PHYSICAL CHEMISTRY QUESTION BANK

KEY

SURFACE CHEMISTRY

1) **1**	2) **3**	3) **2**	4) **2**	5) **2**	6) **1**	7) **2**	8) **3**	9) **1**	10) **2**
11) **1**	12) **2**	13) **1**	14) **4**	15) **1,4**	16) **4**	17) **2**	18) **3**	19) **3**	20) **3**
21) **3**	22) **2**	23) **4**	24) **4**	25) **3**	26) **4**	27) **3**	28) **4**	29) **1**	30) **2**
31) **3**	32) **4**	33) **4**	34) **250**	35) **4**	36) **3**	37) **3**	38) **3**	39) **2**	40) **4**
41) **2**	42) **3**	43) **4**	44) **4**						

SOLUTIONS

1) **3**	2) **1**	3) **2**	4) **3**	5) **2**	6) **3**	7) **4**	8) **2**	9) **2**	10) **3**
11) **1**	12) **4**	13) **3**	14) **1**	15) **3**	16) **1**	17) **3**	18) **4**	19) **3**	20) **2**
21) **2**	22) **2**	23) **2**	24) **4**	25) **4**	26) **3**	27) **2**	28) **3**	29) **1**	30) **3**
31) **1**	32) **1**	33) **4**	34) **1**	35) **1**	36) **1**	37) **2**	38) **1**	39) **1**	40) **1**
41) **2**	42) **2**	43) **3**	44) **1**	45) **3**	46) **3**	47) **2**	48) **1**	49) **3**	50) **1**

SOLID STATE

1) **3**	2) **1**	3) **3**	4) **3**	5) **4**	6) **1**	7) **2**	8) **1**	9) **1**	10) **2**
11) **1**	12) **2**	13) **2**	14) **3**	15) **2**	16) **4**	17) **1**	18) **2**	19) **2**	20) **2**
21) **3**	22) **1**	23) **1**	24) **4**	25) **3**					

26) **7.53**	27) **2.1655**	28) **1.2594**	29) **1.122**	30) **117.2**
31) **6.023**	32) **530**	33) **3.643**	34) **a.3.6764**	**b.49.43**
c.4	**d.8.54**	35) **a.1.5458**	**b.1.5427**	36) **2**
37) **14**	38) **1**	39) **1**	40) **0.5236**	

ELECTRO CHEMISTRY

1) **3**	2) **1**	3) **4**	4) **4**	5) **4**	6) **3**	7) **2**	8) **2**	9) **4**	10) **2**
11) **1**	12) **4**	13) **3**	14) **1**	15) **4**	16) **1**	17) **3**	18) **2**	19) **4**	20) **3**
21) **3**	22) **1**	23) **4**	24) **2**	25) **1**	26) **1**	27) **2**	28) **3**		

CHEMICAL KINETICS

1) **1**	2) **2**	3) **3**	4) **4**	5) **1**	6) **2**	7) **3**	8) **1**	9) **2**	10) **2**
11) **3**	12) **4**	13) **1**	14) **2**	15) **3**	16) **1**	17) **1**	18) **1**	19) **4**	20) **3**
21) **2**	22) **2**	23) **2**	24) **4**	25) **4**	26) **2**	27) **3**	28) **1**	29) **1**	30) **3**
31) **3**	32) **2**	33) **3**	34) **4**	35) **2**	36) **3**	37) **2**	38) **3.12**		

HINTS & SOLUTIONS

SURFACE CHEMISTRY

5. $xNCH_3COOH = xMCH_3COOH$ (Here, n-factor is one)
   Millimoles of CH_3COOH adsorbed on 3g charcoal
   $= M_1V_1 - M_2V_2$
   $= 0.06\times 50 - 0.042\times 50$
   $= 0.018\times 50$ millimoles
   3 g charcoal adsorbs $CH_3COOH = 0.018\times 50\times 60mg$
   1 g charcoal adsorbs $CH_3COOH = \frac{0.018\times 50\times 60}{3} = 18mg$
7. Please, refer to the text article 11.7(d)(i)
8. Please, refer to the text article 11.8(h)
9. Preferential adsorption of anticatalyst blocks the active sites/free valencies of catalyst that restricts the binding of main reactants
10. Amylase converts starch to glucose. It is diastase that converts starch to maltose.
12. $AgNO_3 + KI \rightarrow Agl + KNO_3$
    $AgI + AgNO_3(excess) \rightarrow [AgI]Ag^+|NO_3^-$
15. Lyophobic colloids have charge of adsorbed ions on surface whose repulsion stabilizes them. Higher the zeta potential between fixed and diffused layers, higher is the stability.
17. Please, refer to the text article 11.18(g)
18. Lower the gold number, higher is the protective power. Hence, the choice(3).
19. 10 mL gold sol requires gelation = 0.01 mg
    100 mL gold sol requires gelation = $\frac{0.01\times 100}{10} = 0.1\,mg$
20. Mud particle, as colloids, are negatively charged. Hence Al^{3+} is the main coagulator ion in alum.
21. Viscosity and surface tension of lyophobic sol remain equal to that of its dispersion medium.
22. Associated colloids or micells are formed by macro ions.
23. The choice(4) is incorrect, because the size of colloidal particles given is between 1 nm to 100 nm while actual range is 1 nm to 1000 nm.
24. Gases undergo diffusion to give solution and not a colloid. So, the choice (4) is incorrect.
25. In the reaction of oxalic acid with $KMnO_4 / H_2SO_4$, the product $MnSO_4$ acts as autocatalyst.
27. Higher the temperature, lower is the extent of adsorption.
29. $N = \frac{100}{22400}\times 6.023\times 10^{23} = 2.69\times 10^{21}$
    Surface area occupied by one molecule
    $= 0.16\times 10^{-14}\,cm^2$
    Total area covered by N_2(g) /gram of catalyst = $0.16 \times 10^{-14} \times 2.69 \times 10^{21}$
    = 43.04×10^5 cm^2
30. Chemical adsorption is irreversible due to formation of new bonds.
31. Blood is a colloidal solution and $FeCl_3$ is a strong coagulant. Blood contains colloidal impurities and $FeCl_3$ neutralizes the charge on these colloidal impurities and clotting of blood begins which blocks the vessels and prevents any further flow of blood.
32. Adsorption is process where randomness
    decreases and energy is released. Hence, ΔS will be negative (as randomness is decreasing) and ΔH will also be negative (ΔH is negative for exothermic processes). Depending on the values of Entropy and enthalpy, the Gibbs energy can either be negative or positive.
33. As_2S_3 and TiO_2 sol are examples of negatively and positively charged sols respectively.

34. 0.25 gm prevents coagulation of 10 ml of gold sol by 1 ml of 10% NaCl
milligrams at starch = 250
Gold number = 250

35. Mass of O2 adsorbed
$$\frac{PVM}{RT}=\frac{(10-2)\times1\times32}{400\times0.08}=8\,g$$
$$\frac{x}{m}=\frac{8}{2}=4$$

36. (3)
(I, II, and III) are correct.

37. (3)
(I, II, and III) are correct.

38. (3)
(I, II, and IV) are correct.

39. (2)
More effective anion SO_4^{-2}

40. (4)
(I, II, and IV)

41. (2)

42. (3)
Electrophoresis means moment of colloidal particles under the influence of electric field.

43. (4)

44. (4)
Gelatin, Haemoglobin, Gum, Starch are protective colloids. (Lyophilic sol)

SOLUTIONS

1. $\alpha=\frac{i-1}{n-1}$
$$0.9=\frac{i-1}{2-1}$$
$$\therefore\ i=1.9$$
$$\pi=iCRT$$
$$=1.9\times0.002\times0.082\times300$$
$$=0.094\ \text{bar}$$

2. For isotonic solutions $\pi_1=\pi_2$
If solutions are non electrolytic $C_1=C_2$
$$\therefore\ \frac{5\times1000}{342\times100}=\frac{1\times1000}{M.w_2\times100}$$
$$\therefore M.w_2=68.4$$

3. $\pi=7.40\,atm$ T = 27+273 = 300 V= 1 litre R = 0.0821
$$\pi=\text{CRT}\quad \pi=\frac{n}{V}RT$$
$$n=\frac{\pi V}{RT}$$
$$=\frac{7.40\times1}{0.0821\times300}=0.3$$

4. KNO_3 is 100% ionized while CH_3COOH is a weak electrolyte

5. $P^H = 2$

$\therefore \left[H^+\right] = 10^{-2} = 0.01M = C_x = 0.1x$

$x = 0.1$

$i = 1 + x$

$= 1 + 0.1$

$\pi = i\frac{n}{v}RT$

$= 1.1 \times 0.1\, RT$

$= 0.11\, RT$

6. According to Henry's law

$\frac{m_1}{m_1} = \frac{P_1}{P_2}$

Hence m_1 and m_2 are masses of ethane at P_1 and P_2 partial pressure, respectively

Form equation $\frac{6.52 \times 10^{-2}}{5 \times 10^{-2}} = \frac{1}{P_2}$

$P_2 = \frac{5}{6.52}$

$\therefore P_2 = 0.762$

7. Lowering in vapour pressure of a solute is given as

$\frac{P^0 - P_{total}}{P_{total}} = \frac{w \times M}{m \times W}$

$P_{total} = \frac{4}{5}P^0$

M = 180 g w = ?

W = 60 g/mol

M = 18 g/mol

$\therefore \frac{P^0 - \frac{4}{5}P^0}{\frac{4}{5}P^0} = \frac{W \times 18}{180 \times 60}$

$\frac{\frac{P^0}{5}}{\frac{4}{5}P^0} = \frac{w \times 18}{180 \times 60}$

$\therefore w = 150g$

8. Given $P_A^0 : P_B^0 = 1:2$

$P_A = X_A.P_A^0 = x\chi_A$

$P_B = X_B.P_B^0 = 2x\chi_B$

$P_{total} = P_A + P_B$

$= x\chi_A + 2x\chi_B$

$\therefore \chi_{A(vapourphase)} = \frac{P_A}{P_{total}} = \frac{x\chi_A}{5 \times \chi_A} = \frac{1}{5} = 0.2$

9. According to Henry's law

$K_H = 76.5\, K.bar$

= 76500 bar

$P_{gas} = K_H \times \chi_{gas}$ $\left[\because\ n_{H_2O} = \frac{1000}{18} = 55.55 \ \&\ n_{gas} << n_{H_2O} \right]$

$$\chi_{gas} = \frac{P_{gas}}{K_H} = \frac{0.98}{76500}$$

$$\chi_{gas} = 1.28 \times 10^{-5}$$

$$\frac{n_{gas}}{n_{gas} + n_{H_2O}} = \frac{n_{gas}}{55.55} = 1.28 \times 10^{-5}$$

$$\therefore n_{gas} = 55.55 \times 1.28 \times 10^{-5}$$

$$= 7.11 \times 10^{-4} moles/litre$$

10. $\pi_1 = C_1RT_1$ $\pi_2 = C_2RT_2$

$400 = C_1 \times R \times 293$ $105 = C_2 \times R \times 303$

$\frac{400}{105} = \frac{C_1 \times R \times 293}{C_2 \times R \times 303}$ $\frac{\pi_1}{\pi_2} = \frac{C_1RT_1}{C_2RT_2}$

$$\frac{C_1}{C_2} = \frac{400 \times 303}{105 \times 293}$$

$$= 3.93 \approx 4$$

$$\Rightarrow C_1 = 4C_2$$

The solution is diluted by 4 times it's initial con.

11. Mass of urea = 5g Wt. of glucose = 10 g

Mol. wt of urea = 60g Mol.wt of glucose = 180

Mass of water = 100-15 $K_f = 1.86 K\ kg\ mol^{-1}$

$$\Delta T_f = 1.86 \times \left[\frac{5}{60} + \frac{10}{180} \right] \times \frac{1000}{85}$$

$$= 3.03K$$

$$\Delta T_f = -3.03K$$

12. $\alpha = \frac{1-i}{1-\frac{1}{n}}$

$$0.8 = \frac{1-i}{1-\frac{1}{4}}$$

$$\therefore\ i = 0.4$$

$$\Delta T_f = i \times K_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{W_B \times 1000}{W_{w_B} \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5_B \times 1000}{W_{w_B} \times 100}$$

$$Mw_B = 62$$

13. $n_A = 1.5$ $n_B = 4.5$

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

$= \frac{1.5}{1.5+4.5} = \frac{1.5}{6.0} = \frac{1}{4}$

$\chi_B = 1-\frac{1}{4} = \frac{3}{4}$

$P = P_A^0 \chi_A + P_B^0 \chi_B$

$P = 116\times\frac{1}{4} + 0.14\times\frac{3}{4}$

$P = 0.029 + 0.105$

$P = 0.134$

14. The inter particle forces in between $CHCl_3$ and acetone increases due to H-bonding and thus $\Delta_{mix}V$ becomes –ve.

15. $\frac{\Delta T_{f_A}}{\Delta T_{f_B}} = \frac{2}{1} = \frac{1}{\frac{1}{2}}$

i.e "B" should associate to show higher ΔT

16. $P^0 - P_S \propto$ loss of wt. of water chamber and $P_S \propto$ loss in wt of solution chamber

$\frac{P^0 - P_S}{P_S} = \frac{n_2}{n_1} = \frac{w_2 \times Mw_1}{Mw_2 \times w_1}$

$= \frac{0.04}{2.50} = \frac{5\times 18}{Mw_2 \times 180}$

$\therefore Mw_2 = 31.25$

17. $P_{total} = P_A \chi_A^0 + P_B \chi_B^0$

$= P_A \chi_A^0 + P_B^0 (1-\chi_A)$

$= P_B^0 - \left(P_B^0 - P_A^0\right)\chi_A$

Given equation = $254 - 119\chi_A$

Compare with the given equation

$\therefore\ P_B^0 = 254$

$\therefore\ P_B^0 - P_A^0 = 119$

$\therefore P_A^0 = 254 - 119 = 135$

18. C_2H_5OH show H-bonding as well as polarity both.

19. $\frac{P^0 - P}{P^0} = \chi_2 =$ mole fraction of solute

$\frac{P^0 - P}{P^0} = 0.0125$

$m = \frac{\chi_2 \times 1000}{\chi_1 \times Mw_1}$

$= \frac{0.0125\times 1000}{(1-0.0125)\times 18}$

$m = \frac{0.0125\times 1000}{0.9875\times 18}$

$m = 0.70$

20. $\Delta T_f = K_f m$

When $\Delta T_f = -4^0 F$

$= -4^0 F = -20^0 C \qquad \left(-4^0 F = -20^0 C\right)$

$\therefore\ m = \dfrac{\Delta T_f}{K_f} = \dfrac{20}{1.86} \qquad \left[\because\ {}^oC = \dfrac{5}{9}(F-32)\right]$

$\therefore m = 10.7$

$\therefore$ Amount of ethyl alcohol to be added

$= m \times mol.wt$

$= 10.7 \times 46.0$

$= 495\ g$

21. $M = \dfrac{w_B \times 1000}{m_B \times V}$

$M = 0.25 \qquad m_B = 32 \qquad V = 2500\ ml$

$\therefore\ 0.25 = \dfrac{w_B \times 1000}{32 \times 2500}$

$w_B = 20g$

Mass = vol×density

$20 = V \times 0.793$

$\therefore\ V = 25.22\ ml$

23. $M_1 = 0.5M \qquad M_2 = 2M$

$V_1 = 750ml \qquad V_2 = 250$

$M_R = \dfrac{M_1V_1 + M_2V_2}{V_1 + V_2} = \dfrac{0.5 \times 750 + 2 \times 250}{250 + 750}$

$M_R = 0.875$

24. Addition of water will increase the mole fraction of solvent. Hence, vapour pressure of solution will increase $\qquad P = P^0 \chi_A$

25. $\Delta T = i \times k_f \times m$

$0.00732 = i \times 1.86 \times 0.02$

$\therefore i = \dfrac{0.00732}{1.86 \times 0.02} = 2$

26. Vapour pressure of Solution

= mole fraction of heptane $\times$92+mole fraction of octane $\times$ 31

27. $\dfrac{S_1}{S_2} = \dfrac{P_1}{P_2}$

$\dfrac{0.034}{S_2} = \dfrac{1}{0.0003}$

$\therefore\ S_2 = 0.034 \times 0.0003$

$= 1.02 \times 10^{-5}\ mol/L$

28. $M = \dfrac{x \times d \times 10}{M_B} = \dfrac{96 \times 1.83 \times 10}{98}$

M=17.93

$M_1V_1 = M_2V_2$

$1.793 \times V_1 = 3 \times 4000$

$V_1 = 669ml$

29. $M = \dfrac{W_B \times 1000}{M_B \times V}$

$2 = \frac{W_B \times 1000}{63 \times 250}$

$\therefore\ W_B = \frac{2 \times 63}{4} = 31.5g$

$\therefore$ mass of HNO_3 required = 31.5 g

Mass of conc. HNO_3 required $= \frac{100}{70} \times 31.5$

$= 45g$

30. $K_f = \frac{RT_0^2}{1000 \Delta H_f}$ $\qquad R = 8.314\ JK^{-1}mol^{-1}$

$T = 16.6 + 273 = 289.6K$

$T = 16.6 + 273 = 289.6K$

31. Molarity (M) $= \frac{\%\text{ of solute} \times 10}{\text{Mol.wt. of solute}}$

$M = \frac{93 \times 10}{98} = 9.48$

$\therefore\ molality(m) = \frac{M}{D - \frac{M \times w}{1000}}$

$= \frac{9.48}{1.84 - \frac{9.48 \times 98}{1000}}$

M = 10.43

32. For an ideal solution ΔS_{mix} is not equal to zero.

33. $\pi \propto T$ $\qquad \pi = iCRT$

$\therefore$ If T is doubled π is also doubled

34. Vant Haff's factor of $Al_2\left(SO_4\right)_3$ is maximum i.e 5

$i = 5$

35. Mol. wt of naphthoic acid $\left(C_{11}8_8O_2\right) = 172\ g/mol$

The theoretical value of depression in freezing point

$= K_f \times \text{molality}$

$= K_f \times \text{molality} = 1.72 \times \frac{20 \times 1000}{172 \times 50}$

$= 4k$

$\therefore$ Vant Haff factor $i = \frac{\text{observed value of colligative property}}{\text{Theoritical value of colligative property}}$

$= \frac{2}{4} = \frac{1}{2} = 0.5$

36. $A_xBy \rightarrow xA^{y+} + yB^{x-}$

$1-\alpha \qquad x\alpha \qquad y\alpha$

$i = 1 - \alpha + x\alpha + y\alpha$

$i = 1 + \alpha\left(x + y - 1\right)$

$\therefore\ \alpha = \frac{i-1}{\left(x+y-1\right)}$

37. w = 0.15 g $\qquad$ W = 15 g $\qquad$ $\Delta T_b = 0.216^0 C$ $\qquad$ $K_b = 2.16$ $\qquad$ $m = ?$

$\Delta T_b = \frac{1000 \times K_b \times W}{m \times W}$

$\therefore\ m = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15} = 100$

$\therefore\ m = 100$

38. $3X \quad \rightarrow \quad X_3$

3mol $\quad$ 1 mol

1 mol $\quad \frac{1}{3}$ mol

$\alpha = \frac{1-i}{1-\frac{1}{n}}$

$\alpha = \frac{1-i}{1-\frac{1}{3}}$

$\alpha = \frac{1-i}{\frac{2}{3}}$

$\alpha = \frac{3}{2}(1-i)$

39. $\frac{\Delta P_1}{\Delta P_2} = \frac{(RLVP)_1}{(RLVP)_2} = \frac{(\chi_B)_1}{(\chi_B)_2} = \frac{(n_B)_1}{(n_B)_2}$

$= \frac{\frac{12}{60}}{\frac{68.4}{342}} = \frac{\frac{1}{5}}{\frac{1}{5}} = 1$

40. Isotonic solutions have equal moles in equal volumes

$\frac{5.25}{M_B} = \frac{1.5}{60}$

$M_B = \frac{52.5 \times 60}{15}$

$M_B = 210\ g\ mol^{-1}$

41. $\Delta T_b = iK_b m$

$\therefore T_b \propto i$ (for equal values of k_b and m)

Hence $T_3 > T_2 > T_1$

42. Strength of the solution = molarity $\times$ mol.wt

$= 2.03 \times 60$

$= 121.8\ g\ /\ L$

Density of solution $= 1.017\ g\ /\ ml$

Mass of 1litre of solution $= 1000\ \text{ml} \times 1.017\ \text{g/ml}$

= 1017 g

Mass of water = 1017-121.8 = 895.2g

$= \frac{895.2}{1000} kg$

Molality(m) $= \frac{2.03}{895.2} \times 1000 = 2.267m$

43. $\Delta T = K_f \times m$ $\Delta T = 2$

Molality(m) = 0.25

$2 = K_f \times 0.25$

$K_f = \frac{2}{0.25}$

$K_f = 8K$ kg mol^{-1}

44. C = 0.1 M $\pi = 4.6\, atm$ T = 300K

S = 0.0821 litre atm $k^{-1}\, mol^{-1}$

$\pi = iCST$

$i = \frac{\pi}{CST} = \frac{4.6}{0.1 \times 0.0821 \times 300} = 1.87$

For dissociation

$\alpha = \frac{i-1}{n-1}$ for $NaCl = 2$

$= \frac{1.87-1}{2-1}$

$\alpha = 0.87$

$\therefore$ % dissociation = 87

45. $P_A^0 = 173\, torr$ $\chi_a^0 = 0.5$

$P_B^0 = 127\, torr$ $\chi_B^0 = 0.5$

$P = P_A^0 \chi_A + P_B^0 \chi_B$

$= (173 \times 0.5) + (127 \times 0.5)$

$= 86.5 + 63.5$

= 150 torr

Let mole fraction of the components in vapour state are y_A and y_B respectively.

$P_A = y_A \times P$

86.5×150

$y_A = 0.577$

$\therefore y_B = 1 - 0.577$

$= 0.423$

46. conc in ppm= $\frac{\text{Mass of solute in gm}}{\text{Mass of solvent in gm}} \times 10^6$

$= \frac{0.2}{500} \times 10^6 = 400$

47. $\pi = CST$

$\pi V = nST$

Case –I: $500 \times V_1 = n \times S \times 283$ …….. (1)

Case-II: $105.3 \times V_2 = n \times S \times 298$ …….. (2)

Dividing eqn (1) by eqn (2) we get

$\frac{500}{105.3} \times \frac{V_1}{V_2} = \frac{283}{298}$

$\frac{V_2}{V_1} = \frac{500 \times 298}{105.3 \times 283} = 5$

48.

	Sucrose	Urea	Glucose	NaCl
Strength	34.2 g/L	60 g/L	90 g/L	58.5 g/L

Molarity	$\frac{34.2}{342}$ = 0.1	$\frac{60}{60}$ = 1	$\frac{90}{180}$ = 0.5	$\frac{58.5}{58.5}$ = 1
i	1	1	1	2

We know that $\pi = iCRT$

$\therefore$ Osmotic pressure of these solutions will lie in following sequence

Sucrose < glucose < Urea < NaCl

49. $P_{CH_4} = K_H \times m_{CH_4}$

$760 = 4.27 \times 10^5 \times m_{CH_4}$

$m_{CH_4} = 1.779 \times 10^{-3}$

50. $\Delta T = 9.3 \quad K_f = 1.86\, K\, kg\, mol^{-1}$

$w_B = 50g \qquad w_B = 62$

$$\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times 62}$$

$$9.3 = 1.86 \times \frac{50 \times 1000}{62 \times w_A}$$

$w_A = 161.3g$

Mass of ice separated = 200 -161.3=38.7g

SOLID STATE

1. for octahedral void

$$\frac{r_B}{r_A} = 0.414 (or)\, r_\beta = 0.414\, r_A$$

$\therefore r_B = 0.414\, r_A$

2. $58.5gr \rightarrow 'N'$ Formula units

$1gr \rightarrow ?$

$\frac{N \times 1}{58.5}$ Formula units

$(ii)\, 4-$Formula unit's $\rightarrow 1$ unit cell

$\frac{N}{58.5}$ Formula units $\rightarrow ?$

$$= \frac{N}{58.5 \times 4} = \frac{6 \times 10^{23}}{234} = 2.57 \times 10^{21} \text{ Unit cells}$$

3. $a = 400\, pm : length\ of\ \ face\ diagonal = \sqrt{2}a$

4. Length of body diagonal $= \sqrt{3}a$

5. Edge length $= 2(r_c + r_a)$

6. Closest approach between two atoms in BCC=

$$\therefore \frac{\sqrt{3}a}{2} = 1.73A^0$$

$$a = \frac{1.73A^0 \times 2}{\sqrt{3}} = \frac{3.45}{1.732} = 2A^0$$

$a = 2 \times 10^2\, pm = 200\, pm \left(\therefore 1A^0 = 10^2\, pm\right)$

7. Let, the sample contains 93 Iron ions and 100 oxide ions

Total negative charge on oxide ions $= 100 \times -2 =$ -200

$no\ of\ Fe^{+3} ions = x$

$no\ of\ Fe^{+2}\ iron\ ions = 93 - x$

Total positive charge $= x(+3) + (93 - x)(+2)$

Numerically $+ve$ charge and $-ve$ charge are Equal $3x + (93 - x)2 = 200$

$\therefore x = 14$

$\%\ of\ Fe^{+3} = \frac{14}{93} \times 100 = 15.05\%$

8. Due to Schottky defects No.of atoms decreases

$z = 4 - \left(4 \times \frac{0.2}{100}\right) = 3.992$

$$\boxed{d = \frac{z.m}{No.a^3}}$$

9. $d = \frac{ZM}{N_0.a^3} = \frac{4 \times 63.5 g\ mol^{-1}}{(3.61 \times 10^{-8} cm)^3 \times (6.022 \times 10^{23} mol^{-1})} = 8.97 gm/cc$

10. The complex $\left[Ni(CN)_4\right]^{-2}$ is square planar so it has limiting radius ratio as octahedral structure i,e 0.414-0.732

11. If 'a' is the length of the face, then face diagonal = $\sqrt{a^2 + a^2} = \sqrt{2}a$

$\therefore$ Face length, $a = \frac{Face\ diagonal}{\sqrt{2}} = \frac{4.25}{1.44} = 3.01 A^0$

12. Density (d) = $\frac{Z \times M}{No \times a^3} \Rightarrow 2.7 = \frac{Z \times 27}{(4.05 \times 10^{-8}) \times (6.022 \times 10^{23})}$

$Z = 4$

Since $Z = 4$,the unit cell is face centered cubic (fcc) unit cell

13. Suppose the no of Anions $\bar{Y} = N$

Then number of Tetrahedral voids =2N

Then number of octahedral voids =N

Octahedral voids and tetrahedral voids are equally occupied by cations X^+ are present in octahedral voids and N cations X^+ are present in tetrahedral voids then

No. of Cations present = $N + N = 2N$

Ratio of cations and anions = 2 : 1

Formula of the compound = X_2Y

14. Suppose the no of oxide ions = N

No.of Octahedral voids = N

No.of tehedral voids = 2N

No of cations 'A' present $= \frac{1}{6} \times 2N = \frac{1}{3}N$

No of cations 'B' present $= \frac{1}{3} \times N = \frac{N}{3}$

Ratio A: B: $o^{-2} = \frac{N}{3} : \frac{N}{3} : N (or) 1:1:3$

Formula of compound ABO_3

15. 'B' forms ccp Structure So, B=4

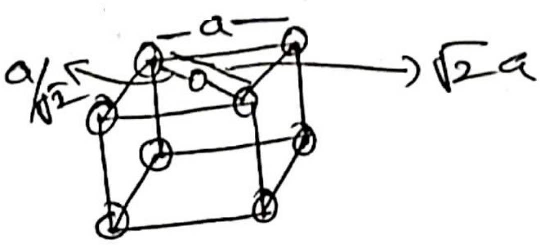
'A' occupies half of the octahedral voids A=2

Oxygen atoms occupy all the tetrahedral voids $0 = 2 \times 4 = 8$

The structure (or) formula of the bimetallic oxide is $A_2B_4O_8$

AB_2O_4

16.



17. For octahedral void

$\frac{r_+}{r_-} = 0.414$

$r_+ = 0.414 \times 250$

18. $M = \left(\cancel{4} \times \frac{1}{\cancel{4}} \right) + (1 \times 1) = 2$

$X = \left(\cancel{8} \times \frac{1}{\cancel{8}} \right) + \left(\overset{3}{\cancel{6}} \times \frac{1}{\cancel{2}} \right) = 4$

The emphecicol formula of the
Compound is $M_2X_4 = MX_2$

20. Rock salt $\rightarrow NaCl$

$Na^+\overline{CI} \rightarrow Fcc\ Structure$

Na^+ Occupies all octahedral voids

CI^- Occupies all corners and face center

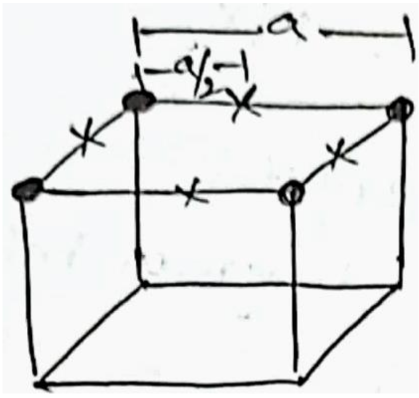
For FCC $z = 4$

No of octahedral voids $= 4$

No of Tetrahedral voids $= 2 \times 4 = 8$

$\rightarrow$ All the octahedral voids are filled by

Na^+ $\bullet \rightarrow \overline{CI}$



21. $\underset{0.85}{Fe}O$

No of voids = no of Fe^{+2} missing =15

No of $Fe(III) = 2 \times 15 = 30$

% $Fe(III) = \frac{30}{85} \times 100 = 35.3\%$

22. $a = 8 \times \frac{1}{8} = 1$

$B=(6-1)\times\frac{1}{2}=\frac{5}{2}$

The formula of the compound is

$=A$	B
1	$\frac{5}{2}$

$=(2\times 1)\left(2\times\frac{5}{2}\right)$

$=A_2B_5$

23. $4r=\sqrt{3}a$

$r=\frac{\sqrt{3}a}{4}=\frac{1.732\times 4.29}{4}=1.857A^0$

26. For Tetrahedral voids $\frac{r^+}{r^-}=0.414$

$r^+=0.414\times\overline{r}=0.414\times 0.182$

$r^+=0.075348nm=7.53\times 10^{-2}nm$

27. Density of $NaCl=\frac{Z\times M}{No\times a^3}=\frac{4\times 58.5}{6.023\times 10^{23}\times\left(5.64\times 10^{-8}\right)^3}$

$=\frac{234}{1080.563\times 10^{23}\times 10^{-24}}$

$=\frac{234}{108.056}=2.1655g/cm^3$

28. FCC unit cell length = $3.5A^0$

BCC unit cell length $=3.0A^0$

Density in fcc= $\frac{n_1\times atomic\, mass}{a_1^3\times N}$

Density in BCC $=\frac{n_2\times atomic\ mass}{a_2^3\times N}$

$\frac{dfcc}{dBcc}=\frac{n_1}{n_2}\times\frac{a_2^3}{a_1^3}$

n_1 For $fcc=4$ $\qquad a_1^3=\left(3.5\times 10^{-8}\right)^3=$

n_2 For $Bcc=2$ $\qquad a_2^3=\left(3.0\times 10^{-8}\right)^3$

$\frac{dfcc}{dBcc}=\frac{4}{2}\times\frac{\left(3\times 10^{-8}\right)^3}{\left(3.5\times 10^{-8}\right)^3}=\frac{4\times 27\times 10^{-24}}{2\times 42.875\times 10^{-24}}$

$\frac{dfcc}{dBcc}=\frac{108}{85.75}=1.2594$

29. $\frac{r_{Na^+}}{r_{ci}^-}=0.55$ $\qquad \frac{r_k^+}{r_{ci}^-}=0.74$

$\frac{r_{Na}^+}{r_{ci}^-}+1=1.55---(1)\frac{r_k^+}{r_{ci}^-}+1=1.74--(2)$

$(2) by (1)$

$$\frac{1.74}{1.55} = \frac{r_{k^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}}$$

$$\frac{r_k^{-1} + r_{ci}^-}{r_{Na}^+ + r_{ci}^-} = \frac{1.74}{1.55} = 1.122$$

30. In fcc unit cell, $4r = \sqrt{2}a$

$$r = \frac{a\sqrt{2}}{4} = \frac{400\sqrt{2}}{4} = 141.4\,pm$$

For octahedral void

$2(r+R) = a \Rightarrow 2R = a - 2r$

$2R = 400 - 2\times141.4 = 400 - 282.8 = 117.2\,pm$

Diameters of greatest sphere $= 117.2\,pm$

31. $Na^+ \;\; cl^- \;\; Na^+ \;\; cl^-$

$cl^- \qquad cl^- \;\; Na^+$

$sr^{+2} \;\; cl^- \;\; Na^+ \;\; cl^-$

$cl^- \;\; Na^+ \;\; cl^- \;\; Na^+$

Number of cationic vacancies per mol

$$= \frac{10^{-3}\times6.023\times10^{23}}{100} = 6.023\times10^{18}\,vacncies\ per\ mol$$

32. Edge length $= 2\times$ distance between Na^+ and Cl^- ions

$= 2\times265 = 530\,pm$

33. Density $(d) = \dfrac{Z\ M}{N\times a^3} = \dfrac{4\times50}{\left(450\times10^{-10}\right)^3\times6.023\times10^{23}}$

$d = 3.643\,g/cm^3$

34. As we know

$$d = \frac{Z\times M}{N\times a^3}$$

(a) For Fcc structure $4r = \sqrt{2}a$

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

$a = 2\sqrt{2}\times130\,pm = 367.64\,pm = 3.67\times10^{-8}\,cm$

(b) Volume of unit cell $\left(a^3\right) = \left(3.67\times10^{-8}\right)^3 cm^3$

$a^3 = 49.43\times10^{-24}\,cm^3$

For fcc $z = 4$

$$d = \frac{ZM}{Nxa^3} = \frac{4\times63.54}{6.023\times10^{23}\times\left(3.67\times10^{-8}\,cm\right)^3} = 8.54\,g/cm^3$$

35. (i) Frenkel defects have no effect on the density because number of atoms per unit cell remains the same

For fcc $z = 4$; for Ca, $M = 40\,g/mol$

Also $a = 0.556nm = 0.556 \times 10^{-7} cm$

Density $(d) = \dfrac{ZM}{No \times a^3} = \dfrac{4 \times 40g\ mol^-}{(6.023 \times 10^{23})mol^- \times (0.556 \times 10^{-7} cm)^3}$

$d = 1.5458 g/cm^3$

(ii) If there were no defects (or there were only Frenkel defects) number of atoms per unit cell=4(being FCC) There would have been no change n density
Due to 0.2% defect, number of atoms per unit cell decreases
Thus, now number of atoms per unit cell=

$4 - \dfrac{0.2}{100} \times 4 = 3.992$

$d = \dfrac{zm}{N \times a^3} = \dfrac{(3.992)(40gmol^-)}{(6.022 \times 10^{23} mol^-)(0.556 \times 10^{-7} cm)^3} = 1.5427 g/cm^3$

36. Edge length $(a) = 2(r_c + r_a)$

$2r_a = a - 2r_c \Rightarrow r_a = \dfrac{a - 2rc}{2}$

$r_a = \dfrac{7.2 - 2(1.6)}{2} = \dfrac{7.2 - 3.2}{2} = \dfrac{4}{2} = 2A^0$

37. Ans: 14
38. for FCC $z = 4$
No of octahedral sites =4
The no of octahedral sites per sphere in $FCC = \dfrac{4}{4} = 1$
39. Ans: 1
40. $\dfrac{\pi}{6} = \dfrac{3.142}{6} = 0.5236$

ELECTRO CHEMISTRY

6.

$CuCI_2 \rightarrow Cu^2 + 2CI^-$

At anode: - $2CI \rightarrow CI_2 + 2e^-$

At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

9.

Fused $NaH \rightarrow Na^+ + H^-$

$At\ anode\ 2H \rightarrow H_2 + 2e^- (oxidn)$

10.

$m = \dfrac{EQ}{96500} = \dfrac{8 \times 1}{96500}$

$E_{O_2} = 8$

14.

$H_2O \rightarrow H_2 \quad + \dfrac{1}{2} O_2$

(Cathode) (Anode)

Hence the ratio is H_2 and $O_2 = 2:1$

16.

The potential of SHE=0. Hence the potential of their electrode is 1.2 volts but it may be present above or below the hydrogen. Hence the value is ± 1.2 volts.

17.

Most negative reduction potential $(-0.74v) = \text{Anode}$

Least negative reduction potential $(-0.46v) =$

Cathode

$E^0 = E^0$

$-E^0$

cathode *Anode*

$= 0.46 - (-0.74) = 0.28v$

18.

Negative potential $(-0.76v) = Anode$

Positive potential $(+0.34v) = cathode$

$E^0 = E^0{}_{cat} - E^0 Ano$

$= 0.4 - -(-0.76) = 1.1.v.$

20.

EMF of Galvanic cell>battery =current flows into the battery.

21.

No of moles of $AgNO_3$ =Molarity $\times$Volume in lit $= 1 \times 0.2 = 0.2 moles$

$AgNO_3 \rightarrow Ag^+ + NO_3$

0.2 0.2 0.2

Wt. of 1mole Ag=108

$0.2 \rightarrow ?$

We want the time require to reduce half of the amount is $\frac{21.6}{2} = 10.8$

$m = \frac{E}{F} i \times t; 10.8 = \frac{108}{96500} \times 1 \times t$

$in \min = \frac{10.8 \times 96500}{108 \times 60} = 160 \min$

22. On passing 96500 C of electricity one equivalent weight of substance is deposited.

$E_H = 1.008 gm$

$E_{cl} = 35.5 gm$

24. $\frac{W_1}{E_1} = \frac{W_2}{E_2} \quad \therefore E_{Ag^+} = 108$

$\frac{0.54}{108} = \frac{w_2}{31.77} E_{Cu^{+2}} = \frac{63.54}{2} = 31.77$

$W_2 = 0.1589 gms$

25. **:** $E = E^0 + \frac{0.06}{n} \log c$

$0.34 + \frac{0.06}{2} \log^{-1}$

$0.4 + (0.03 \times -1)$

$0.31v$

26. $E = E^0 + \frac{0.06}{n}\log C$

$= 0 + \frac{0.06}{1}\log\left(10^{-2}\right)$

$= 0.06 \times -2 = -0.12v$

27. $Mn\,O_4^- \to Mn^{+2}$

$x^1 + (-8) = -1$

$x = +7$

The change is $= 7 - 2 = 5$ moles of electrons.

No of coulombs required $= 5 \times 96500\,C$

28. $1\,H_2O \to H_2 + \frac{1}{2}O_2$

$2H_2O \to 2H_2 + O_2$

CHEMICAL KINETICS

1. For first order reaction

$t_{1/2} = \frac{0.693}{k}$

$t_{1/2} = \frac{0.693}{1.155 \times 10^{-3}}$

= 600 seconds

2. $t_2 = \frac{2.303}{k}\log\frac{100}{0.1}\left(For\ 99.9\%\ completion\right)$

$t = \frac{2.303}{k}\log\frac{100}{10}\left(For\ 90\%\ completion\right)$

$\therefore t_2 = 3t$

3. $\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$\frac{k_2}{k_1} =$ Temperature coefficient =2

4. $t_{1/2} = \frac{0.693}{k}$

$k \times t_{1/2} = 0.693$

$= 2.303 \times \log 2$

5. $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$\therefore \log\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \frac{Ea}{2.303 \times 2 \times 10^{-3}}$

$\left[\frac{10}{300 \times 310}\right]$

$E_a = 12 - 13$

6. $t_{1/2} = 50\min$

$1 \to \frac{1}{2} \to \frac{1}{4} \to \frac{1}{8}$

$\therefore\ for\ 3t_{1/2} = 3 \times 50 = 150\min$

7. For a radioactive decay the energy of activation is almost zero

8. For 20% decomposition $a=100, \quad (a-x)=80$

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

$$5=\frac{2.303}{k}\log\frac{100}{80}$$

$$k=\frac{2.303}{5}(1-0.9030)$$

$$t_{1/2}=\frac{0.693}{k}=15.52\,\text{min}$$

9. $K=\dfrac{2.303}{t}\log\dfrac{a}{(a-x)}$

$$a=0.2(a-x)=0.02$$

$$\therefore k=\frac{2.303}{100}\log\frac{0.2}{0.02}$$

$$=2.303\times10^{-2}$$

10. for a second order reaction $t_{1/2}=\dfrac{1}{ka}$

$$\Rightarrow t_{1/2}\times a=\text{Constant}$$

$$\therefore order=2$$

11. Remaining $\%=100-87.5=12.5\%$

$100\rightarrow 50\rightarrow 25\rightarrow 12.5\%$

$$\therefore 3t_{1/2}=90\,\text{min}\,(or)\,t_{1/2}=\frac{90}{3}=30\,\text{min}.$$

12. If $[A]$ is double rate is doubled order w.r.t $A=1$

If $[B]$ is increased by 9 times rate is increased by '3 ' times

$$\therefore w.r.t\,'B'\,is\,'1/2'$$

$$\therefore r=k[A][B]^{1/2}$$

13. For first order reaction $r=k.C$

$$\therefore 8\times10^{-5}=k\times4\times10^{-3}$$

$$\therefore k=\frac{8\times10^{-5}}{4\times10^{-3}}=2\times10^{-2}\,\text{sec}^{1}$$

14. for every 10^0c raise in temperature rate constant increases by 3 times

$$\therefore 30^0C=K$$

$$40^0C=3K$$

$$50^0C=9k$$

$$60^0C=27k$$

15. FOR $4NH_3+5O_2\rightarrow 4NO+6H_2O$

$$\frac{-1d(O_2)}{5\ dt}=\frac{1d(NO)}{dt}$$

$$\therefore \frac{d(O_2)}{dt}=\frac{5}{4}\frac{5d(NO)}{dt}$$

$$=\frac{5}{4}\times10^{-3}=1.25\times10^{-3}$$

16. Given that $r = k[A]^n$ ....(1)

$4r = k(2[A])^n$ ....(2)

Dividing $(2) by (1)$

$n = 2$ $\therefore order = 2$

17. In acid medium hydrolysis of ethyl acetate is found to be first order reaction because water is in excess

$r = K[CH_3COOC_2C_3H_5]^1[H_2O]^0$

18. More the rate constant more the extent of reaction

19. In first order reaction half-life period is independent of initial concentration

$t_{1/2} = \frac{0.693}{k}$

$t_{1/2} \alpha a^{1-n} (a = initial\ conc.)(n = order)$

$If\ n = 1$

$t_{1/2} \alpha a^{1-1}$

$t_{1/2} \alpha a^0$

20. $If\ n = 2$

$t_{1/2} = \alpha a^{1/n}$

$t_{1/2} = \alpha a^{1/n}\ or\ t_{1/2} \alpha a^{-1} (or) t_{1/2} \alpha^{1/n}$

21. For first order reaction

$t_{1/2} = \frac{0.693}{k}$

$t_{1/2} = \frac{0.693}{k}$

$\therefore half\ life = \frac{0.693}{0.693} = 1\sec$

22. Order and half-life of a reaction are related as $t_{1/2} = \alpha \frac{1}{a^{(n-1)}}$

23. $\frac{C}{C^1} = \frac{1}{2^n}\ and\ n = \frac{1}{t^{1/2}}$

C=Concentration after 1 Co=initial concentration

$\therefore \frac{1}{16} = \frac{1}{2} = \frac{1}{2^4}$

$\Rightarrow$ Since $t = 2 \times 60 \min$

$4 = \frac{2 \times 60}{t_{1/2}}$

$\therefore t_{1/2} = \frac{2 \times 60}{4} = 30 \min$

or

$1 \to \frac{1}{2} \to \frac{1}{4} \to \frac{1}{8} \to \frac{1}{16}$

$\therefore 4t^{1/2} = 2h$

$t\frac{1}{2} = \frac{2}{4} = \frac{1}{2}h \Rightarrow 30 \min$

$\therefore t_{1/2} = \frac{2 \times 60}{4} = 30 \min$

24. If $r = K[A]^0[B]^M$
Order $= n + m$
Since $2+1=3$
$1+2=3$
$1.5+1.5=3$

25. rate constant units depends on order of the reaction.
$unit\ if\ k = mol^{1m} lit^{n-1} \sec^{-1}$
$where\ n = order$

26. Order w.r.t A=1
Order w.r.t B=2
$rate = K[A][B]^2$

27. In $N_2 + 3H_2 \rightleftharpoons 2NH_3$
$$\therefore \frac{d(N_2)}{dt} = \frac{-1}{3}\frac{(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}$$
$$\therefore \frac{d(NH_3)}{dt} = \frac{-2}{3}\frac{d(H_2)}{dt}$$

28. Dimensions of rate constant of first order reaction $= time^{-1}$

29. rate constant of a reaction is constant irrespective of time
$$K = A.e^{-E_a/RT}, K = \frac{0.693}{t\frac{1}{2}}$$

30. $\therefore r = k(c)^2$
$\therefore r = k.if\ c = 1$

31. A catalyst increases the reaction by decreasing the activation energy

33. As per Arrhenius expression
$k = Ae^{-Ea/RT}$
$\frac{K}{A} = e^{-Ea/RT} =$ Fraction of fruitful collisions

34. $CH_4 + 2O_2 + 2H_2O$
Is the slowest, because more number of bonds involved in the reactions

35. $r = {k[A]^3}/{B}$
$= k[A]^3[B]^{-1}$
Order sum of the powers of concentration terms
$= 3 - 1 = 2$

36. $r = k[A]^{0.5}[B][C]^{1.5}$
Order =sum of the powers of concentration terms
$= 0.5 + 1 + 1.5 = 3$

37. $$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$
$$\frac{5}{50} = \left[\frac{0.01}{0.1}\right]^{n-1}$$
$$\frac{1}{10} = \left(\frac{1}{10}\right)^{n-1}$$
$\therefore 1 = n - 1$

38. Let the initial amt $amt = 100.87.5\%$ decomposition always requires there half lifes is first order reaction

$\therefore 3t_{1/2} = 72\,\text{min}$

Half-life = $\frac{72}{3} = 24$

$\therefore$ No of life's in 120 minutes $= \frac{120}{24}$

For a half life's

$100 \rightarrow 50 \rightarrow 25 \rightarrow 12.5 \rightarrow 6.25 \rightarrow 3.125$

Amount left $= 3.125 gms$