

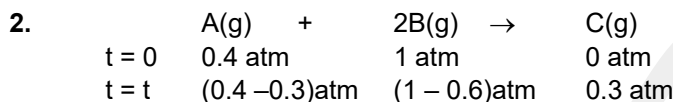
DPP No. # 51

1.  $k t = \ln \left( \frac{C_0}{C_t} \right)$

	$2 \text{N}_2\text{O}_5$	$\longrightarrow$	$2\text{N}_2\text{O}_4$	$+$	$\text{O}_2$
t=0	200 cm <sup>3</sup>		0		0
t=t	20 cm <sup>3</sup>		180cm <sup>3</sup>		90 cm <sup>3</sup>
t=∞	0		200cm <sup>3</sup>		100 cm <sup>3</sup>

Initial volume of  $\text{N}_2\text{O}_5 = 200 \text{ cm}^3$ .  
because Max. volume of  $\text{O}_2 = 100 \text{ cm}^3$ .

$$\therefore K \times 500 = \ln \left( \frac{200}{20} \right) \Rightarrow k = \frac{\ln 10}{500} = \frac{2.303}{500}$$



Since reaction is elementary.

So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient

$$\text{Rate} = K [\text{A}] [\text{B}]^2$$

$$\text{Rate}_{(\text{Initial})} = K [0.4] [1]^2$$

$$\text{Rate}_{(\text{after } t = t)} = K [0.1][0.4]^2$$

$$\frac{R_{(t=t)}}{R_{(t=0)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]} = \frac{1}{25}$$

3. We know

$$\text{Rate} = k [\text{conc.}]$$

Given Rxn catalysed by HA and HB

$$\text{Rate constant } k_A = k_1 [\text{H}^+]_A$$

$$k_B = k_1 [\text{H}^+]_B$$

Then relative strength of acids A and B is

$$\frac{k_A}{k_B} = \frac{[\text{H}^+]_A}{[\text{H}^+]_B} \quad \frac{2}{1} = \frac{[\text{H}^+]_A}{[\text{H}^+]_B} = \text{strength of } \frac{[\text{AcidA}]}{[\text{AcidB}]}$$



Let initial pressure  $P_0$                       0                      0

After 10 min.  $(P_0 - x)$                       2x                      x

After long time  $(t \rightarrow \infty)$  0                      2P<sub>0</sub>                      P<sub>0</sub>

as per given  $(P_0 - x) + 2x + x + \text{vaour pressure of H}_2\text{O} = 188$

$$P_0 + 2x = 160 \text{ and } 3P_0 + 28 = 388$$

so,  $P_0 = 120$  and  $x = 20$  torr

$$k = \frac{1}{t} \ln \left( \frac{P_0}{P_0 - x} \right)$$

$$\Rightarrow \frac{1}{10} \ln \left( \frac{120}{100} \right) = \frac{1}{10} \times (\ln 4 + \ln 3 - \ln 10) = 0.02 \text{ min}^{-1} = 1.2 \text{ hr}^{-1}$$

5.  $Kt = \ln \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right)$

$$K = \frac{1}{84} \ln \left( \frac{-10 - 50}{-10 - 20} \right) = \frac{1}{84} \ln (2)$$

Solution is optically inactive i.e. optical rotation is zero.

$$\left( \frac{1}{84} \ln 2 \right) t = \ln \left( \frac{-10 - 50}{-10 - 0} \right) \Rightarrow t = 84 \frac{\ln 6}{\ln 2} = 218$$

6.  $A \rightarrow$  Products.

$$t_{1/2} = [\text{conc.}]^{1-n} \quad n \rightarrow \text{order of reaction.}$$

$$\frac{100}{50} = \left(\frac{0.1}{0.025}\right)^{1-n}$$

$$\Rightarrow 2 = 2 - 2n$$

$$\Rightarrow 2n = 1.$$

$$\Rightarrow n = \frac{1}{2}.$$

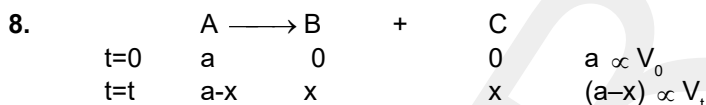
$$\text{order of reaction is } \frac{1}{2}.$$

$$\Rightarrow t_{1/2} = 100\sqrt{10} \text{ min for } [A_0] = 1M.$$

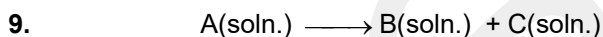
7. Slope =  $\frac{(1-1.75)}{25-0} = -0.03$

$$k = -2.303 (\text{slope}) \text{ min}^{-1}$$

$$= -2.303 (-0.03) \text{ min}^{-1} = 0.06909 \text{ min}^{-1} = 4.14 \text{ hr}^{-1} \approx 4 \text{ hr}^{-1}$$



$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t} \ln\left(\frac{V_0}{V_t}\right)$$



t=0	a	0	0
t=t	a-x	x	x
t=∞	0	a	a

Let n-factor of A, B & C are  $n_1, n_2$  &  $n_3$  & that of reagent is n & molarity of reagent is M

At  $t=0$ ,

meq. of A = meq. of reagent

$$n_1 \times a = M \times n \times V_0 \quad \dots\dots (i)$$

At  $t=t$ ,

meq. of reagent = meq. of A + meq of B + meq of C

$$MV_t n = (a-x)n_1 + xn_2 + xn_3 \quad \dots\dots (ii)$$

At  $t=\infty$ ,

meq. of reagent = meq of B + meq of C

$$MV_\infty n = an_2 + an_3 \quad \dots\dots (iii)$$

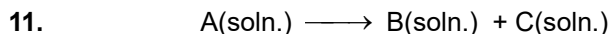
From (iii) & (i)

$$(n_2 + n_3) = \frac{MV_\infty n}{a} \quad \& \quad n_1 = \frac{MV_0 n}{a}$$

$$\Rightarrow MV_t n = (a-x) \frac{MV_0 n}{a} + x \frac{MV_\infty n}{a} \Rightarrow \frac{a}{a-x} = \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

$$Kt = \ln \frac{a}{a-x} \Rightarrow K = \frac{1}{t} \ln \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

10. Same as of question 9.



t=0	a	0	0
t=t	a-x	x	x
t=∞	0	a	a

Let  $\alpha$ ,  $\beta$  &  $\gamma$  are specific rotation of A, B & C respectively.

At t=0,  $r_0 = a\alpha$  ..... (i)

At t=t,  $r_t = (a-x)\alpha + x\beta + x\gamma$  ..... (ii)

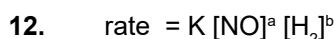
At t=∞,  $r_\infty = a\beta + a\gamma$  ..... (iii)

From (i) & (iii)

$$\alpha = \frac{r_0}{a} \quad \& \quad (\beta + \gamma) = \frac{r_\infty}{a}$$

Putting in (ii)

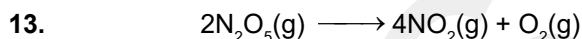
$$r_t = (a-x) \frac{r_0}{a} + \frac{r_\infty}{a} x \Rightarrow \frac{a}{a-x} = \frac{r_\infty - r_0}{r_\infty - r_t} \Rightarrow Kt = \ln \frac{a}{a-x} \Rightarrow k = \frac{1}{t} \ln \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right)$$



$$\frac{r_1}{r_2} = \frac{1.5}{0.25} = \left( \frac{359}{152} \right)^a \Rightarrow \frac{6}{1} = (2.36)^a \Rightarrow a = 2$$

$$\frac{r_3}{r_4} = \frac{1.6}{0.79} = \left( \frac{289}{147} \right)^b \Rightarrow 2 = (1.966)^b \Rightarrow b = 1$$

order of the reaction = 1 + 2 = 3



t = 0	a	0	0	
t = t	a - x	2x	$\frac{x}{2}$	$\left( a + \frac{3x}{2} \right) \propto P_t$

t = ∞	0	2a	$\frac{a}{2}$	$\frac{5a}{2} \propto P_\infty$
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$$kt = \ln \left( \frac{a}{a-x} \right)$$

$$a \propto \frac{2}{5} P_\infty \quad \& \quad x \propto \frac{2}{3} \left( P_t - \frac{2}{5} P_\infty \right)$$

$$k = \frac{1}{t} \ln \left( \frac{\frac{2}{5} P_\infty}{\frac{2}{5} P_\infty - \frac{2}{3} \left( P_t - \frac{2}{5} P_\infty \right)} \right) = \frac{1}{t} \ln \left( \frac{3P_\infty}{5(P_\infty - P_t)} \right)$$

**DPP No. # 52**

1.  $\frac{k_t}{k_0} = (TC)^{t-0/10}$

Taking log gives  $\log_e k_t - \log_e k_0 = \frac{t}{10} \log_e (TC) \Rightarrow \ln k_t = \ln k_0 + \left( \frac{\ln (TC)}{10} \right) t$

Comparison indicates  $\frac{\ln (TC)}{10} = 0.0693 \Rightarrow \ln (TC) = 0.693 \Rightarrow TC = 2$

2.  $k_1 = Ae^{-E_a/RT_1}$  &  $k_2 = Ae^{-E_a/RT_1}$

$k'_1 = Ae^{-E_a/RT_2}$  &  $k'_2 = Ae^{-E_a/RT_2}$

$$\Rightarrow \frac{k'_1}{k_1} = e^{\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \& \quad \frac{k'_2}{k_2} = e^{\frac{E'_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Since  $E_a > E'_a \Rightarrow \frac{k'_1}{k_1} > \frac{k'_2}{k_2}$

3. As temperature increases,  $K_A$  &  $K_B$  tends to A.  
So, they are equal in magnitude.

4. According to Arrhenius equation

$$k = A \cdot e^{-E_a/RT}$$

At temp., T the equation will be

$$k' = A \cdot e^{-E'_a/RT}$$

Given  $E'_a = 4.15 \text{ kJ mol}^{-1}$

..... in the presence of a catalyst

$$\therefore \frac{k'}{k} = e^{(E_a - E'_a)/RT}$$

Given  $k' = (1 + 1.718)k = 2.718k = ek$

Hence  $e = e^{(E_a - E'_a)/RT}$

or  $E_a - E'_a = RT$

or  $E_a = E'_a + RT = 4.15 + 8.3 \times 500 \times 10^{-3} = 8.3 \text{ kJ mol}^{-1}$ .

5. Fraction of molecules which cross over the barrier

$$= e^{-\frac{E_a}{RT}} = e^{-\frac{18428}{8 \times 1000}} = e^{-2.303} = e^{-\ln 10} = \frac{1}{10}$$

6.  $\log k = -\frac{E_a}{2.303 R} \frac{1}{T} + \text{constant}$

$$= -\frac{E_a}{2.303 R} \times 10^{-3} \times \frac{10^3}{T} + \text{constant}$$

thus, slope of graph will be  $-\frac{E_a \times 10^{-3}}{2.303 R} = -\frac{4}{0.4}$

$$\Rightarrow E_a = 2.303 \times 1.98 \times 10^4 = 45600 \text{ cal}$$



$t = 0$	800	-	-	
$t = 10 \text{ minutes}$ ,	$800 - 4p$	$p$	$2p$	
	$800 - p = 650$	$\therefore p = 150$	Pressure of A = 200, so	
$\therefore$	$2 \times t_{1/2} = 10 \text{ minutes}$	$\Rightarrow$	$t_{1/2} = 5 \text{ minutes}$	

8. As only A is optically active. So conc. of A at  $t = 20 \text{ min} \propto 40^\circ$

While concentration of A at  $t = 50 \text{ min} \propto 10^\circ$

so  $t_{1/2} = 15 \text{ min}$ .

So volume consumed of  $H_2O_2$  at  $t = 15 \text{ min} = t_{1/2}$ , is according to 50% production of B.  
at  $t = 60 \text{ min}$ . production of B = 94.75% (four half lives)

So volume consumed =  $(40 \text{ ml}) + \left(\frac{40}{2}\right) \text{ ml} + \left(\frac{40}{4}\right) \text{ ml} + \left(\frac{40}{8}\right) \text{ ml} = 75 \text{ ml ans.}$

9.  $S_1$   $k = Ae^{-E_a/RT}$   
 $S_2$  rate =  $k_n [C]^n \Rightarrow \ln \text{rate} = \ln k_n + n \ln C$   
 $S_3$   $A \rightarrow \text{product}$

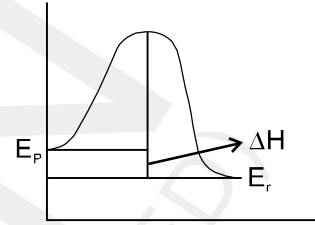
$$a \xrightarrow{\frac{1}{2} \text{hr}} \frac{a}{2} \xrightarrow{\frac{1}{2} \text{hr}} \frac{a}{4} \xrightarrow{\frac{1}{2} \text{hr}} \frac{a}{8} \Rightarrow \text{1st order reaction.}$$

10.  $K_f = A_f e^{-E_{a_f}/RT}$ ;  $K_b = A_b e^{-E_{a_b}/RT}$ .

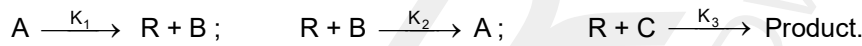
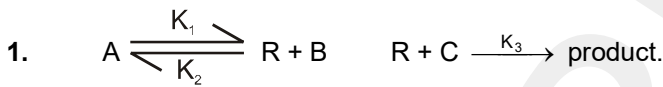
$$K_c = \frac{K_f}{K_b} = \frac{A_f}{A_b} e^{-(E_{a_f} - E_{a_b})/RT}$$

$$K_c = \frac{4 \times 10^{-4}}{2 \times 10^{-3}} e^{-(167000 - 180000) / 8.314 \times 300}$$

$$K_c = 2 \times 10^{-1} \times 183 = 36.6$$



### DPP No. # 53



$$\frac{d[A]}{dt} = -k_1[A] + K_2[R][B] \quad \dots\dots (i)$$

$$\frac{d[R]}{dt} = K_1[A] - K_2[R][B] - K_3[R][C] \quad \dots\dots (ii)$$

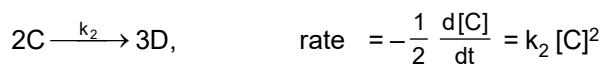
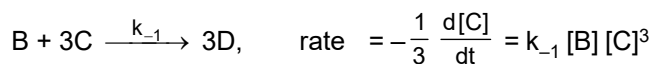
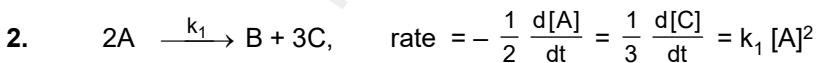
At steady state  $\frac{d[R]}{dt} = 0$

$$[R] = \frac{K_1[A]}{K_2[B] + K_3[C]}$$

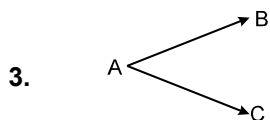
$$\frac{d[A]}{dt} = -K_1[A] + \frac{K_2[B] K_1[A]}{K_2[B] + K_3[C]} = \frac{-K_1[A]\{K_2[B] + K_3[C]\} + K_2[B]K_1[A]}{K_2[B] + K_3[C]}$$

$$\frac{d[A]}{dt} = \frac{-K_1[A]K_3[C]}{K_2[B] + K_3[C]}$$

$$\Rightarrow \frac{d[a-x]}{dt} = \frac{-K_1[A]K_3[C]}{K_2[B] + K_3[C]} \Rightarrow \frac{dx}{dt} = \frac{K_1[A]K_3[C]}{K_2[B] + K_3[C]} = \frac{K_1[A]}{1 + \frac{K_2[B]}{K_3[C]}}$$



$$\frac{d[C]}{dt} = 3k_1 [A]^2 - 3k_{-1} [B][C]^3 - 2k_2 [C]^2$$



$$\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{0.4}{0.6} = \frac{2}{3}$$

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

$$\Rightarrow k_{\text{eff.}} = k_1 + k_2$$

$$\frac{\ln 2}{(t_{1/2})_{\text{overall}}} = k_1 + \frac{3}{2} k_1 = \frac{5}{2} k_1$$

$$\Rightarrow \frac{\ln 2}{12} = \frac{5}{2} \frac{\ln 2}{(t_{1/2})_{A \rightarrow B}}$$

$$\Rightarrow (t_{1/2})_{A \rightarrow B} = 30 \text{ hrs.}$$

4.  $[B] + [C] = 2 \text{ M}$

$$\frac{[B]}{[C]} = \frac{2k_1}{3k_2} = \frac{4}{9}$$

$$\Rightarrow \frac{4}{9} [C] + [C] = 2 \text{ M} \quad \Rightarrow \quad \frac{13}{9} [C] = 2 \quad \Rightarrow \quad [C] = \frac{18}{13} \text{ M}$$

$$\therefore [B] = 2 - [C] = 2 - \frac{18}{13} = \frac{8}{13} \text{ M.}$$

5.  $\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{k_1[\text{CH}_4][\text{Br}_2]}{1 + k_2[\text{HBr}]/[\text{Br}_2]}$

At initial stages ( $[\text{HBr}] \approx 0$ )

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = K_1 [\text{CH}_4] [\text{Br}_2] \longrightarrow \text{2nd order}$$

At final stages ( $[\text{Br}_2] \approx 0$ )

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{K_1[\text{CH}_4][\text{Br}_2]^2}{[\text{Br}_2] + K_2[\text{HBr}]} = \frac{K_1[\text{CH}_4][\text{Br}_2]^2}{K_2[\text{HBr}]} \longrightarrow \text{2nd order}$$

6.  $k_1 = k_2$  (Since  $[C] = [D]$  at all the times)

$$\Rightarrow \frac{2}{3} \text{rd of A has reacted for } [A] = [C] = [D]$$

$$\therefore k_1 + k_2 = \frac{1}{t} \ln \frac{[A]_0}{\frac{1}{3}[A]_0}$$

$$\Rightarrow t = \frac{1}{k_1 + k_2} \ln 3 = \frac{1}{2k_1} \ln 3 = \frac{1}{2k_2} \ln 3$$

7. Using the r.d.s. approximation method

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3 [\text{ClCO}]^1 [\text{Cl}_2]^1$$

but  $K_1 = \frac{[Cl]^2 [M]}{[Cl_2] [M]}$  and  $K_2 = \frac{[ClCO] [M]}{[Cl] [CO] [M]}$

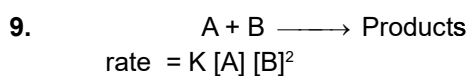
$\Rightarrow [ClCO] = K_2 [Cl] [CO]$  and  $[Cl] = \sqrt{K_1} \sqrt{[Cl_2]}$

$\therefore \frac{d[Cl_2CO]}{dt} = k_3 K_2 [Cl] [CO] [Cl_2]$   
 $= k_3 K_2 \sqrt{K_1} \sqrt{[Cl_2]} [CO] [Cl_2]$   
 $= k_3 K_2 \sqrt{K_1} [Cl_2]^{3/2} [CO]$

comparison with the rate law given shows that

$$k = k_3 K_2 \sqrt{K_1}$$

8.  $\frac{dC_D}{dt} = K_1 C_A + K_3 C_B - K_2 C_D - K_4 C_D$



$r_0 = K [1] [1]^2 = 10^{-2} \Rightarrow K = 10^{-2} \text{ M}^{-2} \text{ S}^{-1} \Rightarrow r = 10^{-2} \left[ \frac{1}{2} \right] \left[ \frac{1}{2} \right]^2 = 1.25 \times 10^{-3} \text{ Ms}^{-1}$

10. 50% completion in 50 minutes.  
 73% completion in 100 minutes.  
 Checking for zero order :

$$t_{1/2} = \frac{C_0}{2K}$$

$53 \text{ min.} = \frac{200}{2K} \Rightarrow K = \frac{100}{53} \text{ min}^{-1}$

$C_t = C_0 - 2 K t$

$C_t = 200 - \frac{200}{53} \times 100 = - \text{ve.}$

So, it is not zero order.

For I<sup>st</sup> order :

$t_{1/2} = \frac{\ln 2}{K} \Rightarrow K = \frac{\ln 2}{53} = \frac{0.693}{53}$

$Kt = \ln \left( \frac{a_0}{a} \right) \Rightarrow \frac{\ln 2}{53} \times 100 = \ln \left( \frac{a_0}{a} \right)$

$\frac{a_0}{a} = 3.6972 \Rightarrow a = \frac{200}{3.6972} = 54.1 \text{ mm of Hg.}$

Completion of reaction =  $\frac{a_0 - a}{a_0} \times 100 = 73\%$ .

So, it is I<sup>st</sup> order.

(b) In I<sup>st</sup> order reaction, % completion is independent an initial concentration so, 73% completion takes place.

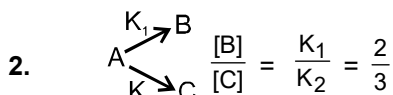
DPP No. # 54

1. We have,

$$\frac{[B]_t}{[C]_t} = \frac{4k_1}{3k_2} = \frac{16}{9} \quad \text{so,} \quad \frac{k_1}{k_2} = \frac{4}{3}$$

$$\text{Now, } k = k_1 + k_2 = [2 \times 10^{-3} + \frac{3}{4} \times 2 \times 10^{-3}] \text{ sec}^{-1}$$

$$= \frac{7}{2} \times 10^{-3} \text{ sec}^{-1} = \frac{7 \times 10^{-3} \times 60}{2} \text{ min}^{-1} \quad \text{so, } T_{1/2} = \frac{\ln 2}{7 \times 30 \times 10^{-3}} \text{ min} = \frac{693}{7 \times 30} = 3.3 \text{ min.}$$



$$K_1 = 4 \times 10^{-4}$$

$$K_2 = \frac{3}{2} \times 4 \times 10^{-4} = 6 \times 10^{-4} \text{ sec}^{-1}.$$

3.  $t_{1/2} = \frac{0.693}{K_1 + K_2} = \frac{0.693}{10^{-3}} = 693 \text{ sec.}$

4.  $t = \frac{1}{K_1 + K_2} = 10^3$

5.  $t = \frac{2.303}{K} \log \left( \frac{C_0}{C_0 - X} \right) \Rightarrow 2303 = \left( \frac{2.303}{10^{-3}} \right) \log \left( \frac{C_0}{C_0 - 5} \right)$

$$\log \frac{C_0}{C_0 - 5} = 1 \Rightarrow \frac{C_0}{C_0 - 5} = 10 \Rightarrow 9C_0 = 50, C_0 = 50/9.$$

6. Rate =  $K [C]$   
 $= 10^{-3} \times [C_0 - x]$   
 $= 10^{-3} \times [50/9 - 5]$   
 $= 10^{-3} \times \frac{5}{9} = 5.55 \times 10^{-4}$

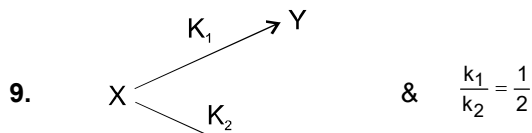
7.  $K = \left( \frac{1}{C_t} - \frac{1}{C_0} \right) \times \frac{1}{t} = \frac{2-1}{5} = \frac{4-1}{15} = \frac{8-1}{35} = \frac{1}{5} = \text{constant}$

8. % of reaction molecules which are =  $e^{-E_a/RT} \times 100$   
able to cross potential barrier  
 $\Rightarrow e^{-E_a/RT} \times 100 = 1.5 \times 10^{-4}$   
 $\Rightarrow e^{-E_a/RT} \times 100 = 1.5 \times 10^{-6}$   
 $\Rightarrow e^{-E_a/2 \times 300} = 1.5 \times 10^{-6} \Rightarrow E_a \text{ (cal)} = 8014.5 \text{ cal.}$   
 $K = Ae^{-E_a/RT}$

$$\frac{dK}{dT} = Ae^{-E_a/RT} \left( \frac{-E_a}{R} \times \frac{-1}{T^2} \right)$$

$$\frac{dK}{dT} = K \frac{E_a}{RT^2} \Rightarrow 0.2 = K \frac{E_a}{2 \times (325)^2}$$

$$\Rightarrow K = \frac{0.2 \times 2 \times (325)^2}{E_a(\text{cal})} = 5.25 \text{ S}^{-1}$$



$$[X]_t = ae^{-(k_1+k_2)t}$$

$$[Y]_t = \frac{k_1 a}{k_1+k_2} (1-e^{-(k_1+k_2)t}) \quad \& \quad [Z]_t = \frac{k_2 a}{k_1+k_2} (1-e^{-(k_1+k_2)t})$$

At  $t = 30$  min.,

$$[X]_t = [Z]_t$$

$$ae^{-(k_1+k_2) \times 30} = \frac{k_2 a}{k_1+k_2} (1-e^{-(k_1+k_2) \times 30})$$

$$\Rightarrow \text{on solving, } (k_1 + k_2) = \frac{1}{30} \ln \frac{5}{2} \quad \dots\dots (i)$$

10. (A)  $\alpha = \frac{x}{a} = \frac{C_{A_0} - C_{A_t}}{C_{A_0}} = 1 - \frac{C_{A_t}}{C_{A_0}}$

$$\therefore C_{A_t} = C_{A_0} e^{-Kt} \Rightarrow \alpha = 1 - \frac{C_{A_0} e^{-Kt}}{C_{A_0}} = 1 - e^{-Kt}$$

$$(B) \frac{1}{C_{A_t}} - \frac{1}{C_{A_0}} = Kt \Rightarrow C_{A_t} = \frac{C_{A_0}}{C_{A_0} Kt + 1} \Rightarrow \alpha = \frac{C_{A_0}}{C_{A_0} Kt + 1} = \frac{C_{A_0} Kt}{C_{A_0} Kt + 1}$$

$$(C) \alpha = 1 - \frac{C_{A_t}}{C_{A_0}} \quad \therefore C_{A_t} = C_{A_0} - Kt$$

$$\alpha = 1 - \frac{C_{A_0} - Kt}{C_{A_0}} = \frac{Kt}{C_{A_0}}$$

$$(D) \alpha = 1 - \frac{C_{A_t}}{C_{A_0}}$$

**DPP No. # 55**

- (a) (A) Cryolite is  $Na_3AlF_6$ ; (B) Carnallite is  $MgCl_2 \cdot KCl \cdot 6H_2O$ .  
 (C) Malachite is  $CuCO_3 \cdot Cu(OH)_2$ ; (D) Cassiterite is  $SnO_2$

(b) Bauxite -  $Al_2O_3 \cdot 2H_2O$  - Al is extracted by Hall's process  
 Carnallite -  $MgCl_2 \cdot KCl \cdot 6H_2O$   
 Malachite -  $CuCO_3 \cdot Cu(OH)_2$   
 Galena - PbS
- (a)  $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} CuO + CO_2 + H_2O$ ;  $CuO + C \longrightarrow Cu + CO$
- (a) Calamine is  $ZnCO_3$ .  
 (b) Haematite is  $Fe_2O_3$  which has magnetic property.
- (a) Froth floatation process is used for the concentration of the sulphide ores of zinc, copper, lead, etc.  
 (b) Conversion of carbonate ore in to oxide on heating in absence of air is called calcination.
- (a) Extraction of silver is not a high temperature operation like most metals and is done by the cyanide process in water solution.  
 (b)  $CaCO_3 \longrightarrow CaO + CO_2$ ;  $CaO + SiO_2 \longrightarrow CaSiO_3$
- (a)  $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

8. (A)  $N_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$   
 B.O. =  $\frac{10-4}{2} = 3$ ;  $n = 0$  (D)  
 $N_2^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1$   
 B.O. =  $\frac{9-4}{2} = 2.5$ ;  $n = 1$  (P)
- (B)  $O_2^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^0$   
 B.O. =  $\frac{10-5}{2} = 2.5$ ;  $n = 1$  (P)  
 $O_2^{2+} = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^0 = \pi^* 2p_y^0$   
 B.O. =  $\frac{10-4}{2} = 3$ ;  $n = 0$  (D)
- (C)  $B_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 = \pi 2p_y^1$   
 B.O. =  $\frac{6-4}{2} = 1$ ;  $n = 2$  (P)  
 $B_2^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^1 \sigma 2p_z^0$   
 B.O. =  $\frac{5-4}{2} = 1/2$ ;  $n = 1$  (P)
- (D)  $NO^- = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$   
 B.O. =  $\frac{10-6}{2} = 1.0$ ;  $n = 2$  (P)  
 $NO = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^0$   
 B.O. =  $\frac{10-5}{2} = 2.5$ ;  $n = 1$  (P).

**DPP No. # 56**

- Aluminium is extracted by Hall-Heroult process (electrolytic reduction).
- Serpeck's method is  
 $Al_2O_3 \cdot 2H_2O + 3C + N_2 \xrightarrow{1800^\circ C} 2AlN + 3CO + 2H_2O$   
 $2AlN + 3H_2O \longrightarrow Al(OH)_3 \downarrow + NH_3$   
 $2Al(OH)_3 \xrightarrow{1473K} Al_2O_3 + 3H_2O$
- $PbS + O_2 \longrightarrow PbO + SO_2$   
 $PbS + 2O_2 \longrightarrow PbSO_4$
- Carbon monoxide is better reducing agent than carbon below 983 K.
- SRP zinc = -0.76 ; SRP iron = -0.44 ; SRP copper = +0.34 (highest)  
 Hence only copper deposits, others do not.
- Increasing voltage would cause deposition of  $Fe^{+2}$  and  $Zn^{+2}$  also to occur.
- Water (pure) is a poor electrical conductor.
- (A)  $CuFeS_2$ ;  $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$ ;  $Cu_2O + C \longrightarrow 2Cu + CO$   
 (B)  $PbS$ ;  $PbS + 2PbO \longrightarrow 3Pb + SO_2$ ;  $PbO + C \longrightarrow Pb + CO$ ;  $PbO + CO \longrightarrow Pb + CO_2$   
 (C)  $Ag_2S$ ; Cyanide process, leaching with alkali metal cyanide followed by displacement with zinc dust.  
 (D)  $CuCO_3$ ;  $Cu(OH)_2$ ; Calcination  $\longrightarrow CuO + C \longrightarrow Cu + CO$

**DPP No. # 57**

2. (D)  $Al_2O_3$  is a poor conductor of electricity and having very high melting point. so to increase the conductivity  $Na_3AlF_6$  is added and to decreases the melting point  $Na_3AlF_6$  and  $CaF_2$ , are added so that melting point of electrolyte comes to around  $930^\circ C$ .
5. In the Bayer's process pure aluminium oxide is obtained from the bauxite ore. A low melting metal like tin can be refined by liquation method. Electrolysis is used in the refining of gold.
7. (A) In steel making. pure  $O_2$  is purged into molten iron, where all impurities like C, S, Si, Mn converted into oxides then forming as slag, which is removed after wards.
8. (a)  $\rightarrow$  van – Arkel method for Zr – Hg  
 $\rightarrow$  Based on volatile nature of halides of methods.

9. for  $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \Delta S = +ve$

10.  $\Delta G = -439 - (-941) = +502 \text{ KJ/mol}^{-1}$  so reaction will non-spontaneous

12. Force of attraction =  $\frac{KZe \times 2e}{r_1^2} = \frac{2KZe^2}{r_1^2}$  ; Force of repulsion =  $\frac{mv^2}{r_1} = \frac{2m_e \times v^2}{r_1}$

$$\therefore \frac{2KZe^2}{r_1^2} = \frac{2m_e \times v^2}{r_1}$$

$$\text{or } r_1 = \frac{KZe^2}{m_e v^2} = \frac{KZe^2}{m_e \times v^2} = \frac{KZe^2}{m_e \times \frac{n^2 h^2}{4\pi^2 m^2 r_1^2}} \quad \left[ \because mvr = \frac{nh}{2\pi} \text{ or } v = \frac{nh}{2\pi mr} \right]$$

$$\text{or } r_1 = \frac{KZe^2 \times 4\pi^2 \times 4m_e^2 \times r_1^2}{m_e \times n^2 h^2} \quad \text{or } r_1 = \frac{n^2 h^2}{4\pi^2 m_e KZe^2 \times 4} = \frac{r}{4}$$

$$\text{or } \frac{r_1}{r} = \frac{1}{4}$$

13.  $v_1 = \frac{nh}{2\pi mr} = \frac{nh}{2\pi \times 2m_e \times r_1} = \frac{nh}{2\pi \times 2m_e \times \frac{r}{4}} = 2 \times \frac{nh}{2\pi m_e r} = 2 \times v \quad \text{or} \quad \frac{v_1}{v} = 2.$

14.  $TE = -\frac{1}{2} KE = -\frac{1}{2} mv^2 = -\frac{1}{2} \times 2m_e \times \frac{n^2 h^2}{\pi^2 \times m_e^2 \times r^2} = -\frac{1}{2} \times 2m_e \times \frac{n^2 h^2}{\pi^2 \times m_e^2 \times \frac{n^4 h^4}{4^2 \pi^4 m_e^2 K^2 Z^2 e^4}}$

$$TE = -\frac{16 \times \pi^2 \times K^2 \times e^4 \times Z^2 \times m_e}{n^2 h^2}$$

$$TE = \left[ -\frac{2 \times \pi^2 \times K^2 \times e^4 \times Z^2 \times m_e}{n^2 h^2} \right] \times 8$$

$$E_1 = E \times 8 \quad \text{or} \quad \frac{E_1}{E} = 8.$$

### DPP No. # 58

- (a)  $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$

(b) Matte mostly contains  $\text{Cu}_2\text{S}$  and a little  $\text{FeS}$ .
- (a)  $\text{Ag} + 2\text{CN}^- \longrightarrow [\text{Ag}(\text{CN})_2]^-$  ;  $2[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag} \downarrow$

(b) Highest temperature 2170 K is found in the lower most part of the blast furnace, where carbon burns to form  $\text{CO}_2$ .  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
- (a) Cathode :  $\text{Al}^{3+} (\text{melt}) + 3\text{e}^- \longrightarrow \text{Al}$

Anode :  $\text{C} + \text{O}^{2-} (\text{melt}) \longrightarrow \text{CO} + 2\text{e}^-$  ;  $\text{C} + 2\text{O}^{2-} (\text{melt}) \longrightarrow \text{CO}_2 + 4\text{e}^-$

(b) Mg being strong reducing agent cannot be obtained by any chemical reduction method.
- (a)  $\text{O}^{2-} (\text{melt}) \longrightarrow \frac{1}{2} \text{O}_2 (\text{g}) + 2\text{e}^- (\text{melt})$

(b) Zinc blende or sphalerite is  $\text{ZnS}$ .
- (a) (A)  $\text{Al}_2\text{O}_3 (\text{s}) + 2\text{NaOH} (\text{aq}) + 2\text{H}_2\text{O} (\ell) \xrightarrow{\Delta} 2\text{NaAlO}_2 (\text{aq}) + 3\text{H}_2\text{O} (\ell)$

(B)  $\text{Ag}_2\text{S} (\text{s}) + 4\text{CN}^- (\text{aq}) \longrightarrow [\text{Ag}(\text{CN})_2]^- (\text{aq}) + \text{S}^{2-} (\text{aq})$

(C)  $\text{MgCl}_2$  (anhydrous) – No leaching is required.

(D)  $\text{Cu}_2\text{O} (\text{s}) + 4\text{H}_2\text{SO}_4 + \text{O}_2 \longrightarrow 4\text{CuSO}_4 + 4\text{H}_2\text{O}$

(b) It is extracted by the electrolysis of alumina mixed with molten cryolite.
- $\text{MgCl}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{Cl}^-$

At cathode :  $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$

At anode :  $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$

$4\text{Ag} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4[\text{Ag}(\text{CN})_2]^- + 4\text{OH}^-$

$2[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow 2\text{Ag} \downarrow + [\text{Zn}(\text{CN})_4]^{2-}$
- All are correctly matched.
- $\text{Ag}_2\text{S} + 4\text{KCN} \xrightleftharpoons{\text{O}_2} 2\text{K}[\text{Ag}(\text{CN})_2] + \text{K}_2\text{S}$

$4\text{K}_2\text{S} + 5\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{K}_2\text{SO}_4 + 4\text{KOH} + 2\text{S} \downarrow$
- Statement-1 : Haematite :  $\text{Fe}_2\text{O}_3$ , limonite :  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and magnetite :  $\text{Fe}_3\text{O}_4$ .

Statement-2 :  $\text{Fe}_2\text{O}_3 + \text{CO} \xrightarrow{\Delta} 2\text{Fe}_3\text{O}_4 + \text{CO}_2$  ;  $\text{Fe}_3\text{O}_4 + \text{CO} \xrightarrow{\Delta} 3\text{Fe} + 4\text{CO}_2$
- Haematite :  $\text{Fe}_2\text{O}_3$  ; Limonite :  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  ; Magnetite :  $\text{Fe}_3\text{O}_4$

Magnesite :  $\text{MgCO}_3$  ; Cuprite :  $\text{Cu}_2\text{O}$  ; Argentite :  $\text{Ag}_2\text{S}$

Bauxite :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  ; Sphalerite :  $\text{ZnS}$  ; Zincite :  $\text{ZnO}$
- $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 2\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{NaAlO}_2 + 3\text{H}_2\text{O}$  ;  $\text{Ag}_2\text{S} + 2\text{CN}^- \longrightarrow [\text{Ag}(\text{CN})_2]^- + \text{S}^{2-}$

$\text{Au} + 2\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow [\text{Au}(\text{CN})_2]^- + 4\text{OH}^-$  ;  $\text{CuFeS}_2 \longrightarrow \text{No leaching}$

$\text{PbS} \longrightarrow \text{No leaching}$  ;  $\text{MgCl}_2 \longrightarrow \text{No leaching}$  ;  $\text{FeCO}_3 \longrightarrow \text{No leaching}$

$2\text{Cu}_2\text{O} (\text{s}) + 4\text{H}_2\text{SO}_4 (\text{aq}) + \text{O}_2 (\text{g}) \longrightarrow 4\text{CuSO}_4 (\text{aq}) + 4\text{H}_2\text{O} (\ell)$  ;  $\text{HgS} \longrightarrow \text{No leaching}$
- Cryolite is  $3\text{NaF} \cdot \text{AlF}_3$  or  $\text{Na}_3[\text{AlF}_6]$ . It gives that coordination number of aluminium is six. It can expand its covalency by using empty d-orbitals.

### DPP No. # 59

- (a)  $\text{Ag/Au} + 8\text{CN}^- (\text{aq}) + 2\text{H}_2\text{O} (\text{aq}) + \text{O}_2 (\text{g}) \longrightarrow [\text{Ag/Au}(\text{CN})_2]^- (\text{aq}) + 4\text{OH}^- (\text{aq})$ .

(b)  $2\text{Cu}_2\text{O} (\text{cuprite}) + 4\text{H}_2\text{SO}_4 (\text{aq}) + \text{O}_2 (\text{g}) \longrightarrow 4\text{CuSO}_4 (\text{aq}) + 4\text{H}_2\text{O} (\ell)$   
 $\text{CuSO}_4 (\text{aq}) + \text{Fe} (\text{s}) \longrightarrow \text{FeSO}_4 (\text{aq}) + \text{Cu} (\text{s}) \downarrow$
- (a) (B) is correct statement.

(b) (A) Bauxite is leached with NaOH (concentrated) to form soluble  $\text{Na}[\text{Al}(\text{OH})_4]$  complex and insoluble impurities are filtered off.  
 (B) Carbonate and hydroxide ores are heated in absence of air below their melting point to convert in to their oxides in reverberatory furnace. This is called calcination. So magnesite,  $\text{MgCO}_3$  is subjected to calcination.  
 (C) This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper iron pyrites  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{CuFeS}_2$  (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.  
 (D) Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) having magnetic properties is separated from non-magnetic silicious impurities by magnetic separator.
- (a) (i) Extraction of tin (carbon reduction) :  
 $\text{SnO}_2 + \text{C} \rightarrow \text{SnO} + \text{CO} \uparrow$

(ii) Extraction of zinc (carbon reduction) :  
 $\text{ZnO} + \text{C} \xrightarrow{\text{coke, 673}} \text{Zn} + \text{CO}$

(iii) Extraction of lead (self reduction) :  
 $\text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4$  ;  $\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$   
 $\text{PbS} + 2\text{PbO} \longrightarrow 3\text{Pb} + \text{SO}_2$  ;  $\text{PbS} + \text{PbSO}_4 \longrightarrow 2\text{Pb} + 2\text{SO}_2$

(iv) Extraction of copper (self reduction) :  
 $2\text{CuFeS}_2 + 4\text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2$   
 $\text{Cu}_2\text{S} + \text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3 (\text{fusible slag}) + \text{Cu}_2\text{S} (\text{matte})$   
 $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$  ;  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$

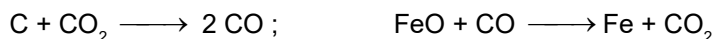
(v) Extraction of aluminium (electrolytic reduction, Hall-Heroult process) :  
 The purified  $\text{Al}_2\text{O}_3$  is mixed with  $\text{Na}_3\text{AlF}_6$  (cryolite) or  $\text{CaF}_2$  (fluorspar) ) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed.  
 Cathode :  $\text{Al}^{3+} (\text{melt}) + 3\text{e}^- \longrightarrow \text{Al}(\ell)$   
 Anode :  $\text{C}(\text{s}) + \text{O}^{2-} (\text{melt}) \longrightarrow \text{CO}(\text{g}) + 2\text{e}^-$   
 $\text{C}(\text{s}) + 2\text{O}^{2-} (\text{melt}) \longrightarrow \text{CO}_2 (\text{g}) + 4\text{e}^-$

(vi) Extraction of lead (leaching and displacement method) :  
 $4\text{Au} / \text{Ag} (\text{s}) + 8\text{CN}^- (\text{aq}) + 2\text{H}_2\text{O} (\text{aq}) + \text{O}_2 (\text{g}) \longrightarrow 4[\text{Au} / \text{Ag} (\text{CN})_2]^- (\text{aq}) + 4\text{OH}^- (\text{aq})$   
 $2[\text{Au} / \text{Ag} (\text{CN})_2]^- (\text{aq}) + \text{Zn}(\text{s}) \longrightarrow 2\text{Au} / \text{Ag} (\text{s}) + [\text{Zn}(\text{CN})_4]^{2-} (\text{aq})$

(b) Ge, Si and Ga used as semi-conductors are refined by the zone refining method.
- $3\text{PbS} + \text{O}_2 (\text{air}) \longrightarrow \text{PbS} + 2\text{PbO}$
- $\text{PbS} + 2\text{PbO} \xrightarrow[\text{absence of air}]{\Delta} 3\text{Pb} (\ell) + \text{SO}_2 \uparrow$
- $\text{FeSiO}_3$  is obtained as slag in the extraction of copper from copper pyrites.
- Statement-1 :  $\text{MgCl}_2 (\text{sea water}) + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$   
 $\text{Mg}(\text{OH})_2 + 2\text{HCl} \longrightarrow \text{MgCl}_2 + 2\text{H}_2\text{O}$   
 On crystallisation hydrated  $\text{MgCl}_2$  is obtained.

Statement-2 :  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow[\text{dry HCl}]{\Delta} \text{MgCl}_2 + 6\text{H}_2\text{O}$ .
- Carnallite is  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

10. At 500 – 800 K (lower temperature range in the blast furnace)
- $$3 \text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2 \text{Fe}_3\text{O}_4 + \text{CO}_2$$
- $$\text{Fe}_3\text{O}_4 + \text{CO} \longrightarrow 3\text{Fe} + 4 \text{CO}_2$$
- $$\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{FeO} + \text{CO}_2$$
- At 900 – 1500 K (higher temperature range in the blast furnace):



11.  $2\text{HgS} + 3 \text{O}_2 \longrightarrow 2\text{HgO} + 2\text{SO}_2$  ;  $2\text{HgO} + \text{HgS} \longrightarrow 3\text{Hg} + \text{SO}_2$   
 $\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 3\text{Cu}_2\text{O} + 2 \text{SO}_2$  ;  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$   
 $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2 \text{SO}_2$  ;  $2\text{PbO} + \text{PbS} \longrightarrow 3\text{Pb} + \text{SO}_2$

12. Copper pyrites ( $\text{CuFeS}_2$ ) contains copper and iron.

### DPP No. # 62

1.  $\text{BeCl}_2$  is hydrolysed due to high polarising power and presence of vacant p-orbitals in Be-atom. ( $\text{Be} = 1s^2, 2s^2 2p_x^1 2p_y^0 2p_z^0$ )
4.  $\text{M} + (x + y) \text{NH}_3 \longrightarrow [\text{M}(\text{NH}_3)_x]^+ + [\text{e}(\text{NH}_3)_y]^-$   
 The electrical conductivity is due to the solvated ions and blue colour is due to solvated electrons.
5. As metallic character i.e. electropositive character of cations increases thermal stability of their sulphates increases and thus the correct order is  $\text{SrSO}_4 > \text{CaSO}_4 > \text{MgSO}_4 > \text{BeSO}_4$ .
7.  $3\text{M} + \text{N}_2 \rightarrow \text{M}_3\text{N}_2$   
'A'                      'B'  
 $\text{M}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{M}(\text{OH})_2 + 2\text{NH}_3$   
'B'                      'C'                      'D'  
 $\text{M}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MCO}_3 + \text{H}_2\text{O}$   
'C'                      'D'  
 M may be either Ca or Ba. It is not magnesium because  $\text{Mg}(\text{OH})_2$  has very low solubility in water.
9. The increasing thermal stability is  
 $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{K}_2\text{CO}_3$   
(IV)            (II)            (III)            (I)  
 Increasing size of cation decreases its polarization ability towards carbonate, making the compound more stable.
11. Basic strength of the oxides increase in the order  $\text{Li}_2\text{O} < \text{Na}_2\text{O} < \text{K}_2\text{O} < \text{Rb}_2\text{O} < \text{Cs}_2\text{O}$ . The increase in basic strength is due to the decrease in I.E. down the group.  
 The melting point of the halides decrease in the order  $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$ , because of the decrease in lattice energies, as the size of the halide ion increases.
12.  $\text{Li} + \text{N}_2 \longrightarrow \text{Li}_3\text{N} \xrightarrow{\text{H}_2\text{O}} \text{LiOH} + \text{NH}_3$   
A = Lithium Nitride            B            C

### DPP No. # 63

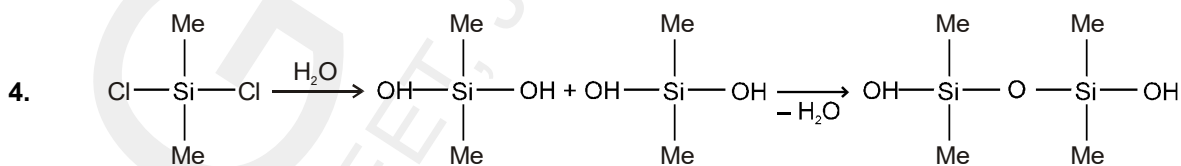
1. When sodium and potassium react with water, the heat evolved causes them to melt, giving a larger area of contact with water, lithium on the other hand, does not melt under these condition and thus reacts more slowly.
- |                    |     |    |     |
|--------------------|-----|----|-----|
|                    | Li  | Na | K   |
| Melting point (°C) | 180 | 98 | 64. |
2. As the size of cation decreases, the extent of polarisation increases so covalent character ↑ and stability ↓
4. (4) Reducing nature increases down the group as their stability decreases down the group  
 $\text{CsH} > \text{RbH} > \text{KH} > \text{NaH} > \text{LiH}$

5. Both statements are correct but  $S_2$  is not correct explanation of  $S_1$ .  
 Statement -1 : The reason for this is that their lattice energies change is more than the hydration energies on descending the group.  
 Statement -2 : Hydration energy  $\propto \frac{1}{\text{size of cation}}$ .
6. The atom becomes larger on descending the group, so the bonds are weaker (metallic bond), the cohesive force/energy decreases and accordingly melting point also decreases.
7. (A) Due to the formation of metal ion clusters (B)  $M + (x + y) \text{NH}_3 \longrightarrow M^+(\text{NH}_3)_x + e^-(\text{NH}_3)_y$   
 (C) due to the formation of metal clusters. (D)  $M (\text{NH}_3)_6 \longrightarrow$  true statement
8. (i)  $E^\circ \text{Li}^+/\text{Li} = -3.04$  ;  $\text{Na}^+ / \text{Na} = -2.71$  which is least among the alkali metals.  
 (ii) Hydration enthalpy /  $\text{KJ mol}^{-1}$   
 $\text{Li} = -506$  ;  $\text{Na} = -406$  ; Cs has the least  $\Delta H_{\text{hyd}} = -276$
9. (A) Bigger anion is stabilised by bigger cation through lattice energy effect.  
 (B) Because of their high reactivity towards air and water.  
 (C) True Statement  
 (D) In concentrated solution, unpaired electrons with opposite spins paired up – forming the solution diamagnetic.
10. Solubility of alkaline earth metal hydroxide increases as the solubility product increases.  
 $\text{Be}(\text{OH})_2 < \text{Ba}(\text{OH})_2$   
 $K_{\text{SP}} \quad 1.6 \times 10^{-26} \quad 5.4 \times 10^{-3}$

#### DPP No. # 64

1. Aluminium becomes passive due to formation of  $\text{Al}_2\text{O}_3$ .
2.  $\text{BF}_3$  undergoes only partial hydrolysis, due to reaction of produced HF with  $\text{H}_3\text{BO}_3$ .
6.  $[\text{CO}_4]^{-4}$  &  $\text{PbBr}_4$  does not exist.
9. 'A' and 'B' are correct on the basis of structure of  $\text{Al}_2(\text{CH}_3)_6$
10. The more stable oxidation state of thallium is +1 on account of inert pair effect.
11. The stable oxidation state of germanium is +3 ; so it has tendency to oxidise to +3 from +2.
12. The stable oxidation state of lead is +2 on account of inert pair effect ; so it has tendency to reduce to +2 from +4.

#### DPP No. # 65



In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by  $-\text{OH}$  groups. Such compounds are generally represented from the following formula.

