

**DPP No. # 25**

$$2. \quad \Delta G = (\Delta H) - T(\Delta S)$$

$$\begin{array}{ccc} \downarrow & & \downarrow \\ -ve & & -ve \end{array}$$

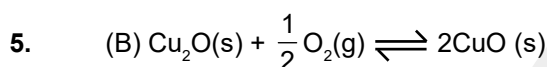
since both are  $-ve$ , the reaction would have a  $-ve$   $\Delta G$  below a temperature of  $\frac{33000}{58}$  K (= 569K)

3. It is because of the fact that for spontaneity, the value of  $\Delta G = (\Delta H - T\Delta S)$  should be  $< 0$ . If  $\Delta S$  is  $-ve$ , the value of  $T\Delta S$  shall have to be less than  $\Delta H$  or the value of  $\Delta S$  has to be less than  $\frac{\Delta H}{T}$  i.e.,  $\frac{x}{298}$ .

$$4. \quad (C) \quad 0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$$

$$S_m = \int_0^{20} \frac{C_{p,m}}{T} dT$$

$$= \int_0^{20} aT^2 dT = \frac{a}{3} [20^3 - 0] = 1.12 \text{ J/K-mol.}$$



$$\Delta G_{\text{reaction}}^0 = [2 \times (-30.4)] - [-34.98] = -25.82 \text{ kcal}$$

$$\text{and } -25.82 \times 10^3 = 2.303 \times 2 \times 298 \log K$$

$\therefore K \approx 10^{19}$ , a very high value, hence reaction will be almost complete with a trace of  $\text{Cu}_2\text{O}$ .

$$6. \quad \Delta G = \Delta H - \Delta(TS)$$

$$= \Delta H - T\Delta S \quad (\text{isothermal})$$

$$= 0 - T\Delta S = -T \left( \int \frac{dq_{\text{rev}}}{T} \right)$$

$$= - \int dq_{\text{rev}} = -q_{\text{rev}} = W_{\text{rev}}$$

as process is isothermal so  $\Delta E = 0 = q_{\text{rev}} + W_{\text{rev}}$

$$\text{so } \Delta G = -nRT \ln \left( \frac{V_f}{V_i} \right)$$

$$= -RT \ln 2 = -8.314 \times 300 \times 0.693 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1}$$

$$= 1.728 \text{ KJ mol}^{-1} \text{ K}^{-1}$$

$$8. \quad 0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$$

$$S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K - mol}$$

9.\* Adiabatic process. So,  $q = 0$ .

Expansion against vacuum. So,  $P_{\text{ext}} = 0$ . Therefore,  $W = 0$ .

So, from 1<sup>st</sup> law,  $\Delta U = 0$ . So,  $\Delta T = 0$ . So,  $\Delta H = 0$ .

$\Delta S_{\text{sys}} > 0$ , since expansion of gas occurs.

10.\* Boiling of a liquid at normal boiling point is a equilibrium process and on decreasing the pressure equilibrium will go forward and  $\Delta G$  will be negative and vice versa.

$$11.* \quad \Delta S = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)$$

$$\Delta H = nC_p \Delta T$$

$$\Delta E = nC_v \Delta T$$

$$\Delta G = \Delta H - \Delta(TS)$$

13.  $\Delta G^\circ = -2.303 \times 8.314 \times 300 \log [2 \times 10^{-7}]$   
 $= 38.48 \text{ KJ/mol}$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = -33.6 \text{ J mol}^{-1} \text{ K}^{-1}.$$

### DPP No. # 26

- Galvanic cells are electro chemical cells which convert chemical energy into electrical energy.
- $E^\circ_{\text{cell}} = [E^\circ_{\text{A}} - E^\circ_{\text{C,OP}}] = 0.76 - 0.41 = 0.35 \text{ V}.$
- $E^\circ_{\text{cell}} = [E^\circ_{\text{C}} - E^\circ_{\text{A,RP}}] = 1.25 + 1.25 = 2.50 \text{ V}.$   
 $E^\circ_{\text{cell}} = [E^\circ_{\text{C}} - E^\circ_{\text{A,RP}}] = 1.25 - (-1.25) = 2.50 \text{ V (Maximum value)}$
- Electrode potential values depend on reference electrode chosen but not cell potential.
- $\text{Sn}^{2+} \longrightarrow \text{Sn}^{+4} + 2e^- \quad E^\circ = -0.15 \text{ V}$   
 $\text{Hg}_2^{2+} \longrightarrow 2\text{Hg}^{2+} + 2e^- \quad E^\circ = -0.92 \text{ V}$   
 $\text{Sn}^{2+} \text{ ] Hg}_2^{2+}$
- $E^\circ(\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}) = 1.33\text{V (A)}$   
 $E^\circ(\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}) = 0.77\text{V (B)}$   
 When these two electrodes are connected, then the electrode with higher reduction potential act as cathode.  
 So (A) is cathode (B) is anode.  
 $e^-$  flow from anode to cathode in external circuit.  
 $E^\circ_{\text{cell}} = 1.33 - 0.77 = 0.56\text{V}$   
 cathode (A) is a +ve electrode in electro chemical cell.
- Higher oxidation potential, higher reducing tendency.
- $E^\circ_{\text{H}^+/\text{H}_2} = 0 \text{ V}.$   
 Hydrogen gas will reduce those metals which have reduction potential greater than  $\text{H}_2$  gas.
- Cu will reduce to those metal which have higher reduction potential than Cu.  
 So,  $\text{Ag}^+$  has higher potential.
- As carbon can reduce XO and YO but not ZO, SRP of X and Y are more than carbon. Y can reduce XO, which means SRP of X is more than Y. Hence the order of SRP is  
 $\text{SRP of X} > \text{SRP of Y} > \text{SRP of C} > \text{SRP of Z}.$   
 More active metal has lesser SRP.  
 So the order of activity of metals is  $\text{Z} > \text{Y} > \text{X}$       **Ans.**
- (A) It is a convention that SRP of standard hydrogen electrode is zero at all temperatures.  
 (B) is incorrect.  
 (C) the difference should be +ve quantity.  
 (D)  $\text{KMnO}_4$  is stronger oxidising agent (SRP values).
- Any temperature can be selected.
- From given SRP values.
- On increasing concentration of  $[\text{H}^+]$  ions the solubility of basic hydroxide  $\text{Fe}(\text{OH})_2$ , will increase.

### DPP No. # 27

- $E^\circ$  is intensive property.
- |  |                             |   |
|--|-----------------------------|---|
| $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$  | $E^\circ = 0.337 \text{ V}$ | $\Delta G^\circ = -2F \times 0.337.$      |
| $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$ | $E^\circ = 0.153 \text{ V}$ | $\Delta G^\circ = -1F \times 0.153.$      |
| $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$  | $E_1^0 = 0.337 \text{ V}$   | $\Delta G_1^0 = -2F \times 0.337.$        |
| $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + e^-$ | $E_2^0 = 0.153 \text{ V}$   | $\Delta G_2^0 = 1 \times F \times 0.153.$ |

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$\text{Cu}^+ + e^- \longrightarrow \text{Cu}$	$E_3^0 = ?$	$\Delta G_3^0 =$
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$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0.$$

$$-F \times E_3^0 = -2F \times 0.337 + F \times 0.153.$$

$$E_3^0 = 2 \times 0.337 - 0.153 = \mathbf{0.521 V}.$$

3.  $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$  (1)  $E_1^0 = 0.77V$   $\Delta G_1^0 = -1 \times F \times 0.77$   
 $\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe}$  (2)  $E_2^0 = -0.036V$   $\Delta G_2^0 = 3 \times F \times 0.036$   
 $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-$  (3)  $E_3^0 = \Delta G_3^0 = -2 \times F \times E_3^0$

$$(1) - (2) = 3$$

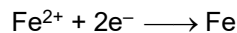
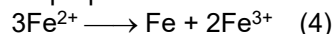
$$\Delta G_1^0 - \Delta G_2^0 = \Delta G_3^0$$

$$\Rightarrow -F \times 0.77 - 3F - 0.036 = -2 \times F \times E_3^0$$

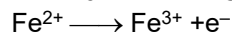
$$\Rightarrow (0.77 \times 0.108) = 2 \times E_3^0$$

$$\Rightarrow E_3^0 \approx 0.44V \text{ Ans.}$$

Disproportionation reaction.



$$E^0 = -0.44V \quad \Delta G^0 = -2 \times F \times (-0.44) \quad (5)$$



$$E^0 = -0.77V \quad \Delta G^0 = -1 \times F \times (-0.77) \quad (6)$$

$$(5) + 2 \times (6) = (4)$$

$$\Rightarrow \Delta G_4^0 = -2 \times F \times (-0.44) + 2(-1 \times F \times (-0.77))$$

$$= +ve$$

$$\therefore \Delta G_4^0 > 0,$$

$\Rightarrow$  Reaction is not spontaneous.

Hence,  $\text{Fe}^{2+}$  is stable to disproportionation.

4. From the given data, we see that  $\text{Fe}^{3+}$  reduces to  $\text{Fe}^{2+}$  as  $E_{(\text{Fe}^{3+}/\text{Fe}^{2+})}^0$  is positive and Fe oxidises to  $\text{Fe}^{2+}$

are  $E_{(\text{Fe}^{2+}/\text{Fe})}^0$  is negative.

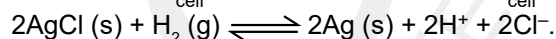
So,  $\text{Fe}^{3+}$  decreases,  $\text{Fe}^{2+}$  increases.

5. Only for this reaction  $E^0$  will come out to be positive, calculate using relation

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0 \quad \text{and} \quad \Delta G^0 = -nFE_{\text{cell}}^0$$

6.  $\text{AgCl} (s) + \frac{1}{2} \text{H}_2 (g) \rightleftharpoons \text{Ag} (s) + \text{H}^+ + \text{Cl}^-.$

$$\Delta G^0 = -nF E_{\text{cell}}^0 = -21.52 \text{ KJ} = -1 \times F E_{\text{cell}}^0.$$



$$\Delta G^0 = -2 \times F \times E_{\text{cell}}^0 = -21.52 \times 2 = \mathbf{-43.04 \text{ kJ.}}$$

7. At anode :  $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$



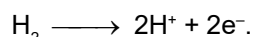
As cell discharges,  $[\text{Zn}^{2+}]$  increase in anode compartment and decrease in cathode compartment, finally becoming equal at equilibrium. Hence, they approach each other.

8.  $\text{Tl}^{3+} + 2e^- \longrightarrow \text{Tl}^+ \quad E_{\text{Cell}} = +1.2496 \text{ V}$

$$E_{\text{Cell}} = 1.2496 \text{ V} = E_{\text{Cell}}^0 - \frac{0.0591}{2} \log \frac{0.01}{0.1}$$

$$E_{\text{Cell}}^0 = 1.22 \text{ V.}$$

9.  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{1}{[\text{H}^+]^2}.$



$$E_{\text{cell}} = -\frac{0.0591}{2} \log [\text{H}^+]^2.$$

Higher the  $[\text{H}^+]$  conc ; less will be emf.

$$\text{or } E_{\text{cell}} = 0 - \frac{0.0591}{2} \log \frac{(C)^2}{(\sqrt{KC})^2}$$

$$E_{\text{cell}} = 0 - \frac{0.0591}{2} \log \frac{(1)^2}{(0.1)^2}$$

$$= - \frac{0.0591}{2} \times 2 = -0.0591.$$

10.  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = 0.8 - (-0.14) - \frac{0.0591}{2} \log \frac{1}{1^2} = \mathbf{0.94 V}.$

11.  $E_{\text{cell}}$  increases by increasing concentration of oxidised species at cathode and by increasing concentration of reduced species at anode.  
 Or by decreasing concentration of reduced species at cathode on decreasing concentration of oxidised species at anode.

12.  $\Delta G^{\circ} = (2 \times 0.34 + 2 \times 1.25)$   
 $- 2 \times E^{\circ} = (2 \times 0.34 + 2 \times 1.25)$   
 $E^{\circ} = -1.59 \text{ V non-spontaneous } E^{\circ} = -ve$

13.  $E_{\text{cell}} = -2.36 - \frac{0.0591}{2} \log \frac{1}{10^{-2}} = -2.4191 \text{ V}.$

### DPP No. # 28

1.  $E_{\text{cell}} = -0.0591 \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}}$

For (A)  $E_{\text{cell}} = 0.0591 \text{ V}$   
 (B)  $E_{\text{cell}} = 0.273 \text{ V}$

$$[\text{H}^+]_{\text{Anode}} = \sqrt{\frac{K_w}{K_b} \cdot C} = \sqrt{\frac{10^{-14}}{18 \times 10^{-5}} \times 10^{-2}} = \sqrt{\frac{10}{1.8}} \times 10^{-6}$$

(C)  $E_{\text{cell}} = -0.0591 \log \frac{1}{2} = 0.0591 \log 2 = 0.0178 \text{ V}$

(D)  $E_{\text{cell}} = -0.0591 \log \frac{1}{1} = 0.$

2.  $E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.46 \text{ V}$

(+)  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = 1.1 \text{ V}$

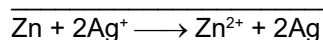
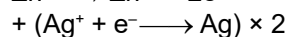
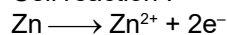
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$$E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = 1.56 \text{ V}$$

$$\text{Zn/Zn}^{2+} (0.1 \text{ M}) \parallel \text{Ag}^+ (1.0 \text{ M}) \mid \text{Ag } E_{\text{cell}}^{\circ} = 1.56$$

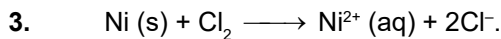
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log Q.$$

Cell reaction :



$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{(0.1)}{(1)^2} = 0.1$$

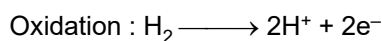
$$\begin{aligned} \Rightarrow E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log 0.1 \\ &= 1.56 - \frac{0.059}{2} \times -1 \\ &= 1.59\text{V Ans.} \end{aligned}$$



$$Q = \frac{[\text{Ni}^{2+}][\text{Cl}^-]^2}{P_{\text{Cl}_2}} = \frac{(0.19)(0.4)^2}{0.1} = \mathbf{0.304.}$$

4.  $\text{pH}_1 = \text{pK}_a + \log \frac{x}{y}$  —(1)

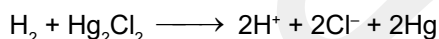
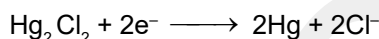
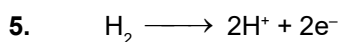
$$\text{pH}_2 = \text{pK}_a + \log \frac{y}{x}$$
 —(2)



$$E_1 = E^{\circ}_{\text{H}_2/\text{H}^+} - \frac{0.0529}{2} \log [\text{H}^+]^2_1 = 0.0529 \text{pH}_1$$

$$\begin{aligned} \Rightarrow E_2 &= 0.0529 \text{pH}_2 \\ \Rightarrow E_1 + E_2 &= 0.1058 (2\text{pK}_a) \end{aligned}$$

$$\Rightarrow \text{pK}_a = \frac{E_1 + E_2}{0.118}$$

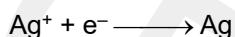


$$E^{\text{initial}} = E^{\circ} + \frac{0.059}{2} \log \frac{1}{[\text{H}^+]^2[\text{Cl}^-]^2} = 0.6 \quad E^{\text{final}} = E^{\circ} + \frac{0.059}{2} \log \frac{1}{(10^{-7})^2[\text{Cl}^-]^2} = 0.718$$

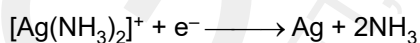
subtracting we get  $0.118 = 0.059 \log \frac{[\text{H}^+]}{10^{-7}} \Rightarrow \frac{[\text{H}^+]}{10^{-7}} = 100 \Rightarrow [\text{H}^+] = 10^{-5} \Rightarrow \text{pH} = 5.$



$$\Delta G_1^{\circ} = RT \ln K_d$$



$$\Delta G_3^{\circ} = -1 \times F \times 0.8$$

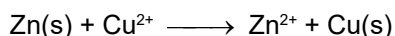
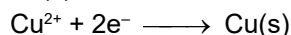
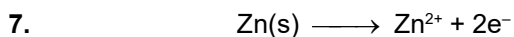


$$\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$-1 \times F \times E^{\circ} = -RT \ln k_d - 1 \times F \times 0.8$$

$$E^{\circ} = -\frac{RT}{F} \ln k_d + 0.8 \Rightarrow \frac{8.314 \times 298}{96500} \times 2.303 \times (-13) + 0.8$$

$$E^{\circ} = 0.0313 \text{ V.}$$

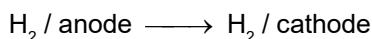
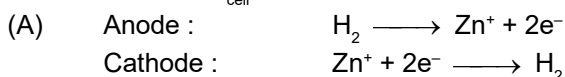


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

Since slope is -ve i.e.  $-\frac{0.0591}{2}$

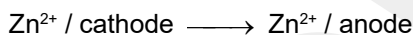
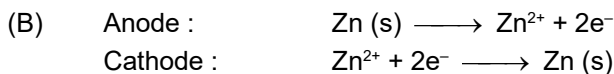
∴ Ans is (B).

8. For spontaneity,  $E_{\text{cell}} > 0$   
 $E_{\text{cell}}^0 = 0$  for concentration cell.



$$E_{\text{cell}} = -\frac{0.0591}{2} \log \frac{\text{H}_2 / \text{cathode}}{\text{H}_2 / \text{anode}} = -\frac{0.0591}{2} \log \frac{P_2}{P_1}$$

= +ve



$$E_{\text{cell}} = -\frac{0.0591}{2} \log \frac{\text{Zn}^{2+} / \text{anode}}{\text{Zn}^{2+} / \text{cathode}} = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$$

= +ve.

9. For urea

$$\Delta T_f = k_f \times m$$

or  $k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$

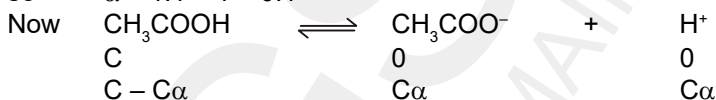
Now for  $\text{CH}_3\text{COOH}$

$$\Delta T_f = i k_f m$$

so  $i = \frac{0.02046}{1.86 \times 0.01} = 1.1$

Now  $i = 1 + \alpha$

so  $\alpha = 1.1 - 1 = 0.1$



$[\text{H}^+] = C\alpha = 0.01 \times 0.1 = 0.001$

so pH = 3.

10. [Acetyl salicylic acid] =  $\frac{0.36}{250} \times 2 \times 1000 \text{ g L}^{-1}$   
 $= \frac{0.36 \times 8}{180} = 0.016 \text{ M}$

By Ostwald's dilution law  $[\text{H}_3\text{O}^+]$

$$= \sqrt{K_a C} = \sqrt{6.25 \times 10^{-9} \times 0.016} = 10^{-5} \text{ M}$$

pH =  $-\log [\text{H}_3\text{O}^+] = 5$

### DPP No. # 29

2.  $\text{Sn} | \text{Sn}^{2+} (1 \text{ M}) || \text{Pb}^{2+} (10^{-3} \text{ M}) | \text{Pb}$ .

$E_{(\text{Sn}^{2+} / \text{Sn})}^0 = -0.14 \text{ V}$  and  $E_{(\text{Pb}^{2+} / \text{Pb})}^0 = -0.13 \text{ V}$ .

$E_{\text{cell}}^0 = -0.13 + 0.14 = 0.01 \text{ V}$ .

$E_{\text{cell}} = 0.01 - \frac{0.0591}{2} \log \frac{1}{10^{-3}} = -0.0785 \text{ V}$ .

3.  $\log K_{\text{eq}} = \frac{2 \times 0.777}{0.0591}$ ,  $K_{\text{eq}} = 2.18 \times 10^{26}$

4.  $E_{\text{cell}} = 3.11 - \frac{0.0591}{2} \log K_{\text{eq.}}$   $E_{\text{cell}} = 0.$

$$\log K_{\text{eq.}} = \frac{3.11 \times 2}{0.0591}$$

$$K_{\text{eq.}} = 1.864 \times 10^{107}$$

$$\Delta G^\circ = -2.303 RT \log 1.864 \times 10^{107} = -2.303 \times 8.314 \times 298 \log 1.86 \times 10^{107}$$

5.  $0 = E^\circ_{\text{cell}} - \frac{0.0591}{1} \log 0.531$

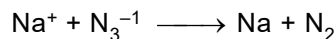
$$E^\circ_{\text{cell}} = 0.0591 \log 0.531 = 0.0591 \log 5.31 \times 10^{-1}$$

$$E^\circ_{\text{C}} - E^\circ_{\text{A}} = -0.01624$$

$$E^\circ_{\text{C}} = -0.01624 + 0.799 = 0.7826 \text{ V.}$$

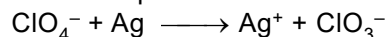
6. For the given options

(A) Sodium ion and azide ion



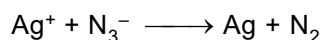
$$E^\circ = -2.71 + 3.09 < 1.7 \text{ V}$$

(B) Silver ion and perchlorate ion



$$E^\circ = 1.23 - 0.80 < 1.7 \text{ V}$$

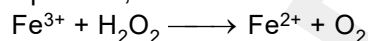
(C) Silver ion and azide ion



$$E^\circ = 0.80 + 3.09 \\ = 3.89 > 1.7 \text{ V}$$

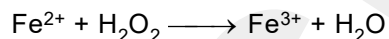
So will lead to explosion

7. If  $\text{Fe}^{3+}$  is present, then



$$E^\circ = 0.77 + 1.03 = 1.8 \text{ V} > 0$$

so spontaneous



$$E^\circ = 1.76 + 0.77 = 0.99 > 0$$

Hence  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  both are capable of decomposing  $\text{H}_2\text{O}_2$ .

8. From SRP values it is clear that  $\text{O}_3$  will oxidise  $\text{H}_2\text{O}_2$  into  $\text{O}_2$ .

9.  $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$

$c(1-h)$   $ch$   $ch$  where h is degree of hydrolysis

$$[\text{OH}^-] = ch ;$$

$$\text{Also; } h = \sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w}{K_a \cdot c}} = \sqrt{\frac{10^{-14}}{4 \times 10^{-4} \times 0.04}} = 2.5 \times 10^{-5}$$

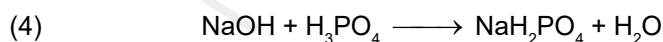
$$\therefore [\text{OH}^-] = 0.04 \times 2.5 \times 10^{-5} \quad \text{or} \quad \text{pOH} = 6$$

$$\therefore \text{pH} = 14 - \text{pOH} = 8$$

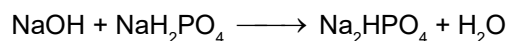
10. (1)  $\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$  ; (2)  $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$



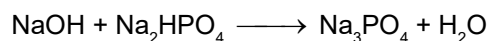
$$\therefore \text{pH}_{\text{WA}} = \frac{1}{2} (\text{p}K_{a_1} - \log C)$$



i	5	2		
f	3	0	2	2

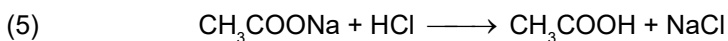


i	3	2		
f	1	0	2	2



i	1	2		
f	0	1	1	1

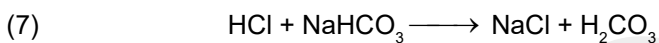
$$\therefore \text{Buffer solution} \quad \therefore \quad \text{pH} = \text{pK}_{a_3} + \log_{10} \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$



i	5	4		
f	1	0	4	4

$$\therefore \text{Acidic buffer} \quad \therefore \quad \text{pH} = \text{pK}_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$(6) \quad \text{pH} = \frac{\text{pK}_{a_2} + \text{pK}_{a_1}}{2}$$

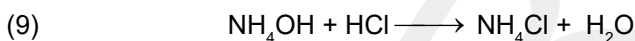


i	2	1		
f	1	0	1	1

For a mixture of WA + SA, major H<sup>+</sup> ions will come from HCl.

$$\therefore \quad \text{pH} = -\log_{10} [\text{H}^+]_{\text{HCl}}$$

$$(8) \quad \text{pH} = \frac{1}{2} (\text{pK}_w + \text{pK}_a - \text{pK}_b)$$



i	4	3		
f	1	0	3	3

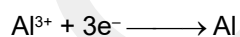
$$\therefore \text{Basic buffer} \quad \therefore \quad \text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

Clearly, pH of solutions 4, 5, 6, 8 and 9 is not affected by dilution.

### DPP No. # 30

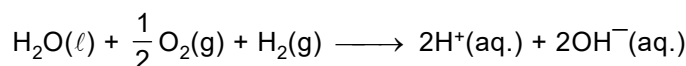
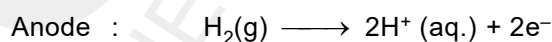
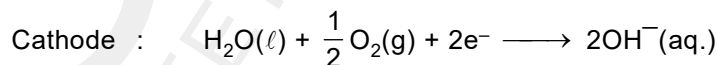
1.  $\text{pH} = 14 \quad \Rightarrow \quad [\text{OH}^-] = 1 \text{ M}$

$$[\text{Al}^{3+}] = \frac{\text{K}_{sp}}{[\text{OH}^-]^3} = 10^{-33}$$

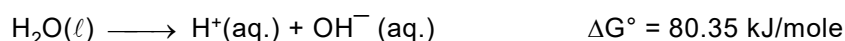


$$E_{\text{cell}} = E_{\text{Al}^{3+}/\text{Al}}^\circ - \frac{0.0591}{3} \log \frac{1}{[\text{Al}^{3+}]}$$

2. Cell reaction



Also we have



Hence for cell reaction

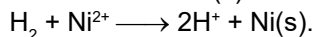
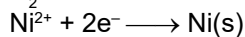
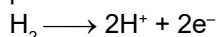
$$\Delta G^\circ = -96.50 \text{ kJ/mole}$$

$$\text{So,} \quad E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{96500}{2 \times 96500} = 0.50 \text{ V}$$

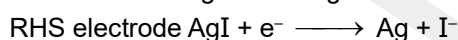
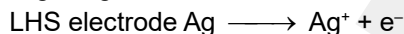
$$3. \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{-0.0591}{2} \log \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}][\text{H}_2]}$$

$$\Rightarrow E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{-0.0591}{1} \log [\text{H}^+] = 0.0591 \times \text{pH}$$

$$\Rightarrow \text{pH} = 1$$



4. For the cell  $\text{Ag} | \text{Ag}^+ || \text{I}^- , \text{AgI} ; \text{Ag}$



Cell reaction,  $\text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^-$

The equilibrium constant (K) = The solubility product  $K_s$

$$\Delta G = -nFE$$

$$\Delta G^{\circ} = -2.303 RT \log K$$

$$\log K = \frac{nFE}{2.303 RT}$$

5.  $\text{Zn} | \text{ZnCl}_2 (0.05\text{M}) | \text{AgCl(s)} | \text{Ag} \quad E_{\text{cell}} = 1.015\text{V}$

$$\left( \frac{dE_{\text{cell}}}{dT} \right) = -4.92 \times 10^{-4} \frac{\text{V}}{\text{K}}$$

$$\begin{aligned} \Delta G &= -nFE_{\text{cell}} = -ve \quad (\text{as } E_{\text{cell}} = +ve) \\ &= -2 \times 96500 \times 1.015 \\ &= -195.895 \text{ kJ.} \end{aligned}$$

$$\Delta S = nF \left( \frac{dE_{\text{cell}}}{dT} \right)$$

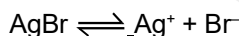
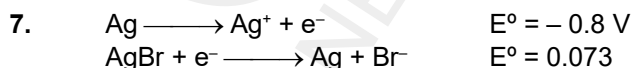
$$\begin{aligned} &= 2 \times 96500 \times -4.92 \times 10^{-4} \\ &= -94.956 \text{ J/K.} \end{aligned}$$

$$\Rightarrow \Delta G = \Delta H - T\Delta S.$$

$$\begin{aligned} &= -198.895 + \frac{298}{1000} \times (-94.956) \\ &= -224.19 \text{ KJ.} \end{aligned}$$

So, all are negative.

$$\begin{aligned} 6. \quad E_{\text{Cl}^- / \text{AgCl, Ag}}^{\circ} &= E_{\text{Ag}^+ / \text{Ag}}^{\circ} + 0.0591 \log k_{\text{sp}} (\text{AgCl}) \\ &= 0.8 + 0.0591 \log 1.56 \times 10^{-10} \\ &= 0.8 + 0.0591 (-10 + \log 1.56) = 0.2204 \text{ V} \end{aligned}$$



$$E_{\text{cell}}^{\circ} = 0.073 - 0.8 - 0.0591 \log [\text{Ag}^+] [\text{Br}^-]$$

$$0.8 - 0.073 = -0.0591 \log K_{\text{sp}} (\text{AgBr})$$

$$K_{\text{sp}} = 4.998 \approx 5 \times 10^{-13}$$

$$[\text{Ag}^+] [\text{Br}^-] = 5 \times 10^{-13}$$

$$[\text{Br}^-] = \frac{5 \times 10^{-13}}{0.1} = 5 \times 10^{-12}$$

Solubility of  $\text{AgBr} = [\text{Br}^-] = 5 \times 10^{-12}\text{M}$

$$8. \quad \Delta S^\circ = nF \left( \frac{dE^\circ}{dT} \right)_p$$

$$= 2 \times 96500 \times [-1.25 \times 10^{-3}] = 241.45 \text{ Jk}^{-1}$$

$$\Delta H^\circ = -nF E^\circ_{\text{cell}} + n F T \frac{dE^\circ_{\text{cell}}}{dT}$$

$$= -2 \times 96500 \times 1.36 + 2 \times 96500 \times 298 \times (-1.25 \times 10^{-3})$$

$$= -3.3437 \times 10^2 \text{ KJ.}$$

10. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.

11.  $S_2$  : Molar entropy of gas is much greater than that of solid and liquid.

$S_3$  : Entropy change is positive if  $\Delta n_g$  is positive.

$S_4$  : Molar entropy of a crystalline solid will be zero at absolute zero temperature.

### DPP No. # 31

1. (a) Solution contains  $\text{Sn}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ .

Anode is tin anode.

$$E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}; E^\circ_{\text{O}_2/\text{H}_2\text{O}} = 1.23\text{V}; E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V.}$$

From the SRP values, it is clear that the reaction for which SRP is least will take place at anode  $E^\circ_{\text{Sn}^{2+}/\text{Sn}}$  is least.

So,  $\text{Sn} \longrightarrow \text{Sn}^{2+} + 2e^-$  **Ans.**

(b) The solution contains  $\text{Ni}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$

$$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = 0.23\text{V}$$

$$E^\circ_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}} = 2.05\text{V}$$

$$E^\circ_{\text{O}_2/\text{H}_2\text{O}} = 1.23\text{V}$$

$$E^\circ_{\text{Au}^{3+}/\text{Au}} = 1.4\text{V}$$

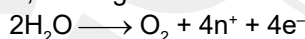
$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$$

If Nickel electrode is used, then Nickel will get oxidised as its SRP is least. So Nickel is not anode. If gold electrode is used, then water will get oxidised as SRP of gold is more than SRP of water. So gold is the anode.

If copper electrode is used, then copper will get oxidised as SRP of Cu is less than that of water.

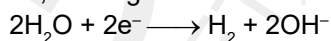
2. (a)  $\text{K}_2\text{SO}_4(\text{aq.})$  contains  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$

At anode ; water gets oxidized



as  $\text{H}^+$  are produced, region around anode has lesser pH.

At cathode, water get reduced.

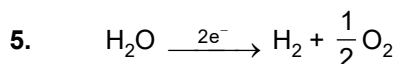
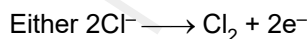


as  $\text{OH}^-$  are produced, region around cathode has higher pH.

Cathode is negatively charged.

(b) In  $\text{CuCl}_2$  solution,

At anode



$$2 \times 96500 \text{ C} \rightarrow 22.4 \times 1000 \text{ cm}^3 \text{ H}_2$$

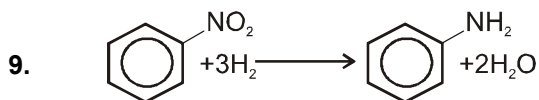
$$\frac{2 \times 96500 \times 224}{22.4 \times 1000} \text{ C} \leftarrow \therefore 224 \text{ cm}^3 \text{ H}_2$$

$$= 1930 \text{ C.}$$

6. Gold chloride  $\text{AuCl}_3$

$$m = \frac{M}{96500 \times n} \times I \times t$$

$$I = \frac{2 \times 96500 \times 3}{197 \times 20 \times 60} = 2.448 \text{ A.}$$



$$\frac{6.15}{123} = 0.05 \text{ mole of nitro benzene}$$

$$V.F = 6$$

electricity of charge required if efficiency is 100%

$$= 0.05 \times 6 = 0.3 \text{ F}$$

But efficiency is 40%

$$\text{charge required} = \frac{0.3}{0.4} = 0.75.$$

11.  $\text{XSO}_4$  (aq.)

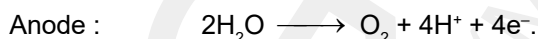
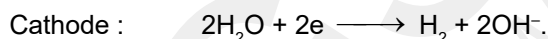
$\text{Y}_2\text{SO}_4$  (aq.)

$$\frac{\text{Mol.mass X}}{\text{Mol.mass Y}} = \frac{2}{1} \quad \Rightarrow \quad \text{eq. wt. of X} = \frac{\text{mol. mass X}}{2} \quad \Rightarrow \quad \text{eq. wt. of Y} = \frac{\text{mol. mass Y}}{2}$$

$$\frac{\text{mass of Y}}{\text{mass of X}} = \frac{\text{eq.wt. of Y}}{\text{eq.wt. of X}} = \frac{\text{mol.mass Y}}{\text{mol.mass X}} \times \frac{2}{1} = 1:1.$$

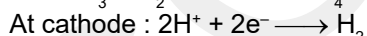
### DPP No. # 32

1. Remains colourless since solution is almost neutral & Hph shows pink colour only in basic medium.



both  $\text{OH}^-$  equivalent =  $\text{H}^+$  equivalent.

2.  $\text{NaClO}_3 + \text{H}_2\text{O} \longrightarrow \text{NaClO}_4 + \text{H}_2$



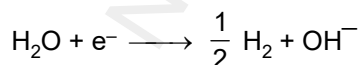
For 1 mole of  $\text{NaClO}_4$  and  $\text{H}_2$  we require 2 F of charge

For 0.5 mole of  $\text{NaClO}_4$  we require 1 F of charge

$\therefore$  Electricity required =  $1 \times 100/60 = 1.67\text{F}$ .

4. The number of Faradays =  $\frac{600 \times 0.2}{96500} = 1.243 \times 10^{-3}$ .

At the cathode, reaction is



$1.243 \times 10^{-3}$  mol of  $\text{OH}^-$  are produced.

The concentration =  $1.243 \times 10^{-3} / 0.05 = 0.02486$  Molar.

5.  $\text{th} \times \text{Area} \times \text{density} = \frac{108 \times 0.2 \times 0.8 \times 3600}{96500}$  ;

$$\text{th} = \frac{108 \times 0.2 \times 0.8 \times 3600}{96500 \times 100 \times 10} \text{ cm} = 6.4 \times 10^{-4} \text{ cm}$$

6. Anode :  $2\text{Cl}^- \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$   $E^\circ = -1.36 \text{ V}$   
 Cathode :  $2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$   $E^\circ = -0.83 \text{ V}$   
 $\text{pH} = 12.24 \Rightarrow [\text{OH}^-] = 0.0174 \text{ M}$   
 Moles of  $\text{OH}^- = 0.3 \times 0.0174 = 5.213 \times 10^{-3}$  moles  
 = Moles of  $\text{e}^-$   
 Total charge =  $5.213 \times 10^{-3} \times 96500 = 503.1 \text{ C}$ .

$$It = 503.1 \quad \Rightarrow \quad I = \frac{503.1}{360} = 1.4 \text{ A.}$$

7. The reduction potential of  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$ .

8. Since, no. of Faraday used

$$= \text{No of equivalent deposited} = (n\text{-factor}) \times \text{mole deposited}$$

$$\therefore \text{mole deposited} = \frac{\text{no. of Faraday used}}{n\text{-factor}} = \frac{i \times t}{96500} \times \frac{1}{n} = \frac{1 \times 96.5 \times 60}{96500 \times 2} = 30 \times 10^{-3} = 0.03.$$

9. If time for the deposition of Zn be t

$$\therefore t = 106.5 - 96.5 = 10 \text{ minute.}$$

$$\therefore \text{mole deposited} = \frac{1 \times 10 \times 60}{96500} \times \frac{1}{2} = 0.0031.$$

10. No. of equivalent of  $\text{O}_2$  evolved = no. of Faraday used

$$= \frac{\left(\frac{50}{100}\right) i \cdot t}{96500} = \frac{0.5 i \cdot t}{96500} \quad \therefore \text{mole of } \text{O}_2 = \frac{0.5 \times 1 \times 96.5 \times 60}{96500} \times \frac{1}{4} = \frac{0.03}{4}$$

$$\therefore \text{volume at NTP} = \frac{0.03}{4} \times 22.4 = 0.168 \text{ L} = 168 \text{ mL.}$$

### DPP No. # 33

1. Weak electrolyte is weakly ionizing substance, dilution promotes ionization thus conductivity. For strong electrolyte, as concentration increases interionic attraction increases and conduction decreases.

2. Normality of resulting solution =  $\frac{0.1 \text{ V}}{2 \text{ V}} = 0.05 \text{ N}$

$$\wedge_{\text{eq.}} = \frac{K \times 1000}{N} = \frac{0.0055 \times 1000}{0.05} = 110$$

3.  $R_A = \frac{1}{0.01} = 100$

$$R_B = \frac{1}{0.005} = 200$$

$$\frac{1}{R_{\text{eq}}} = \frac{1}{R_A} + \frac{1}{R_B}$$

$$\text{Sep} = S_A + S_B = 0.01 + 0.005 = 0.0155$$

6.  $\kappa_{\text{electrolyte}} = \kappa_{\text{solution}} - \kappa_{\text{solvent}}$   
 $= 3.4 \times 10^{-6} - 2.02 \times 10^{-6} = 1.38 \times 10^{-6} \text{ Scm}^{-1}$

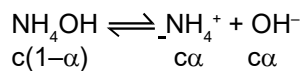
$$\text{Solubility} = \frac{\kappa_{\text{electrolyte}} \times 1000}{\lambda_m^\circ}$$

$$= \frac{1.38 \times 10^{-6} \times 1000}{138} = 10^{-5} \text{ M.}$$

7.  $\Lambda_{\text{eq}}^{\circ} \text{Ba(OH)}_2 = \lambda^{\circ} \text{Ba}^{2+} + \lambda^{\circ} \text{eq, OH}^-$   
 $\lambda^{\circ} \text{eq BaCl}_2 = \lambda^{\circ} \text{eq Ba}^{2+} + \lambda^{\circ} \text{eq, Cl}^-$   
 $\lambda^{\circ} \text{eq NH}_4\text{Cl} = \lambda^{\circ} \text{eq NH}_4^+ + \lambda^{\circ} \text{eq, Cl}^-$   
 $\lambda^{\circ} \text{eq, NH}_4\text{OH} = \lambda^{\circ} \text{eq, NH}_4^+ + \lambda^{\circ} \text{eq, OH}^-$   
 I + III + II  
 $\lambda^{\circ} \text{eq, NH}_4\text{OH} = (228.8 + 129.8) - 120.3 = 238.33 \text{ cm}^2 \text{eq}^{-1}$

$$\lambda_{\text{eq, NH}_4\text{OH}} = \frac{4.766 \times 10^{-14} \times 1000}{0.2} = 2.383$$

$$\alpha = \frac{\lambda_{\text{eq, NH}_4\text{OH}}}{\lambda^{\circ} \text{eq, NH}_4\text{OH}} = 10^{-2}$$



$$[\text{OH}^-] = 0.2 \times 10^{-12} = 2 \times 10^{-3}$$

$$\text{pOH} = 3 - \log 2 \Rightarrow \text{pH} = 14 - (3 - \log 2) = 11.3$$

8.  $R = \frac{1}{\kappa} \frac{\ell}{A} \Rightarrow \kappa = \frac{1}{250} \times \frac{7}{7} = 0.004 \Omega^{-1} \text{ cm}^{-1}$

$$\Lambda_{\text{eq}} = \frac{0.004}{0.1} \times 1000 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1} = 40 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

9. Number of moles of  $\text{Cu}^{2+}$  discharged from anode = number of moles of  $\text{Cu}^{2+}$  deposited at cathode.

### DPP No. # 34

1. In solution A :  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$  ;  $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$  (pH decreases)  
 In solution B :  $2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{e}^-$  ;  $2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$  (pH increases)
2. (D) Ni (dmg)<sub>2</sub> complex is square planar and dimagnetic.  
 Pt (II) – 5d<sup>8</sup> configuration. Complex is square planar and therefore, dimagnetic.  
 So,  $\mu = 0$
4. On increasing dilution, conductivity (k) of solution decreases but molar conductivity ( $\lambda_m$ ) increases.
5. emf of cell is intensive function so do not depend stoichiometric coefficient. In complex formation concentration of cation of decreases, emf and connectivity get change.
7.  $\Lambda_m^{\infty} (\text{Cu}_2[\text{Fe}(\text{CN})_6]) = 2 \lambda_m^{\infty} (\text{Cu}^{2+}) + \lambda_m^{\infty} (\text{Fe}(\text{CN})_6^{4-})$   
 $= 2 \Lambda_m^{\infty} (\text{CuSO}_4) + \Lambda_m^{\infty} (\text{K}_4\text{Fe}(\text{CN})_6) - 2 \Lambda_m^{\infty} (\text{K}_2\text{SO}_4)$   
 $= 640 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m^{\infty} = \frac{\kappa \times 100}{s}$$

$$s = \frac{\kappa \times 1000}{\Lambda_m^{\infty}} = \frac{1.28 \times 10^{-5} \times 1000}{640} = 2 \times 10^{-5}$$

8.  $\lambda_{\text{K}^+}^{\infty} = 96.50$

$$\therefore \text{Ionic mobility } \mu_{\text{K}^+}^{\infty} = \frac{\lambda_{\text{K}^+}^{\infty}}{F} = \frac{96.50}{96500} = 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$$

$$\text{Potential gradient applied} = \frac{6.0}{10} = 0.6 \text{ volt cm}^{-1}$$

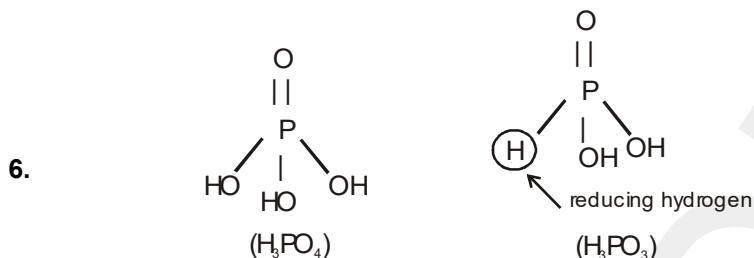
$$\text{Ionic mobility } (\mu) = \left( \frac{\text{speed of ion}}{\text{potential gradient}} \right)$$

So speed of ( $\text{K}^+$ ) =  $(10^{-3} \times 0.6) = 6 \times 10^{-4} \text{ cm/sec}$ .

$\therefore$  Distance travelled in 2 hours 46 minutes and 60 seconds  
 $d = 6 \text{ cm}$ .

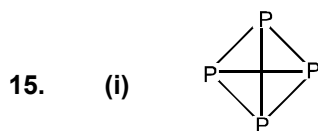
**DPP No. # 35**

1.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
4. (C) oxygen gas is produced.
5. (a)  $\text{Ca}_3\text{P}_2 + 6\text{HCl} \longrightarrow 3\text{CaCl}_2 + 2\text{PH}_3$       (b)  $\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2$

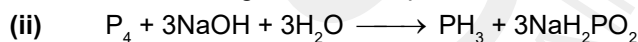


Strength of phosphorus oxy acid depends upon the number of OH groups per P = O group. It is the P = O group which induces polarisation and helps in the release of proton from -OH group.  $\text{H}_3\text{PO}_3 > \text{H}_3\text{P}_4$

8. (A) Burns only in pure dioxygen gas.  
 (D) Availability of electrons for metallic bonding ↓.
10. Both statement are correct but not correct explanation  
 NO solid is dimerised so diamagnetic  $\text{O}=\text{N}-\text{N}=\text{O}$  (s) but gaseous form is paramagnetic.



Six P-P single bonds are present.

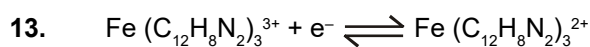


**DPP No. # 36**

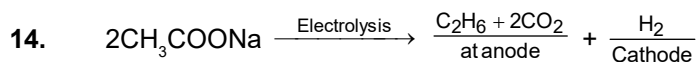
2. (i) Graphite like layered structure.  
 (ii)  $\text{Sb} + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$   
 (iii)  $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
4. Down the group  $\Delta_{\text{dissociation}}(\text{H}-\text{E}-\text{H})$  bond decreases.
6. S<sub>1</sub> -  $\text{N}_2\text{H}_4$  is formed in aqueous dilute solution in presence of glue or gelatin.  
 S<sub>2</sub> -  $\text{PH}_3$  solution in water explodes forming red phosphorous and  $\text{H}_2$ .  
 S<sub>3</sub> -  $\text{Ba}(\text{N}_3)_2 \xrightarrow{\Delta} \text{Ba} + 3\text{N}_2 \uparrow$   
 S<sub>4</sub> -  $\text{H}_4\text{P}_2\text{O}_6 = \text{P}-\text{P}$  bond,  $\text{H}_3\text{PO}_2 = \text{P}-\text{H}$  bond.
7.  $\text{ClO}_2$  does not dimerise because odd electron is present in 'd' orbital and is delocalised not localised as in  $\text{NO}_2$ .
11. (A)  $3\text{H}_3\text{PO}_2 \xrightarrow{415\text{K}} 2\text{H}_3\text{PO}_3 + \text{PH}_3 \uparrow$   
 $4\text{H}_3\text{PO}_3 \xrightarrow{435\text{K}} 3\text{H}_3\text{PO}_4 + \text{PH}_3$   
 (B)  $\text{PCl}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{H}_3\text{PO}_3 + 3\text{HCl}$   
 $4\text{H}_3\text{PO}_3 \xrightarrow{435\text{K}} 3\text{H}_3\text{PO}_4 + \text{PH}_3 \uparrow$   
 (C)  $2\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_2 + \text{HNO}_3$   
 (D)  $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$   
 \*  $\text{PH}_3$  and  $\text{HNO}_2$  act as reducing agents.

$$12. \quad E = 0.76 + \frac{0.0591}{2} \log \frac{10}{1}$$

$$\& \quad E = 0.76 + \frac{0.0591}{2} \log \frac{1}{10}$$



$$\text{range} = 1.14 \pm \frac{0.0591}{1}$$

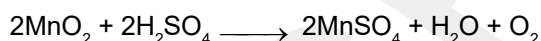
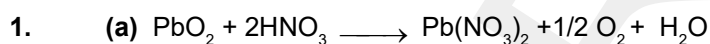


$$\text{Electric supplied} = \frac{0.965 \times 60 \times 60}{96500} = 3.6 \times 10^{-3} \text{ F}$$

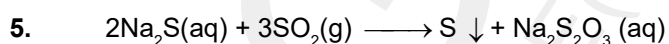
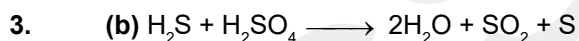
$$V_{\text{H}_2} = \frac{3.6 \times 10^{-3}}{2} \times \frac{0.0821 \times 298}{1} = 0.44 \text{ lit}$$

$$V_{\text{total}} = V_{\text{C}_2\text{H}_6} + V_{\text{CO}_2} + V_{\text{H}_2} = 4 \times 0.44 = 1.76 \text{ lit.}$$

### DPP No. # 37

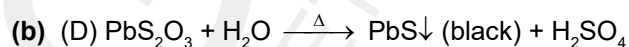


2. (A) and (B). Source NCERT



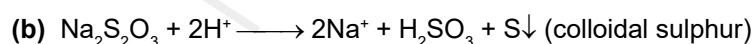
7. (b) (A), (B) (C) can be explained on the basis of decrease in bond (H-E) dissociation enthalpy (D) Hydrogen bonding, and van der Waal's force of attraction.

8. (a) S<sub>1</sub> (NCERT), S<sub>3</sub> β-Sulphur is stable above 369K.



9. Kept in plastic or wax-lined glass containers containing urea or phosphoric acid.

10. (a) on the basis of atomicity, oxygen diatomic where as sulphur is polyatomic.



(c) S<sub>2</sub> (in vapour state) has two unpaired electrons, like O<sub>2</sub>.

11. (A) H<sub>2</sub>O = 273 K, H<sub>2</sub>Te = 222 K; Δ<sub>diss</sub> H (H—E)/kJ mol<sup>-1</sup>  
H<sub>2</sub>O = 463 and H<sub>2</sub>TE = 238;

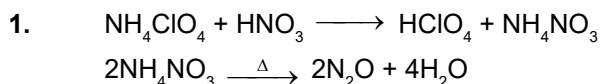
(B) SO<sub>3</sub> = 44.8°C and SO<sub>2</sub> = -10.07°C, SO<sub>2</sub><sup>+4</sup>, SO<sub>3</sub><sup>+6</sup>

SO<sub>3</sub> more acidic than SO<sub>2</sub>

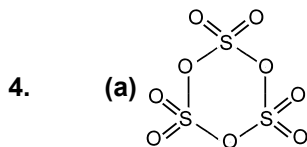
(C) H<sub>2</sub>SO<sub>4</sub> = 338°C; H<sub>2</sub>O<sub>2</sub> = 144°C

(D) NH<sub>3</sub> = 238.5°C, PH<sub>3</sub> = 185.5°C; ↓ down the group thermal stability ↓ acidic character ↑ Reducing character.

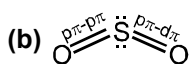
**DPP No. # 38**



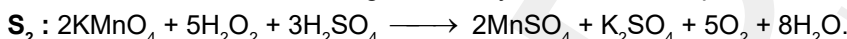
3. During oxidation of  $\text{H}_2\text{O}_2$ , O–O bond is not broken.



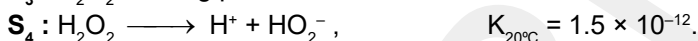
Hence, Ans.(D)



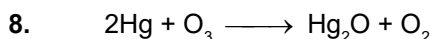
6. **S<sub>1</sub>** : It is correct statement. Dark coloured bottle prevents the auto oxidation of  $\text{H}_2\text{O}_2$  by light. Urea and sodium stannate act as negative catalyst for the decomposition of  $\text{H}_2\text{O}_2$ .



**S<sub>3</sub>** :  $\text{H}_2\text{O}_2$ , boiling point  $152^\circ\text{C}$ .



7. **O<sub>2</sub>** : KK,  $\sigma 2s^2$ ,  $\sigma^* 2s^2$ ,  $\sigma 2px^2$ ,  $\pi 2py^2$ ,  $\pi 2pz^2$ ,  $\pi^* 2py^1$ ,  $\pi^* 2pz^1$



$\text{Hg}_2\text{O}$  dissolves in Hg and thus its mobility decreases.

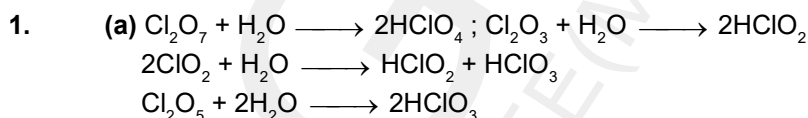
10. (i) Phosphorous acid ( $\text{H}_3\text{PO}_3$ ) Dibasic  $\therefore x = 2$

Tetrathionic acid ( $\text{H}_2\text{S}_4\text{O}_6$ ) Dibasic  $\therefore y = 2$

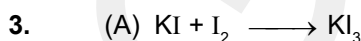
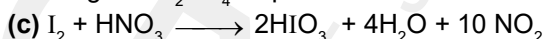
Pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) tetrabasic  $\therefore z = 4$

(iii)  $\text{P}_4\text{O}_6$ ,  $\text{SiO}_2$ ,  $\text{CO}_2$ ,  $\text{NO}_2$  are acidic oxides, CO and NO are neutral oxides and  $\text{PbO}_2$  and  $\text{SnO}_2$  are amphoteric oxides.

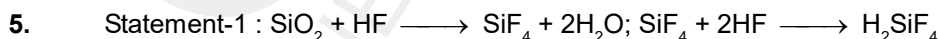
**DPP No. # 39**



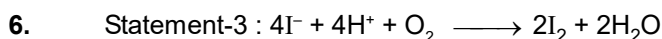
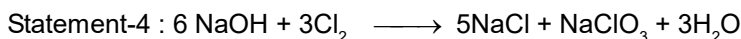
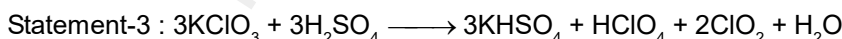
2. (b) In  $\text{H}_2\text{SO}_4$ , intense H-bonding makes it less volatile than HCl. HCl is more volatile as there is no H-bonding. So  $\text{H}_2\text{SO}_4$  displaces HCl from its salt.



$\text{I}_2$  is non-polar covalent compound. So soluble in (C) & (D)



Statement-2 : True.



7. Statement-1 :  $\text{HI} > \text{HBr}$  due to low bond dissociation enthalpy.

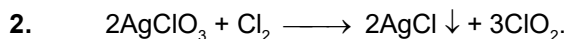
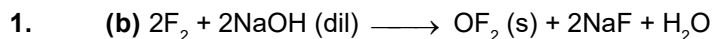
Statement-2 : Due to small size

Statement-3 :  $\text{F}_2 > \text{O}_3$  oxidising agent. Highest SRP of fluorine

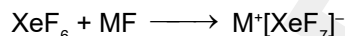
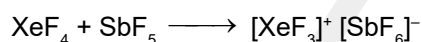
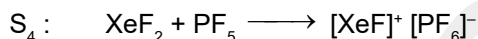
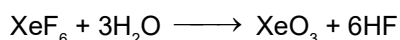
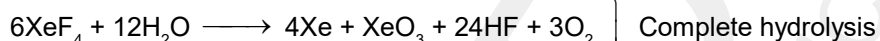
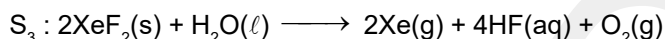
Statement-4 : Fluorine does not have empty d-orbital.

8. (a)  $3\text{Br}_2 + 3\text{Na}_2\text{CO}_3 \longrightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{CO}_2$   
 $\text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O}$
9. (b) Bond energy of  $\text{F}_2$  is less than  $\text{Cl}_2$  because lp-lp repulsion.  
 (c)  $\text{H}_2\text{O} + \text{Cl}_2 \longrightarrow 2\text{HCl} + [\text{O}]$   
 $\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2[\text{H}]$   
 (d)  $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + (\text{colourless}) + \text{Na}_2\text{S}_4\text{O}_6$

**DPP No. # 40**

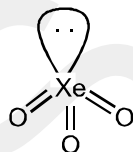


4. (a)  $\text{S}_1$  and  $\text{S}_2$  are correct statements.

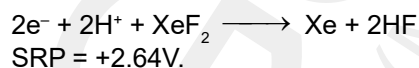


M = Na, K, Rb or Cs

- (b)  $\text{S}_1$  : Statement is correct



- $\text{S}_2$  : Statement is false



$\text{S}_3$ : Statement is false as He atoms being smaller do not trap in the cavities formed by water molecules (ice).

$\text{S}_4$  : Statement is false  $2\text{F}_2 + 2\text{NaOH} \longrightarrow \text{OF}_2(\text{g}) + 2\text{NaF} + \text{H}_2\text{O}$

5. (a)  $\text{Fe} + 2\text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$   
 Liberation of hydrogen prevents the formation of ferric chloride.



10. (A)  $\text{XeF}_4 + 6\text{H}_2\text{O} \longrightarrow 2\text{Xe} + \text{XeO}_3 + 3/2\text{O}_2 + 12\text{HF}$   
 (B)  $2[\text{HXeO}_4]^- + 2\text{OH}^- \longrightarrow [\text{XeO}_6]^{4-} + \text{Xe} + \text{O}_2 + 2\text{H}_2\text{O}$   
 (C)  $3\text{H}_2\text{O} + 3\text{F}_2 \longrightarrow 6\text{HF} + \text{O}_3$   
 $2\text{H}_2\text{O} + 2\text{F}_2 \longrightarrow 4\text{HF} + \text{O}_2$   
 (D)  $2\text{NOCl} + \text{O}_2 \longrightarrow 2\text{NO}_2 + \text{Cl}_2$

12.  $\text{H}_2\text{SO}_5$  and  $\text{Na}_2\text{S}_2\text{O}_3$   
 (+6)                      (+2)

**DPP No. # 41**

2. (a) For triclinic  $a \neq b \neq c$  &  $\alpha \neq \beta \neq \gamma \neq 90^\circ$
3. (b)  $a \neq b \neq c$  &  $\alpha = \beta = \gamma = 90^\circ$  the crystal system is orthorhombic

6. (a)  $P = 8 \times \frac{1}{8} = 1$  ;  $Q = 1 = 1$  ;  $R = 12 \times \frac{1}{4} = 3$  ; formula =  $PQR_3$

(b)  $Au = 8 \times \frac{1}{8} = 1$  ;  $Cu = 6 \times \frac{1}{2} = 3$  formula  $AuCu_3$

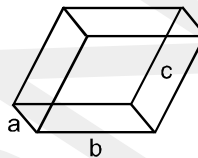
7.  $A = 7 \times \frac{1}{8} = \frac{7}{8}$  ;  $B = 6 \times \frac{1}{2} = 3$

Formula =  $A_{7/8} B_3$  or  $A_7 B_{24}$

10. (a) In triclinic unit cell.

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma$



(b). In simple cubic contribution of one corner =  $\frac{1}{8}$

total corner = 8

effective no. of atom per unit cell =  $\frac{1}{8} \times 8 = 1$

No. of bondy center in simple cubic = 1

No. of atom in body center = 1

AB

### DPP No. # 42

3.  $d = \frac{ZM}{a^3 N_A}$  ;  $\frac{d_1}{d_2} = \frac{4}{(3.5)^3} \times \frac{(3)^3}{2} = 1.26$

7.  $\frac{r_{\text{tetrahedral}}}{r_{\text{octahedral}}} = \frac{0.225R}{0.414R} = 0.543$ .

11. 8, 4, 100%.  
 It has fluorite ( $CaF_2$ ) structure.

12.  $d = \frac{ZM}{a^3 N_A}$  ;  $3.9 = \frac{4 \times 84}{a^3 \times 6.023 \times 10^{23}}$  or  $a^3 = 174.9 \times 10^{-24}$

$a = 5.6 \times 10^{-8}$  cm or 5.6 Å

$2r = \frac{a}{\sqrt{2}} = \frac{5.6}{\sqrt{2}} = 3.95$  Å

13. (A)  $2r = \frac{\sqrt{3} a}{2} = \frac{\sqrt{3} \times 5.2}{2} = 4.5$  Å

(B) Distance =  $a = 5.2$  Å

(C) 8

(D) 6

(E)  $d = \frac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92$  g/ml

14. In bcc unit cell there are 8 atoms at the corners of the cube and one atom at the body centre

$\therefore$  No of atoms per unit =  $8 \times \frac{1}{8} + 1 = 2$

No of atoms is 4.0 g of potassium =  $\frac{4}{39} \times 6.023 \times 10^{23}$

$\therefore$  No of unit cells in 4.0 g potassium =  $\frac{4}{39} \times 6.023 \times 10^{23} / 2 = 3.09 \times 10^{22}$





$$4. \quad 4 d_{c-c} \sin(54^\circ 44') = \sqrt{2} a \quad \Rightarrow \quad r = \frac{d_{c-c}}{2} = 0.78$$

$$5. \quad d = \frac{8 \times 12}{N_A \times a^3} = 3.37 \text{ gm/cc.}$$

$$6. \quad \text{Total number of unit cells} = \frac{1.2 \times N_A}{12 \times 8} = 7.5 \times 10^{21}.$$

7. (a) In zinc blende  $S^{2-}$  form FCC while alternate tetrahedral voids are occupied by  $Zn^{2+}$ .

(b)  $S^{2-}$  ion : number of tetrahedral void

$$1 : 2$$

$$8. \quad \text{We have theoretical density} = \frac{zM}{NV} = \frac{zM}{N(a^3)}$$

For a b.c.c lattice:  $z = 2$  and given that  $a = 3.50 \times 10^{-10}$  and  $M = 7 \times 10^{-3}$  kg / mole

$$d_{\text{cal}} = \frac{2 \times (7 \times 10^{-3})}{6.022 \times 10^{23} \times (3.50 \times 10^{-10})^3} = 5.42 \times 10^2 \text{ kg m}^{-3}$$

$$\therefore \text{percentage occupancy} = \frac{\rho_{\text{exp}}}{\rho_{\text{cal}}} = \frac{5.30 \times 10^2}{5.42 \times 10^2} \times 100 = 97.78 \%$$

9. Let there be 80  $O^{2-}$  in the crystal.

$\therefore$  Octahedral voids = 80 ; Tetrahedral voids = 160

$$A^{2+} \text{ ions} = \frac{1}{8} \times 160 = 20$$

$$B^{3+} \text{ ions} = \frac{1}{2} \times 80 = 40$$

$$A^{2+} : B^{3+} : O^{2-} = 20 : 40 : 80 = 1 : 2 : 4$$

$\therefore$  Formula is  $AB_2O_4$ .

11. In a face-centred cubic cell,

$$\text{radius} = \frac{\sqrt{2}a}{4}$$

$$\therefore \text{the closest distance between two atoms} = \text{diameter} = 2 \times \frac{\sqrt{2}a}{4} = \frac{a}{\sqrt{2}}$$

$$= \frac{4.070}{\sqrt{2}} \text{ \AA} = 2.878 \text{ \AA}.$$

$$\text{Number of atoms in a face-centred unit cell} = 8 \left( \frac{1}{8} \right) + 6 \left( \frac{1}{2} \right) = 4$$

$$\begin{aligned} \text{Mass of 4 atom per unit cell} &= 4 \times 197 \text{ amu} \\ &= 4 \times 197 \times (1.66 \times 10^{-24}) \text{g} \\ &= 1.308 \times 10^{-21} \text{g} \end{aligned}$$

$$\begin{aligned} \text{Volume of the unit cell} &= a^3 \\ &= (4.07 \times 10^{-8})^3 \text{cc.} \end{aligned}$$

$$\therefore \text{density of gold} = \frac{1.308 \times 10^{-21}}{(4.07 \times 10^{-8})^3} = 19.40 \text{ g /cc.}$$





$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = k [A] [B]^2$$

3.  $\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}$

$$\frac{k_1}{2} [A]^2 = K_2 [A]^2 = \frac{k_3}{3} [A]^2$$

$$\Rightarrow \frac{k_1}{2} = k_2 = \frac{k_3}{3}$$

4. Unit of k for first order reaction is  $s^{-1}$ .

5.  $\text{Rate} = k[A]^{1/2} [B]^2$

$$r_1 = k[a]^{1/2} [b]^2 ; \quad r_2 = k[4a]^{1/2} [2b]^2$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{1}{2 \times 4} = \frac{1}{8}$$

$$\Rightarrow r_2 = 8 \times r_1$$



$$\text{rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k [A]^2$$

$$\left(\frac{d[B]}{dt}\right)_1 = \frac{k(a)^2}{k(2a)^2} = \frac{1}{4}$$

7. From the unit of K, it is evident that it is a second order reaction.

$$-\frac{1}{2} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} \Rightarrow \therefore -\frac{d[NO_2]}{dt} = 2 \times \frac{d[O_2]}{dt} = 2 \times 1.5 \times 10^{-4} = 3 \times 10^{-4}$$

$$3 \times 10^{-4} = K [NO_2]^2 = 3 \times 10^{-3} [NO_2]^2 \Rightarrow \therefore [NO_2] = 0.316.$$

8.  $a - 2r = 53.6 \text{ pm}$

$$\text{also } 4r = \sqrt{3}a \Rightarrow a - \frac{\sqrt{3}}{2}a = 53.6$$

$$\Rightarrow a = \frac{53.6 \times 2}{2 - \sqrt{3}} = 400 \text{ pm}$$

$$\text{Density } (\rho) = \frac{2 \times 23}{6.023 \times 10^{23} \times 4^3 \times 10^{-24}} = 1.19 \text{ g/cc}$$

9.  $2.32 = \frac{2 \times M}{6 \times 10^{23} (1.22)^3 \times 10^{-21}}$

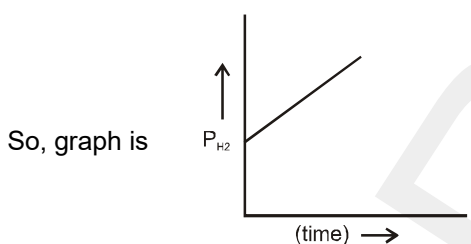
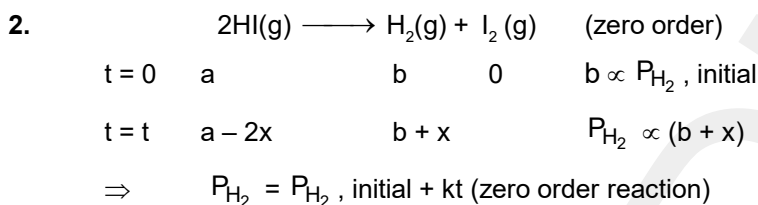
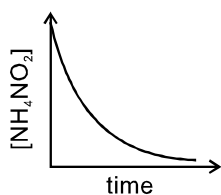
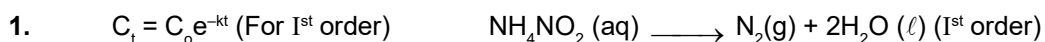
$$\Rightarrow M = 1264 \Rightarrow x \approx 47.$$

10. Given  $a - 2r = 60.3$  and for bcc,  $4r = \sqrt{3}a$

$$\Rightarrow a - \frac{\sqrt{3}}{2}a = 60.3 \Rightarrow a = 450 \text{ pm}$$

$$\text{Density } (\rho) = \frac{2 \times 48}{6.023 \times 10^{23} \times (4.5)^3 \times 10^{-24}} = 1.75 \text{ g/cc.}$$

**DPP No. # 48**



3.  $\therefore C_t = \frac{C_0}{2^n}$

For 75% completion, no. of half lives taken = 2 half life =  $\frac{100}{2} = 50$  min

For 87.5% completion, no. of half lives taken = 3.

$\therefore$  Time taken =  $3 \times 50 = 150$  min.

4. For zero order, rate =  $K = \frac{-(0.08 - 0.1)}{10} = \frac{0.02}{10} \text{ M min}^{-1}$

half life =  $\frac{C_0}{2K} = \frac{0.1 \times 10}{2 \times 0.02} = 25$  min

$\Rightarrow$  completion time =  $\frac{C_0}{K} = \frac{0.1 \times 10}{0.02} = 50$  min.



$t = 0$      $a$          $0$

$t = t$      $a - x$      $x$

At intersection,  $a - x = x$

$\Rightarrow x = \frac{a}{2}$

so, this time represents half life.



$t = 0$      $a$          $0$

$t = t$      $a - x$      $x$

$\frac{a-x}{a} = \text{fraction of A} \Rightarrow (a-x) = a - kt \Rightarrow \frac{a-x}{a} = 1 - kt$

So, it is zero order.



3.  $\frac{dx}{dt} = k [C]^{3/2}$  For  $n^{\text{th}}$  order

$$(n-1) kt = \left[ \frac{1}{[C_t]^{n-1}} - \frac{1}{[C_o]^{n-1}} \right] \Rightarrow \frac{k}{2} t = \left[ \frac{1}{[C_t]^{1/2}} - \frac{1}{[C_o]^{1/2}} \right]$$

$$t = \frac{2}{k} \left[ [C_t]^{-1/2} - [C_o]^{-1/2} \right] \quad t \propto [C_t]^{-1/2}$$

So, For  $C_t^{-1/2}$  Vs  $t$  will give linear plot.

4. For zero order,  $\frac{C_0 - C_t}{t} = k \Rightarrow \frac{0.01 - 0.001}{100} = k \neq 9$

For first order,  $k = \frac{2.303}{t} \log \frac{C_0}{C_t} = \frac{2.303}{100} \log \frac{0.01}{0.001} = 2.303 \times 10^{-2} \neq 9$ .

For second order,  $\frac{1}{t} \left[ \frac{1}{C_t} - \frac{1}{C_0} \right] = k \Rightarrow k = \frac{1}{100} [1000 - 100] = 9$

so, reaction is 2nd order. Unit of rate constant is  $M^{-1}s^{-1}$ .

5.  $t_{1/2} \propto \frac{1}{a^{n-1}}$  [Here  $a \propto P$ ]  $\frac{880}{410} = \left[ \frac{364}{170} \right]^{n-1} \therefore n = 2$ .

6. In 1st order Rxn, decrease in % of concentration same in same interval of Time

$$\left[ \frac{(0.12 - 0.06)}{0.12} \times 100 \right] = 50\%$$

$$\frac{(0.06 - 0.03)}{0.06} \times 100 = 50\%$$

so reaction must be of first order.

7.  $A \rightarrow \text{product}$

$$a \xrightarrow{30\text{min}} \frac{a}{2} \xrightarrow{60\text{min}} \frac{a}{4} \xrightarrow{90\text{min}} \frac{a}{8}$$

So, Order is 1.

8.  $Kt = \ln \left( \frac{C_0}{C_t} \right)$

$$K \times 30 = \ln \left( \frac{C_0}{C_1} \right) \quad \dots(1)$$

$$K \times 40 = \ln \left( \frac{C_0}{C_2} \right) \quad \dots(2)$$

$$\frac{3}{4} = \frac{\ln \left( \frac{C_0}{C_1} \right)}{\ln \left( \frac{C_0}{C_2} \right)} \Rightarrow 3 \ln \left( \frac{C_0}{C_2} \right) = 4 \ln \left( \frac{C_0}{C_1} \right) \Rightarrow \left( \frac{C_0}{C_2} \right)^3 = \left( \frac{C_0}{C_1} \right)^4 \Rightarrow C_o = \frac{C_1^4}{C_2^3}$$

9. Rate =  $K C_t = K C_o e^{-kt}$

$$= 2.303 \times 1 \times e^{-2.303 \times 1} \text{ M min}^{-1} = 2.303 \times e^{-\ln 10} = \frac{2.303}{10} = 0.2303$$

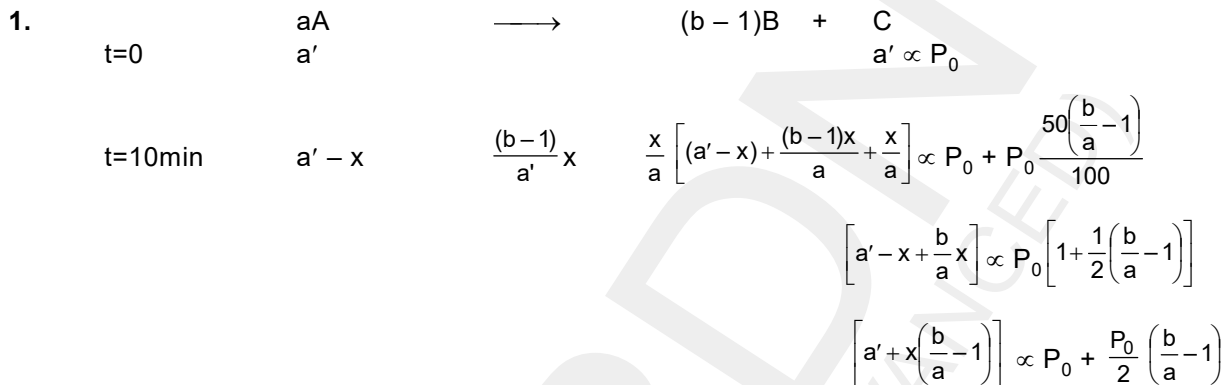
10. For 1st order reaction,

$$[A]_t = [A]_0 e^{-Kt}$$

$$-\frac{d[A]}{dt} = K[A]_t = [A]_0 K e^{-Kt}$$

$$Kt = 2.303 \log [A]_0 - 2.303 \log [A]_t \Rightarrow \log [A]_t = \log [A]_0 - \frac{Kt}{2.303}$$

**DPP No. # 50**



$$\Rightarrow x \propto \frac{P_0}{2} \Rightarrow x \propto \frac{a'}{2}$$

$\Rightarrow$  half life = 10 minute.

2. (C) 
$$t_1 = \frac{(t_{1/2})_1}{0.693} \ln \left( \frac{1}{1-(1/4)} \right)$$

$$t_2 = \frac{(t_{1/2})_2}{0.693} \ln \left( \frac{1}{1-3/4} \right)$$

$$\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\ln(4/3)}{\ln(4)} = 1 : 0.62.$$

3. For 1<sup>st</sup> order reaction

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} \text{ second}^{-1}$$

$$\Rightarrow \frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5$$

For zero order reaction

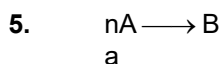
$$k_0 = \frac{C_0}{2 t_{1/2}} = \frac{1.386}{2 \times 20}$$

4. 
$$t = \frac{2.303}{k} \log \left( \frac{100}{0.1} \right) = \frac{2.303}{k} \times 3$$

$$t = \frac{2.303 \times 3}{0.693} = \frac{2.303 \times 3 \times t_{1/2}}{0.693}$$

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

$$\Rightarrow \frac{t_{99.9\%}}{t_{1/2}} = \frac{2.303 \times 3}{0.693} = 10$$



a

$$a-x \quad \frac{x}{n} \quad t_{1/2} = 24 \text{ min}$$

$$\text{at } t = 48 \quad a-x = \frac{x}{n}$$

$$a = \frac{(1+n)x}{n}; \frac{na}{1+n} = x$$

$$\frac{\ln 2}{24} = \frac{1}{48} \ln \frac{a}{a - \frac{na}{(1+n)}}$$

$$4 = \frac{a(1+n)}{a} \Rightarrow n = 3.$$

6. We know,  $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$   
99.9% completion  
 $a = 100$   
 $a - x = (100 - 99.9) = .10$

Then  $t = \frac{2.303}{k} \log \left( \frac{100}{.10} \right)$

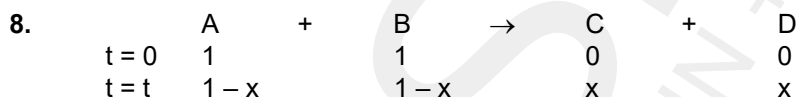
$$t = 2.303 \times 3 \times \left[ \frac{1}{k} \right]; \quad t = 6.9 \times t_{av}$$



$$\frac{-d[A]}{dt} \propto [A] \text{ (1st order)}$$

$$[A]_t \propto t \text{ (zero order)}$$

$$\frac{1}{[A]_t} \propto t \text{ (2nd order)}$$

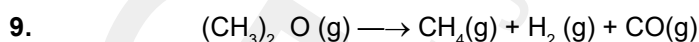


$$r = k[A]^{1/2} [B]^{1/2}$$

$$\Rightarrow \frac{dx}{dt} = k(1-x)^{1/2} (1-x)^{1/2}$$

or  $\frac{dx}{dt} = k(1-x)$

$$\Rightarrow t = \frac{1}{k} \ln \left( \frac{1}{1-x} \right); \quad t = \frac{2.303}{2.303 \times 10^{-2}} \log \left( \frac{1}{0.1} \right) = 100 \text{ sec.}$$



$t=0$	$a$	0	0	0	$a \propto P_0 = 312 \text{ mm}$
$t=400 \text{ sec}$	$a-x$	$x$	$x$	$x$	$a+2x \propto p_{400} = 412 \text{ mm}$
$t=1200 \text{ sec}$	$a-y$	$y$	$y$	$y$	$a+2y \propto p_{1200} = 560 \text{ mm}$
$t = \infty$	0	$a$	$a$	$a$	$3a \propto P_\infty = 935 \text{ mm}$

$$Kt = \ln \left( \frac{C_0}{C_t} \right) = \ln \left( \frac{a}{a-x} \right) \Rightarrow Kt = \ln \left( \frac{p_\infty - p_0}{p_\infty - p_t} \right)$$

$$(t = 400 \text{ sec}) \quad K_1 = \frac{1}{400} \ln \left( \frac{935 - 312}{935 - 412} \right) = \frac{1}{400} \ln \left( \frac{623}{523} \right) \text{ sec}^{-1} = 0.175 \times \frac{1}{400}$$

$$(t = 1200 \text{ sec}) \quad K_2 = \frac{1}{1200} \ln \left( \frac{935 - 312}{935 - 560} \right) = \frac{1}{1200} \ln \left( \frac{623}{375} \right) \text{ sec}^{-1} = 0.5076 \times \frac{1}{1200}$$

$$t_{1/2} = \frac{\ln 2}{\frac{k_1 + k_2}{2}} = \frac{2 \ln 2}{(k_1 + k_2)} = \frac{1584 + 1638}{2} = 1611 \text{ sec.}$$

