuclear transmutation differs from radioactive decay in that the former is brought about by the collision of two particles.

TRANSURANIUM ELEMENTS

Particle acceleration made it possible to synthesis the so-called transuranium elements, elements with atomic numbers greater than 92. Neptunium ($Z = 93$) was first prepared. Since then many other transuranium element have been synthesized. All isotopes of these elements are radioactive.

NEUTRON ACTIVATION ANALYSIS

Quantities of elements that are too small for chemical analysis can be detected by this method. When bombarded with neutrons, many stable nuclides absorb a neutron to become unstable & then undergo ${}^{0}_{-1}\beta$ decay. The energies of ${}^{0}_{-1}\beta$ & ${}^{0}_{0}\gamma$ depend on the unstable nuclide & provide a means of identifying its original stable nuclide.

EXERCISE - I

Single Answer Correct Type

1. $^{238}_{92}U$ (IIIB) undergoes follows emissions

$$^{238}_{92}U \xrightarrow{-\alpha} A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C$$

which is/are correct statement ?

(a) A will of IB group (b) A will be of IIIA group

(c) B will of IIA (alkaline earth metal) group (d) C will of IIIA (boron family) group

2. Beta-emission takes place

(a) when neutron is converted to proton

(b) from the elements above the bond of stability

(c) with shifting of the new element one group towards right

(d) All the facts given above are true

3. Which of the following nuclear reaction is an example of nuclear fusion ?

(a) $^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$ (b) $^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{14}_{7}N + \gamma$

(c) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{12}_{6}C + ^{1}_{1}H$ (d) $^{235}_{92}N + ^{1}_{0}n \longrightarrow ^{142}_{56}Ba + ^{91}_{36}Kr + 3^{1}_{0}n$

4. There are 0.618 μg of ^{206}Pb and 0.238 μg of ^{238}U in a rock. If $T_{1/2}$ of ^{238}U is 1.5×10^9 yr, age of the rock is

(a) 0.75×10^9 yr (b) 1.5×10^9 yr (c) 3.0×10^9 yr (d) 4.5×10^9 yr

5. If half-life period is 100 yr, averge life is nearly

(a) 70 yr (b) 90 yr (c) 100 yr (d) 144 yr

6. In uranium mineral, the atomic ratio $N_{U\text{-}238}/N_{Pb\text{-}206}$ is nearly equal to one. The age (in yr) of the mineral is nearly (half-life period of U-238 is 4.5×10^9 yr)

(a) 3.0×10^8 (b) 3.0×10^9 (c) 4.5×10^8 (d) 4.5×10^9

7. The type of radiation that has the greatest penetrating power thruogh matter is

(a) α (b) β^- (c) γ (d) visible light

8. Of the following nuclides, the one most likely to decay by positron (β^+) emission is

(a) ^{68}Cu (b) ^{63}Cu (c) ^{67}Cu (d) ^{59}Cu

9. The radiation from a naturally occurring radioactive substance, as seen after deflection by a magnet in one direction, are

(a) definitely alpha rays (b) definitely beta rays

(c) both alpha and beta rays (d) either alpha rays or beta rays

10. $^{27}_{13}Al$ is a stable isotope $^{29}_{13}Al$ is expected to decay by

(a) α-emission (b) β-emission (c) positron emission (d) proton emission

11. $^{23}_{11}$Na is the more stable isotope of Na. Find out the process by with $^{24}_{11}$Na can undergo radioactive decay.

(a) β^--emission (b) α-emission (c) β^+-emission (d) K-electron capture

12. The half-life of a radioactive nuclide is 20 years. If a sample of this nuclide has an activity of 6400 disintegrations per minute (dis/min) today, its activity (dis/min) after 100 years would be

(a) 850 (b) 1600 (c) 200 (d) 400

13. In the following equation X is $^{241}_{95}\text{Am} + \alpha \rightarrow ^{243}_{97}\text{Bk} + \text{X}$

(a) $2\,^1_0\text{n}$ (b) ^1_0n (c) $2\,^1_1\text{H}$ (d) ^4_2He

14. If uranium (mass number 238 and atomic number92) emits an α-particle, the product has mass number and atomic number

(a) 236 and 92 (b) 234 and 90 (c) 238 and 90 (d) 236 and 90

15. An isotope of Ge_{32}^{76} is

(a) Ge_{32}^{77} (b) As_{33}^{77} (c) Se_{34}^{77} (d) Se_{34}^{78}

16. The number of neutrons accompanying the formation of $^{139}_{54}$Xe and $^{94}_{38}$Sr from the absorption of a slow neutron by $^{235}_{92}$U, followed by nuclear fission is

(a) 0 (b) 2 (c) 1 (d) 3

17. A positron is emitted from $^{23}_{11}$Na. The ratio of the atomic mass and atomic number of the resulting nuclide is

(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12

18. In boron neutron capture therapy, the initial boron isotope used and the particle generated after neutron capture respectively are:

(a) ^{11}B and α particle (b) ^{10}B and α particle

(c) ^{11}B and β particle (d) ^{10}B and β particle

19. The number of α and β particle(s), generated in the following radioactive decay process, are:

$$^{238}_{92}\text{U} \rightarrow ^{234}_{92}\text{U}$$

(a) one α and two β particle (b) two α and one β particles

(c) one α and four β particles (d) no α and four β particles

EXERCISE - II

Numerical and Subjective Answer Type

1. An element $_Z M^A$ undergoes an α-emission followed by two successive β-emissions. The element formed is ....

2. The number of neutrons in the parent nucleus which gives N^{14} on beta emission is ....

3. A radioactive nucleus decay by emitting one alpha and two beta particles, the daughter nucleus is .... of the parent.

4. (a) ${}^{235}_{92}U + {}_0n^1 \rightarrow {}^{137}_{52}A + {}^{97}_{40}B +$ .... (b) ${}^{82}_{34}Se \rightarrow 2\ {}_{-1}e^0 +$ ....

5. The number of neutrons emitted when ${}^{235}_{92}U$ undergoes controlled nuclear fission to ${}^{142}_{54}Xe$ and ${}^{90}_{38}Sr$ is

6. ${}_{90}Th^{234}$ disintegrates to give ${}_{82}Pb^{206}$ as the final product. How many alpha and beta particles are emitted during this process ?

7. Write a balanced equation for the reaction of N^{14} with α-particle.

8. ${}_{92}U^{238}$ is radioactive and it emits α and β particles to form ${}_{82}Pb^{206}$. Calculate the number of α and β particles emitted in this conversion. An ore of ${}_{92}U^{238}$ is found to contain ${}_{92}U^{238}$ and ${}_{82}Pb^{206}$ in the weight ratio of 1 : 0.1. The half-life period of ${}_{92}U^{238}$ is 4.5×10^9 yr. Calculate the age of the ore.

9. Complete the following nuclear reactions :

(a) ${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{1}_{1}H +$ .... (b) ${}^{7}_{3}Li + {}^{1}_{1}H \rightarrow$ ....

10. ${}^{215}_{84}Po$ undergoes an α emission to give element X followed by a β emission to give element Y.

(i) Write the valence shell electronic configuration of Y.

(ii) Indicate the groups of the periodic table to which X and Y belong.

11. (a) The radioactive element Ra (Z = 88) emits three alpha particles in succession. Deduce in which group the resulting element will be found ?

(b) A radioisotope sample ~~has an~~ initial activity of 23 dis/min. After 1/2 h, the activity is 11.5 dis/min. How many atoms of the radioactive nuclide were present originally ? [$\lambda t_{1/2} = 0.69$]

12. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr^{-1}) for the decay? What fraction would remain after 11540 yr?

13. ${}^{234}_{90}Th$ disintegrates to give ${}^{206}_{82}Pb$ as the final product. How many alpha and beta particles are emitted during this process?

14. The nuclidic ratio, ${}^{3}_{1}H$ to ${}^{1}_{1}H$ in a sample of water is 8.0×10^{-18} : 1. Tritium undergoes decay with a half-life period of 12.3 yr. How many tritium atoms would 10.0 g of such a sample contain 40 yr after the original sample is collected.

15. One of the hazards of nuclear explosion is the generation of ${}^{90}Sr$ and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 yr. Suppose one microgram was absorbed by a new-born child, how much ${}^{90}Sr$ will remain in his bones after 20 yr.

16. ${}^{227}Ac$ has a half-life of 22.0 yr with respect to radioactive decay. The decay follows two parallel paths, one leading to ${}^{227}Th$ and the other to ${}^{227}Fr$. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths?

17. Write a balanced equation for the reaction of N^{14} with α-particles.

18. A radioactive element undergoes 80% radioactive decay in 300 min. The half-life for this species in minutes is ______

19. The isotope $^{214}_{84}Po$ undergoes one alpha and one beta particle emission sequentially to form an isotope "X". The number of neutrons in "X" is _____.

20. A wood specimen containing ^{14}C taken from an ancient palace showed 24 counts in 3 minutes per gram of carbon in a detector. however, a fresh wood showed 52 counts in 2 minutes per gram of carbon. Assuming no background signal in the detector and half life of ^{14}C as 5730 years, the age (in years) of the wood specimen is

ANSWER KEY

EXERCISE - I

1. b 2. d 3. a 4. c 5. d 6. d 7. c
8. d 9. d 10. b 11. a 12. c 13. a 14. b
15. a 16. d 17. c 18. b 19. a

EXERCISE - II

1. $_{Z}M^{A-4}$
2. 8
3. isotope
4. (a) $2\,_{0}n^{1}$, (b) $_{36}Kr^{82}$, $\alpha = 8, \beta = 6$
5. 3
6. 7, 6
7. $_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{9}F^{18}$
8. 7.1×10^{8} yr
9. (a) $_{8}O^{17}$ (b) 2α
10. (a) $Y = {}_{83}Bi^{211}$, $6s^{2}\,4f^{14}\,5d^{10}\,6p^{3}$
    (b) X = group 14 and Y = group 15
11. (a) Group 14, (b) 10^{3}
12. 1/4
13. $\alpha = 7, \beta = 6$
14. 5.62×10^{5}
15. 0.6102 μg
16. $\lambda_1 = 6.3 \times 10^{-4}\ yr^{-1}$, $\lambda_2 = 0.03087\ yr^{-1}$
17. $^{14}_{7}N + ^{4}_{2}He \left[\underset{\text{unstable}}{^{18}_{9}F}\right] \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$
18. 129.15
19. 127
20. 9745.58 years

CHAPTER

15

TITRATIONS

CONDUCTOMETRIC TITRATIONS

PRINCIPLE

The principle of conductometric titrations is based on the fact that during the titrations, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration.

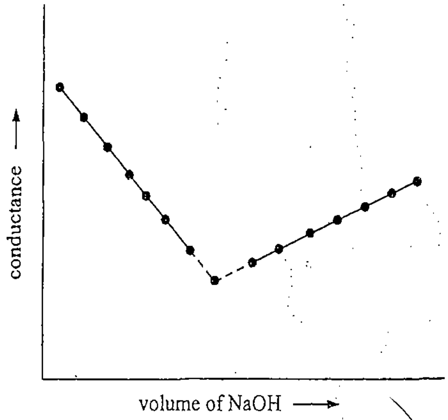
Types

1. Acid base titration
2. Replacement Titration
3. Redox Titrations
4. Precipitation Titration

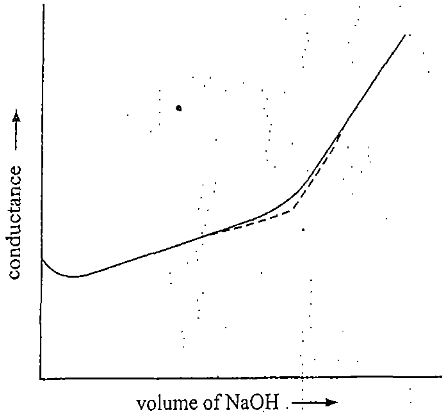
1. **Acid Base Titration:**

(a) Titration of Strong Acid vs Strong Base: Take an example of the titration of a strong acid, say HCl with a strong base, say NaOH, the following changes in conductance is observed during the course of titration.

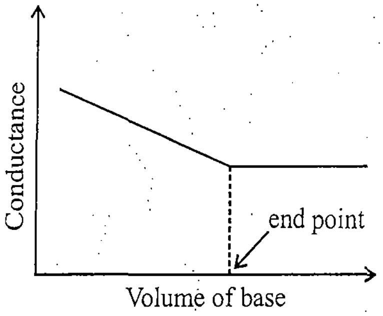
Before NaOH is added, the conductance of HCl solution has a high value due to the presence of highly mobile hydrogen ions. As NaOH is added, H^+ ions combine with OH^- ions to form undissociated water and thus the faster moving H^+ ions are replaced by relatively slower moving Na^+ ions. Consequently, the conductance of the solution decreases and this continues right up to the equivalence point where the solution decreases and this condinues right up to the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains an excess of the fast moving OH^- ions with the result that its conductance is increased and it continues to increase as more and more of NaOH added.



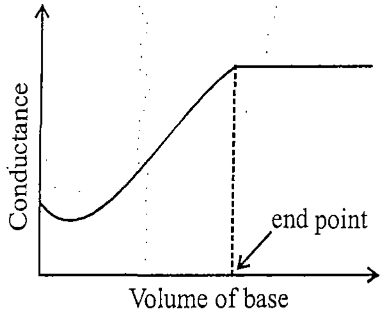
due to feeble ionization of acetic acid. Initially the addition of alkali causes not only the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to the common ion Ac^- and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc to Na^+Ac^- thus causing the replacement of non-conducting HAc with strong-conducting electrolyte Na^+Ac^-. The increase in conductance continues right up to the equivalence point. Beyond this point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. The graph near the equivalence point can, as usual, be obtained by the extrapolation method. The nature of curve obtained is shown in Figure.



(c) Titration of Strong Acid with Weak Base: In this case, initially conductance decreases on addition of base (e.g. NH_4OH) because fast moving H^+ ions are replaced by slow NH_4^+ ions. After end point the conductance remains constant because NH_4OH is a weak base, hence it dissociate to a very small extent moreover the NH_4^+ ions present in the solution exerts common ion effect thus decreasing the extent of dissoication. Hence a constant value is observed



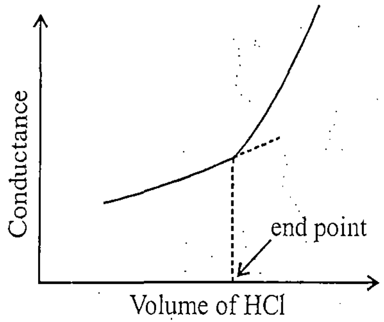
(d) Weak Acid vs Weak base: The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid vs strong base. After equivalence point, conductance virtually remains same as the weak base is feebly ionised, moreover common ion effect of NH_4^+ (coming from CH_3COONH_4) supressed the dissociation. Thus a constant value is obtained.



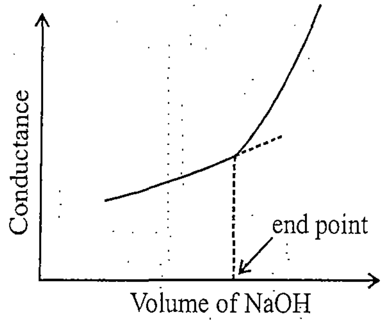
2. Displacement or Replacement Titration:

When a salt of weak acid is titrated with strong acid, the anion of weak acid is replaced by that of the strong acid and weak acid itself is liberated in undissociated form. For e.g. If HCl is added to solution of sodium acetate, the acetate ions is replaced by chloride ion after the end point. The initial increase in conductivity is due to the fact that chloride ion is slightly greater than acetate ion. Until the replacement is complete the solution contains enough sodium acetate to supress the ionization of liberated acid (CH_3COOH). However near the equivalence point acetic acid is sufficiently ionized to affect the conductivity and a rounded portion in curve is obtained. Beyond equivalence point, when excess of HCl is added, the conductivity increases rapidly as HCl is a strong electrolyte.

So the curve obtained is shown as

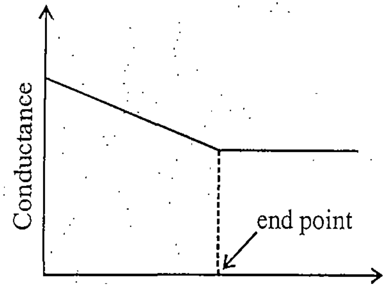


Same type of curve is obtained when a strong base is added to salt of weak base. e.g. NH_4Cl with NaOH.



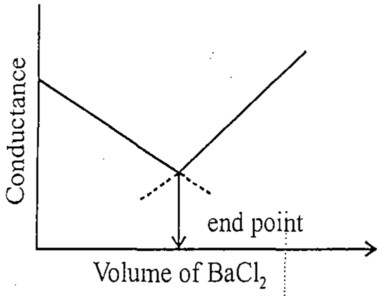
3. Redox Reaction

These are usefull for studying the complex compounds. In these titrations, there will be reduction in the number of hydrogen ions, so the conductivity will reduce as the number of H^+ ions are reduced. Beyond the end point, a constant curve is obtained. e.g. $KMnO_4$ with oxalic acid.



4. Precipitation Titration

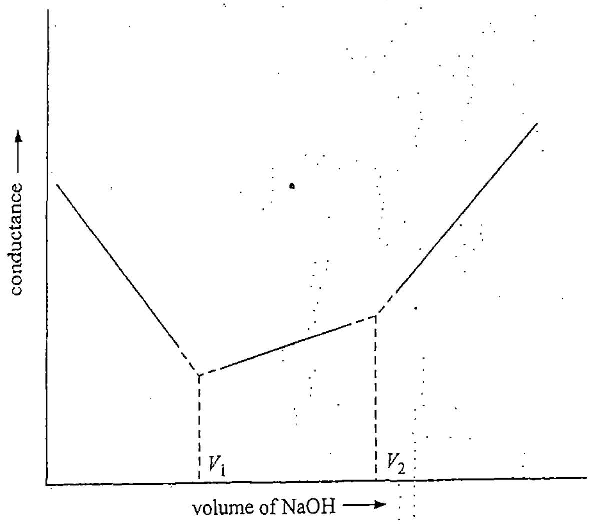
In this type of titration, the ion is replaced by another and the replaced ion forms a precipitate. e.g. in titration of $MgSO_4$ and $BaCl_2$ when $BaCl_2$ is added to $MgSO_4$ and $BaCl_2$ when $BaCl_2$ is added to $MgSO_4$ the conductance decreases as $BaSO_4$ is formed as a precipitate. After end point conductance increases rapidly because of fast moving Ba^{2+} and Cl^- ions.



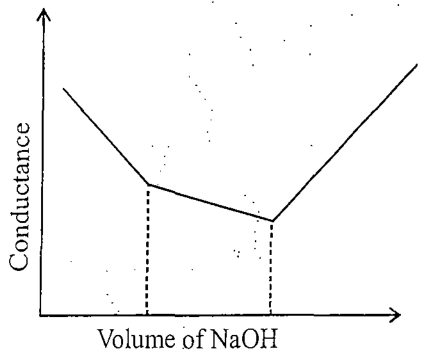
MIXTURES

1. **Mixture of strong and weak acid vs strong / weak base:**

In this case, the strong acid is first neutralized and only when this has been completely neutralized, the weak acid starts neutralizing. Thus, we have the neutralization reaction in two stages and the curve contains two breaks as shown in Figure. The first break corresponds to the neutralization of the strong acid and the second corresponds to that of the weak acid. From these the individual concentrations of the strong acid and the weak acid can be calculated.



2 **Mixture of HNO_3 and $AgNO_3$ vs NaOH.** Initially the NaOH reacts with HNO_3 and hence acid-base reaction occur. Fast moving H^+ ions replaced by slow Na^+ ions hence conductance decreases. After acid is neutralized the NaOH reacts with $AgNO_3$ and precipitate of AgOH is formed, this conductance decreases slightly. After end point. Conductance increases rapidly because of fast moving $\overset{\ominus}{OH}$ ions.

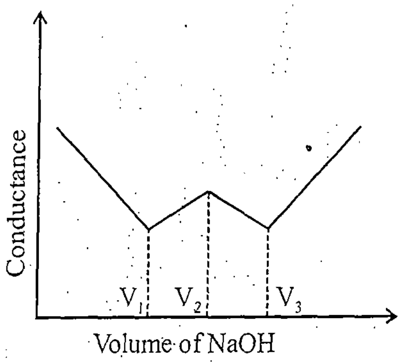


V_1 = volume of NaOH required to neutralise HNO_3

$V_2 - V_1$ = Volume of NaOH required to neutralise $AgNO_3$

Miscellaneous Curves

1. Mixture of HCl, CH_3COOH and $CuSO_4$ vs NaOH

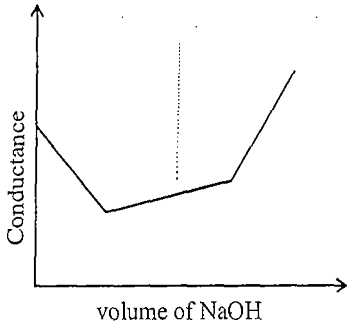


V_1 = Volume of NaOH required to neutralise HCl

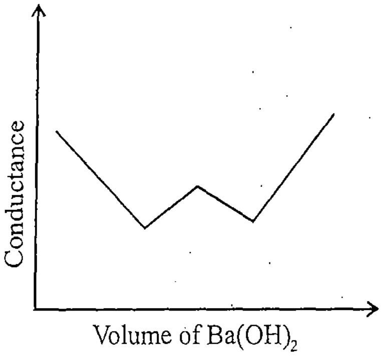
$V_2 - V_1$ = Volume of NaOH required to neutralize CH_3COOH

$V_3 - V_2$ = volume of NaOH required to neutralize $CuSO_4$

2. (a) Titration of H_3PO_4 vs NaOH



(b) Titration of H_3PO_4 vs $Ba(OH)_2$



REDOX TITRATIONS

1. **Iodometric Titrations :** (i) It is used to estiamte strength of unknown oxidising agent

(ii) It involve the in direct titration of iodine with hypo solution.

$$O.A. + \underset{\text{excess}}{KI} \longrightarrow I_2 \quad ...(1)$$

$$I_2 + \underset{\text{(hypo solution)}}{2Na_2S_2O_3} \longrightarrow 2NaI + Na_2S_4O_6 \quad ...(2)$$

at equivalence point

From reaction (2) gram equivalent of I_2 = gram equivalent of $Na_2S_2O_3$

So, from above equation we can estiamte strength of oxidising agent.

Example

$$I_2 + 2e^- \longrightarrow 2I^-$$

$\downarrow$ Reduction

Oxidising agent

$$2I^{-1} \longrightarrow I_2(s) + 2e^-$$

$\downarrow$ Oxidation

Reducing agent

$$MnO_4^- + I^- \longrightarrow I_2 + Mn^{+2}$$

Gram equivalent $KMnO_4$ = gram equivalent of I_2

$$5e^- + 5MnO_4^- \longrightarrow Mn^{+2}$$

$$2I^- \xrightarrow{\text{Reduction}} I_2 + 2e^-$$

$$I_2 + Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

gram equivalent of I_2 = gram equivalent $Na_2S_2O_2$

$x \times 2$ = gram equivalent $Na_2S_2O_2$

Iodometric titration is used for determination of conc. of oxising agent.

In this oxidising agent is allowed to react with excess of KI. The I_2 liberated in the reaction is titrated with hypo solution.

Illustration: 50 ml of $KMNO_4$ is mixed completely with excess of KI. The I_2 liberatd require 30 ml of 0.1 M $Na_2S_2O_3$. Calculate the molarity of $KMnO_4$ solution.

Solution:

$$\underset{n_f = 5}{MnO_4^-} + KI \xrightarrow{\text{excess}} \underset{n_f = 2}{I_2} + Mn^{2+}$$

gram equivalent of $KMnO_4$ = gram equivalent of I_2

$$\frac{5 \times M \times 50}{1000} = x \times 2$$

$$\underset{n_f = 2}{I_2} + \underset{n_f = 1}{2Na_2S_2O_3} \rightarrow 2NaI + Na_2S_4O_6$$

gram equivalent I_2 = gram eq. of $Na_2S_2O_3$

$$x \times 2 = \frac{30 \times 0.1 \times 1}{1000}$$

$$5 \times M \times 50 = 30 \times 0.1 \times 1$$

$$M_{KMnO_4} = \frac{3}{250} M$$

Illustration: Certain amount of KIO_3 was mixed with excess of KI solution. the liberated I_2 was titrated with 50 ml of 0.2 M $Na_2S_2O_3$ solution. Calculate the moles of KIO_3 added.

Solution: $\underset{n_f = 5}{IO_3^-} + I^{-1} \longrightarrow \underset{n_f = 5/3}{I_2}$

Gram eq. of KIO_3 = gram eq. of I_2

$$M_{KIO_3} \times 5 = x \times \frac{5}{3}$$

$$x = 3 \times M_{KIO_3} \qquad ....(1)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

gm eq. of I_2 = gm eq. of $Na_2S_2O_3$

$$x \times 2 = \frac{50 \times 2 \times 1}{10000}$$

$$x = \frac{5}{1000}$$

$$x = 3 \times M_{KIO_3}$$

$$\left[\text{Mole of } KIO_3 = \frac{5}{3000}\right]$$

2. **Iodimetric Titrations :** (i) It is used to estimate strength of unknown reducing agent.

(ii) It is also a type of back titration.

(iii) It involve direct tiration of iodine with hypo solution.

$$R.A. + \underset{\text{excess}}{I_2} \longrightarrow I^-$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Since it is a type of back titration

Σ gram equvialent of R.A. = Σ gram equivalent of O.A.

$$\boxed{\text{Gram equivalent of unknown R.A. + gram equivalent of } Na_2S_2O_3 = \text{gram equivalent of } I_2}$$

Illustration: 10 ml of unknown reducing agent is reacted with 500 ml, 0.1 M excess iodine solution. If the remaining iodine requires 0.1 M, 200 ml hypo solution ($Na_2S_2O_3$) for its complete neutralisation. Calculate the normality of unknown reducing agent?

Solution: $R.A. + \underset{\text{excess}}{I_2} \rightarrow I^-$

Batch Exam-[illegible]

According to equivalent concept,

Gram equivalent of unknown R.A. + gram equivalent of $Na_2S_2O_3$ = gram equivalent of I_2

$$N\times\frac{10}{1000}+0.1\times\frac{200}{1000}\times 1 = 0.1\times\frac{500}{1000}\times 2$$

$$\Rightarrow \quad N = 8$$

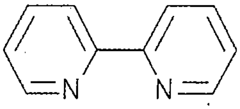
Hence, normality of the unknown reducing agent is 8 N.

REDOX INDICATORS

Definition: A redox indicator is an indicator compound that changes color at specific potential differences.

A redox indicator compound must have a reduced and oxidized form with different colors and the redox process must be reversible

Examples: The molecule 2,2'-Bipyridine is a redox indicator. In solution, it changes from light blue to red at an electrode potential of 0.97 V.



2,2'-Bipyridine

Almost all redox indicators involve a proton as a participant in their electrochemical reaction. Therefore sometimes redox indicators are also divided into two general groups: independent or dependent on pH.

pH independent Redox Indicators

Indicator	E^0, V	Color of Oxidized form	Color of Reduced form
2,2'-bipyridine (Ru complex)	+1.33	Colorless	Yellow
Nitrophenanthroline (Fe complex)	+1.25	Cyan	Red
N-Phenylanthranilic acid	+1.08	violet-red	Colorless
1,10-Phenanthroline iron(II) sulfate complex (Ferroin)	+1.06	Cyan	Red
N-Ethoxychrysoidine	+1.00	Red	Yellow
2,2`-Bipyridine (Fe complex)	+0.97	Cyan	Red
5,6-Dimethylphenanthroline (Fe complex)	+0.97	yellow-green	Red
o-Dianisidine	+0.85	Red	Colorless
Sodium diphenylamine sulfonate	+0.84	red-violet	Colorless
Diphenylbenzidine	+0.76	Violet	Colorless
Diphenylamine	+0.76	Violet	Colorless
Viologen	-0.43	Colorless	blue

2, 2' -Bipyridine

Ferroin

pH Dependent Redox Indicators

Indicator	E^0, V at pH=0	E^0, V at pH=7	Color of Oxidized form	Color of Reduced form
Sodium 2,6-Dibromophenol-indophenol or Sodium 2,6-Dichlorophenol-indophenol	+0.64	+0.22	Blue	Colorless
Sodium o-Cresol indophenol	+0.62	+0.19	Blue	Colorless
Thionine (syn. Lauth's violet)	+0.56	+0.06	Violet	Colorless
Methylene blue	+0.53	+0.01	Blue	Colorless
Indigotetrasulfonic acid	+0.37	-0.05	Blue	Colorless
Indigotrisulfonic acid	+0.33	-0.08	Blue	Colorless
Indigo carmine (syn. Indigodisulfonic acid	+0.29	-0.13	Blue	Colorless
Indigomono sulfonic acid	+0.26	-0.16	Blue	Colorless
Phenosafranin	+0.28	-0.25	Red	Colorless
Safranin **T**	+0.24	-0.29	red-violet	Colorless
Neutral red	+0.24	-0.33	Red	colorless

Safranin T
methylene Blue.

Indicator	Colour change		pH transition range	
	Acid form	Base form	Acid form predominate of pH	Base form predominate at pH
Picric acid	Colourless	Yellow	0.0	1.2
Malachite green	Yellow	Green	0.0	2.0
Methyl violet	Yellow	Violet	0.1	3.2
m-Cresol purple	Red	Yellow	1.2	2.8
Thymol blue	Red	Yellow	1.2	2.8
Bromophenol blue	Yellow	Blue	3.0	4.6
Congo red	Blue	Red	3.0	5.0
Methyl orange	Red	Yellow	3.1	4.4
Bromocresol green	Yellow	Blue	3.8	5.4
Methyl red	Red	Yellow	4.2	6.3
Litmus	Red	Blue	4.5	8.3
Propyl red	Red	Yellow	4.6	6.4
Chlorophenol red	Yellow	Red	4.8	6.4
Hematoxylin	Yellow	Red	5.0	6.0
p-Nitrophenol	Colourless	Yellow	5.0	7.0
Bromocresol purple	Yellow	Purple	5.2	6.8
Bromothymol blue	Yellow	Blue	6.0	7.6
Phenol red	Yellow	Red	6.8	8.4
m-Cresol purple	Yellow	Purple	7.4	9.0
Thymol blue	Yellow	Blue	8.0	9.6
Phenolphthalein	Colourless	Red	8.3	10.0
Thymolphthalein	Colourless	Blue	9.3	10.5
Alizarin yellow R	Yellow	Lavender	10.0	12.1
Alizarin blue S	Green	Blue	11.0	13.0
Malachite green	Green	Colourless	11.4	13.0

COMPLEXOMETRIC

- Calcein with EDTA for calcium
- Curcumin for boron, although the red color change of curcumin also occurs for pH > 8.4
- Eriochrome Black T for calcium, magnesium and aluminium
- Fast Sulphon Black with EDTA for copper
- Hematoxylin for copper
- Murexide calcium and rare earths
- Xylenol orange for gallium, indium and scandium

POTENTIOMETRIC

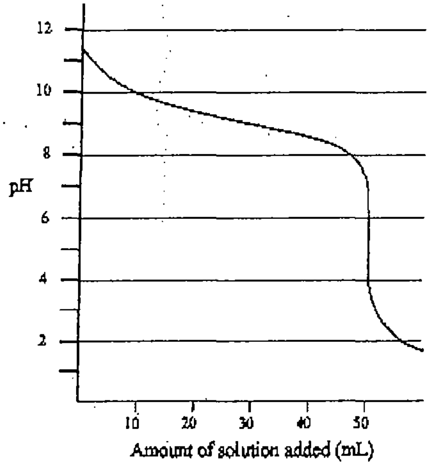
Indicator name	Reduced form colour	Oxidized form colour	Normal potential at pH 0 (V)	Normal potential at pH 7 (V)
Safranin T	Colourless	Red	0.24	-0.29
Neutral red	Colourless	Red	0.24	-0.33
Indigomonosulfonic acid	Colourless	Blue	0.26	-0.16
Phenosafranin	Colourless	Red	0.28	-0.25
Indigotetrasulfonic acid	Colourless	Blue	0.36	-0.05
Methylene blue	Colourless	Green-blue	0.36	???
Nile blue	Colourless	Blue	0.41	???
Benzidine	Colourless	Blue	0.92	???
Variamine blue B	Colourless	Blue	0.69	???
Dipehnylbenzidine	Colourless	Violet	0.76	TS
Diphenylamine sulfonic acid	Colourless	Red-violet	0.85	TS
Erioglaucine A	Green	Red	1.00	???
p-ethoxychrysoidine	Red	Light yellow	1.00	TS
Setoglaucine	Yellow-green	Light red	1.06	???
p-Nitrodiphenylamine	Colourless	Violet	1.06	???
Ferroin	Red	Light blue	1.06	???
5-Nitroferroin	Red-violet	Light blue	1.25	???
2,2′-Bipyridine (Ru complex)	Colourless	Yellow	1.33	TS

EXERCISE

1. Conductance of a solution depends on
   (a) concentration and types of ions (b) temperature
   (c) construction of device (d) All of them

2. In the titration of a strong acid with a strong base, the equivalence point is represented by
   (a) a maxima in the plot of conductance vs volume of titrant
   (b) a minima in the plot of conductance vs volume of titrant
   (c) second maxima in the plot of conductance vs volume of titrant
   (d) second minima in the plot of conductance vs volume of titrant

In answering questions 3-7, consider the following titration curve.



3. Which one of the following combinations does the titration curve represent?
   (a) addition of a strong base to a weak acid
   (b) addition of a weak base to a strong acid
   (c) addition of a strong acid to a weak base
   (d) addition of a weak acid to a strong base

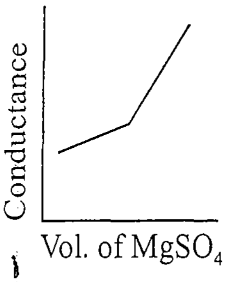
4. What is the value of pK_a that can be obtained from this titration curve?
   (a) 11.3 (b) 10.0 (c) 9.3 (d) 5.3

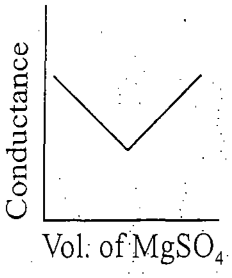
5. What is the pH of the solution at the point of maximum buffering?
   (a) 11.3 (b) 10.0 (c) 9.3 (d) 5.3

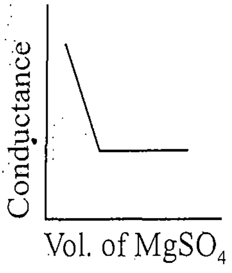
6. What is the pH of the solution at the equivalence point?
   (a) 11.3 (b) 10.0 (c) 9.3 (d) 5.3

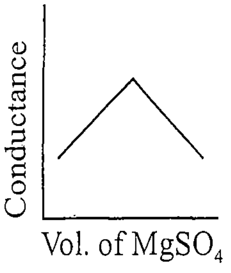
7. Which one of the following indicators would be most suitable for this titration?
   (a) any acid/base indicator is suitable (b) phenolphthalein ($pK_a = 9.6$)
   (c) cresol red ($pK_a = 8.3$) (d) methyl red ($pK_a = 5.1$)

8. In the conductometric titration experiment, a solution of 0.1 M $Ba(OH)_2$ is titrated against a solution of 0.1 M $MgSO_4$, and the conductance of the conductance of the mixture is continuously measured. The correct variation of conductance of the reaction mixture with the titration volume of $MgSO_4$ is best represented by

(a)


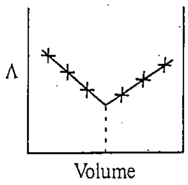
(b)


(c)


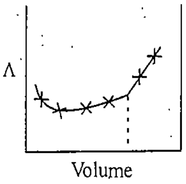
(d)


9. $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) *versus* the volume of $AgNO_3$ is :

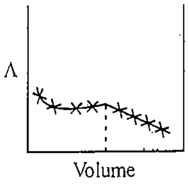
pH – BM



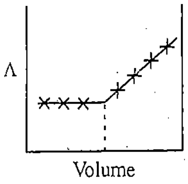
(P)



(Q)



(R)



(S)

(a) P (b) Q (c) R (d) S

10. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in column I. The variation in conductivity of these reactions is given in column II. Match column I with column II and select the correct answer using the codes given below the columns.

	Column I	Column II
P.	$\underset{X}{(C_2H_5)_3N}+\underset{Y}{CH_3COOH}$	1. Conductivity decreases and then increases
Q.	$\underset{X}{KI(0.1M)}+\underset{Y}{AgNO_3(0.01M)}$	2. Conductivity decreases and then does not change much
R.	$\underset{X}{CH_3COOH}+\underset{Y}{KOH}$	3. Conductivity increases and then does not change much
S.	$\underset{X}{NaOH}+\underset{Y}{HI}$	4. Conductivity does not change much and then increases

Codes

	P	Q	R	S		P	Q	R	S
(a)	3	4	2	1	(b)	4	3	2	1
(c)	2	3	4	1	(d)	1	4	3	2

11. Which of the indicator is best for titration of HCl vs NaOH, if the HCl is in burette and NaOH in conical flask

(a) Phenolphthalein (b) Methyl orange (c) EBT (d) congo red

12. The suitable pH range for phenolphthalein for its action is

(a) 4-5 (b) 6-8 (c) 8-11 (d) 12-14

13. Which of the following is an external indicator

(a) Alizarin (b) Pottasium ferricyanide

(c) methyl red (d) salochromic black-T

Pot. Ferrocyanide is external indicator

14. Which of the following is used as an indicator in Redox reaction

(a) EBT (b) Methyl orange (c) Phenolphthalein (d) methylene blue

Diphenylamine → Internal of [illegible]

(a) methyl orange (b) methyl red

(c) $KMnO_4$ itself can act as indicator (d) Mohr's salt can act as indicator

16. The best suitable indicator for titration of metal ions with EDTA in a slightly acidic medium is

(a) Eriochronic Black-T (b) Alizarin

(c) Xylenol orange (d) None of the above

17. For the working of xylenol orange indicator in a metal EDTA titration, the buffer used is

(a) $NH_4OH - NH_4Cl$ (b) $CH_3COOH - CH_3COONa$

(c) Hexamine (d) All of the above

18. The indicator used in titration of Mohr's salt with $K_2Cr_2O_7$ is (Redox Rxn)

(a) Solochrome Black-T (b) Xylenol orange

(c) diphenyl amine (d) phenolphtalein

diphenyl amine is redox

19. In a titration of EDTA with metal ions, if we do not have a metal indicator, then

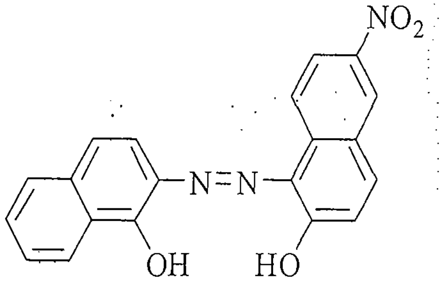
(a) we can use acid base indicator

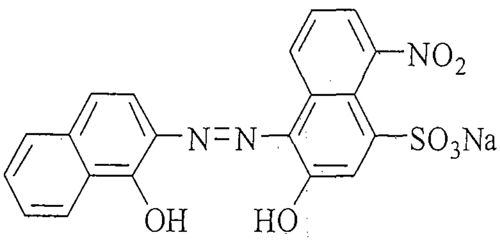
(b) we can use Redox indicator

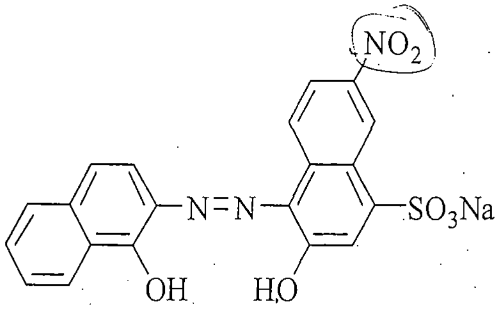
(c) we can used both acid base as well as redox indicator

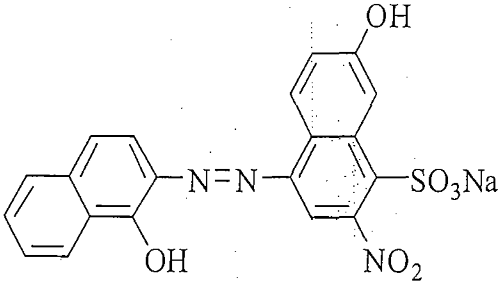
(d) we can't titrate without a metal indicator

20. The structure of Eriochrome Black-T is

(a)


(b)


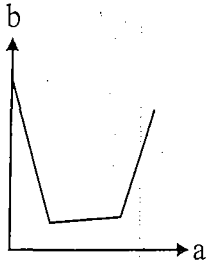
(c)


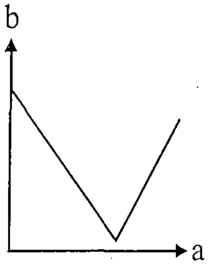
(d)


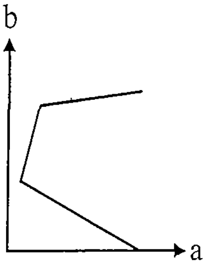
21. The naturally occuring indicator among the following is

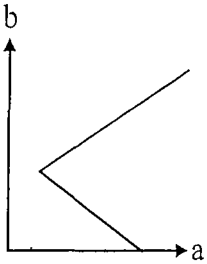
(a) Litmus (b) Anthraquinone (c) Methyl Red (d) Fluoroscein

22. On titrating conductometrically a NaOH solution with a mixture of HCl and CH_3CO_2H solutions, plot of the volume of mixed acid addded (b) in y-axis against the conductance (a) in x-axis is expected to look like

(a)


(b)


(c)


(d)


23. Conductometric titration of a strong acid with a strong alkali (MOH) shows linear fall of conductance upto neutralisation point because of

(a) formation of water (b) increase in alkali concentration

(c) Faster moving H^+ being replaced by slower moving M^+

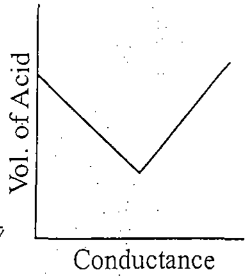
(d) Neutralisation of acid

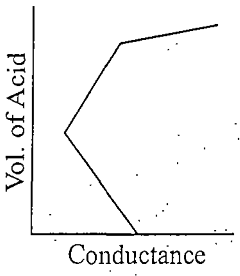
1 ml
10x

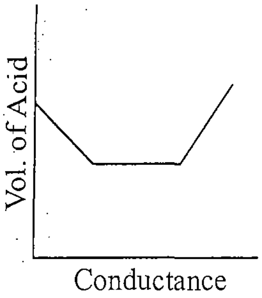
24. 10 mL aliquots of mixture of HCl and HNO_3 are titrated conductometrically using a 0.1M NaOH and 0.1M $AgNO_3$ seperately. The titre volumes are V_1 and V_2 m^2 respectively. The concentration of HNO_3 in the mixture is

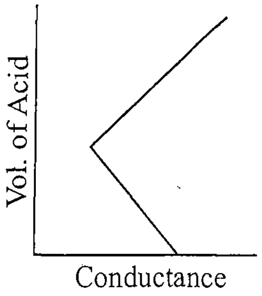
(a) $V_1 - V_2$ (b) $2V_1 - V_2$ (c) $V_2 - V_1$ (d) $2V_2 - V_1$

25. A solution of NaOH was titrated with a mixture of HCl and HNO_3 which of the plot correctly represent it

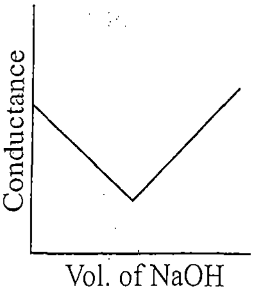
(a)


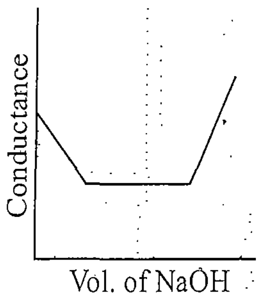
(b)


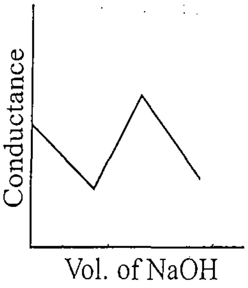
(c)


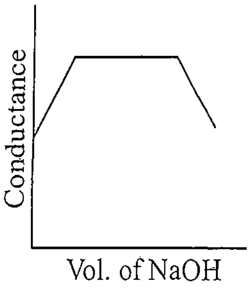
(d)


26. A solution of HCl and $CuSO_4$ was titrated with NaOH. What will be the nature of curve

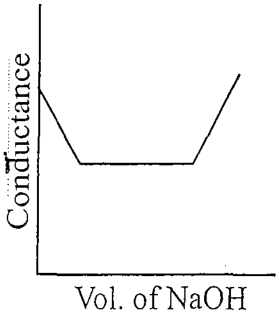
(a)


(b)


(c)


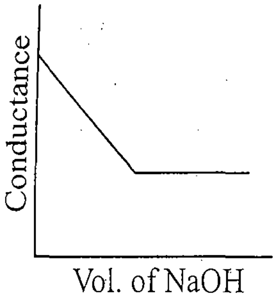
(d)


27. Which of the following curves are correctly represented?

(a)


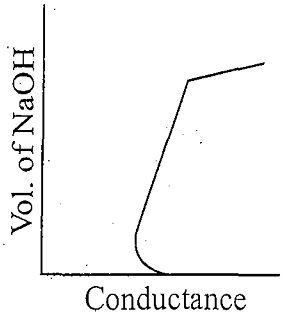
(mixture of HCl + H_2SO_4 vs NaOH)

(b)



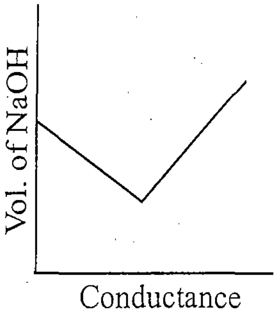
$(CH_3COOH \text{ vs } NH_4OH)$

(c)



(Acetic acid vs NaOH)

(d)



(HCl vs NaOH)

ANSWER KEY

1. d	2. b	3. c	4. c	5. c	6. d	7. d
8. b	9. d	10. a	11. b	12. c	13. b	14. d
15. c	16. c	17. c	18. c	19. a	20. c	21. a
22. c	23. c	24. a	25. d	26. c	27. b,c	