

# Chemical Equilibrium

## ELEMENTARY

**Q.1** (3)

When rate of forward reaction is equal to rate of backward reaction the reaction is said to be in equilibrium.

**Q.2** (1)

**Q.3** (1)

**Q.4** (4)

**Q.5** (4)

**Q.6** (1)

$H_2 + I_2 \rightleftharpoons 2HI$ ;  $[HI] = 0.80$ ,  $[H_2] = 0.10$ ,  $[I_2] = 0.10$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.80 \times 0.80}{0.10 \times 0.10} = 64$$

**Q.7** (1)

For reaction  $A + 2B \rightleftharpoons C$

$$K = \frac{[C]}{[A][B]^2} = \frac{0.216}{0.06 \times 0.12 \times 0.12} = 250$$

**Q.8** (4)

**Q.9** (3)

**Q.10** (3)

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left[ \frac{2 \times 10^{-3}}{2} \right]^2}{\left[ \frac{.2}{2} \right]} = \frac{10^{-6}}{10^{-1}} = 10^{-5}$$

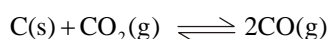
**Q.11** (2)

For  $A + B \rightleftharpoons C + D$

$$K = \frac{[C][D]}{[A][B]} = \frac{0.4 \times 1}{0.5 \times 0.8} = 1$$

**Q.12** (2)

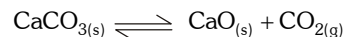
Given,  $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \uparrow$



$$K_{p_2} = \frac{[pCO]^2}{[pCO_2]}; pCO = \sqrt{[K_{p_1} \times K_{p_2}]}$$

$$pCO = \sqrt{[8 \times 10^{-2} \times 2]} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-1} = 0.4$$

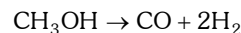
**Q.13** (2)



$$K_p = P_{CO_2}$$

Solid molecule does not have partial pressure so in calculation of  $K_p$  only  $P_{CO_2}$  is applicable.

**Q.14** (4)



$$\frac{[H_2]^2[CO]}{[CH_3OH]} = \frac{0.1 \times 0.1 \times 1}{2} = \frac{0.01}{2} = \frac{10 \times 10^{-3}}{2} = 5 \times 10^{-3}$$

**Q.15** (1)

$$n_p = n_r \text{ then } K_p = K_c$$

where  $n_p$  = no. of moles of product

$n_r$  = no. of moles of reactant.

**Q.16** (3)

$$K_p = K_c (RT)^{\Delta n}; \Delta n = 2 - 2 = 0$$

**Q.17** (3)

For the reaction  $H_2 + I_2 \rightleftharpoons 2HI$

$$\Delta n = 0$$

$$\text{So } K_p = K_c \approx 50.0$$

**Q.18** (4)

For reaction  $2SO_3 \rightleftharpoons O_2 + 2SO_2$

is + ve so  $K_p$  is more than  $K_c$

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

**Q.19** (3)

$$\Delta n = 2 - 1 = 1$$

$$K_p = K_c (RT)$$

**Q.20** (3)

If  $\Delta n = 0$  then  $K_p = K_c$

**Q.21** (2)

**Q.22** (3)

For this reaction there is no change in equilibrium constant by change of volume.

**Q.23** (3)

Equilibrium constant is independent of original concentration of reactant.

**Q.24** (3)

$$K_1 = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} \text{ and } K_2 = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}; K_2 = \frac{1}{K_1^2}$$

**Q.25** (2)

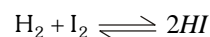
$$K' = K^n; \text{ Hence } n = \frac{1}{2}$$

$$\therefore K' = K^{1/2} = \sqrt{K}$$

**Q.26** (3)

**Q.27** (4)

$K$  for dissociation of  $\text{HI} = ?$



$$K_a = 50, K_b = \frac{1}{50} = 0.02$$

**Q.28** (1)

**Q.29** (2)

**Q.30** (1)

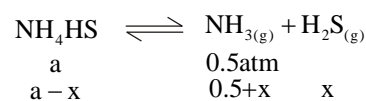
$$\frac{22}{100} \times 3.2 = 0.704$$

$$\text{at equil. moles of HI} = 3.2 - 0.704 = 2.496$$

**Q.31** (2)

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left[\frac{20}{100}\right] \times \left[\frac{20}{100}\right]}{\left[\frac{80}{100}\right]}$$

$$= \frac{0.2 \times 0.2}{0.8} = \frac{0.04}{0.8} = 0.05$$

**Q.32** (4)


$$\text{Total pressure} = 0.5 + 2x = 0.84$$

$$\text{i.e., } x = 0.17$$

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = 0.1139 = (0.67) \cdot (0.17) = 0.1139$$

**Q.33** (2)

**Q.34** (3)

According to Le-chatelier principle when concentration of reactant increases, the equilibrium shift in favour of forward reaction.

**Q.35** (4)

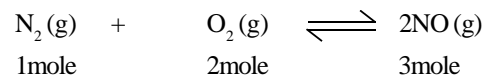
Equilibrium constant changes with temperature, pressure and the concentration of either reactant or product.

**Q.36** (2)

**Q.37** (4)

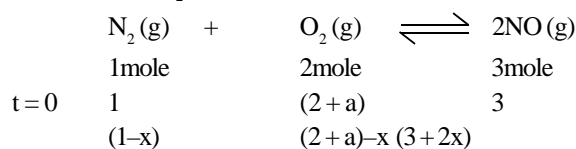
According to Le-chatelier's principle.

**Q.38** (3)

**JEE-MAIN**
**OBJECTIVE QUESTIONS**
**Q.17** (A)


$$K_c = \frac{(3)^2}{1 \times 2} = \left(\frac{9}{2}\right)$$

Let a mole of  $\text{O}_2$  is added, Then,



$$[\text{NO}] = \left[\frac{3+2x}{100}\right] = 0.04; \quad (3+2x) = 4.$$

$$2x = 1, \quad x = 0.5.$$

$$K_c = \frac{(3+x)^2}{(1-x)(2+a-x)} = \frac{9}{2}$$

$$K_c = \frac{(4)^2}{0.5[(1.5)-a]} = \frac{9}{2}$$

$$= \frac{16}{0.5(1.5+a)} = \frac{9}{2}$$

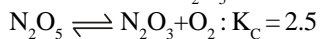
$$= \frac{35}{4.5} = [1.5+a]$$

$$7.11 = 1.5 + a.$$

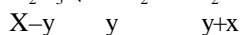
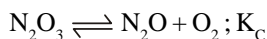
$$a = \frac{101}{18} = 5.61$$

**Q.18** (D)

Given:- When  $N_2O_5$  is heated T, its dissociates



and



$$\boxed{x + y = 2.5}$$

$$K_c = \frac{(x+y)(x-y)}{4-x}$$

$$\Rightarrow \frac{2.5(x-y)}{4-x} = 2.5 \text{ [from eq. (1)]}$$

$$\Rightarrow x-y = 4-x$$

$$\Rightarrow \boxed{2x - y = 4} \text{ -----(2)}$$

$\Rightarrow$  from (1) and (2)

$$3x = 6.5$$

$$x = 2.17$$

from (1)

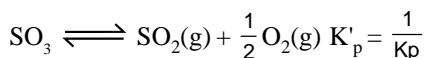
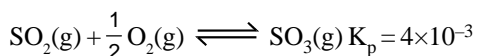
$$2.17 + y = 2.5$$

$$y = 2.5 - 2.17$$

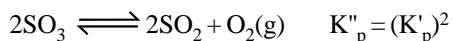
$$y = 0.334$$

Equilibrium concentration of  $N_2O$  is 0.334.

**Q.19** (D)



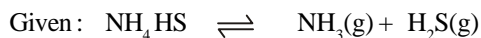
$$K'_p = \left( \frac{1}{4 \times 10^{-3}} \right)$$



$$= \left[ \frac{1}{4 \times 10^{-3}} \right]^2 = \left[ \frac{1000}{4} \right]^2 = 6250 = 625 \times 10^2$$

$$\mathbf{6.25 \times 10^4 \text{ atm.}}$$

**Q.20** (D)



$$\text{atm} \qquad \qquad \text{atm}$$

$$\text{total pressure} = 0.5+x+x=0.84$$

$$2x = 0.34$$

$$x = .17$$

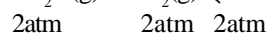
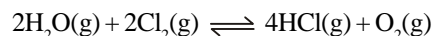
$$P_{NH_3} = 0.5 + x$$

$$= 0.5 + .17 \Rightarrow .67$$

**Q.24** (C)

Given :-

$$K_p = 12 \times 10^8 \text{ atm for reaction}$$



$$\frac{380}{760} = \frac{1}{2} \quad 2-2y \qquad \qquad 2+4x \quad 2+x$$

$$K_p = 12 \times 10^8; K_p \gg 1$$

$$\Rightarrow x \approx 1$$

$$\Rightarrow 12 \times 10^8 = \frac{(3) \times (6)^4}{y^2 \times (1/2)^2}$$

$$\Rightarrow \frac{12 \times 10^8}{3 \times 36 \times 36 \times 4} = \frac{1}{y^2}$$

$$\Rightarrow y = \frac{36 \times 2}{2 \times 10^4} = 2 \times 18 \times 10^{-4}$$

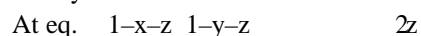
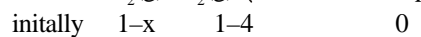
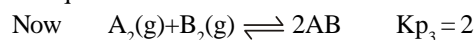
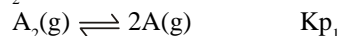
$$y = 36 \times 10^{-4} \text{ atm}$$

$$y = 3.6 \times 10^{-3} \text{ atm}$$

**Q.25** (A)

Given - Equimolar mixture of two given

$A_2$  and  $B_2$



$$P_{e_v} = P_{A_2} + P_{B_2} + P_B + P_A + P_{AB}$$

$$\Rightarrow 1-x-z+1-y-z+2x+24+2z$$

$$P_{e_v} \Rightarrow 2+x+y$$

$$2+x+y=2.75$$

$$x+y=0.75 \qquad \qquad \qquad [\text{as } P_{e_v} = 2.75]$$

$$x+y=0.75 \qquad \qquad \qquad \dots(1)$$

As partial pressure of  $AB(g)$

$$P_{AB} = 0.5$$

$$27 = 0.5$$

$$7 = 0.25$$

$$\dots(2)$$

$$K_{p_3} = \frac{(P_{AB})^2}{P_{A_2} \times P_{B_2}} = \frac{(0.5)^2}{(0.75-x)(0.75-y)} \dots(3)$$

$$K_{p_1} = \frac{(P_A)^2}{P_{A_2}} = \frac{(2x)^2}{(0.75-x)}$$

$$K_{p_2} = \frac{(P_B)^2}{P_{B_2}} = \frac{(2y)^2}{(0.75-y)}$$

$$K_{p_1} \times K_{p_2} = \frac{(2x)^2(2y)^2}{(0.75-x)(0.75-y)}$$

$$\Rightarrow \frac{16x^2y^2}{(0.75-x)(0.75-y)} \dots(4)$$

Now equate with eq. (3)

$$K_{p_1} \times K_{p_2} = K_{p_3}$$

$$\Rightarrow .5 = 4xy \quad \Rightarrow \quad xy = \frac{1}{8}$$

$$x + y = .75 \quad \left[ \text{put } y = \frac{1}{8x} \right]$$

$$\Rightarrow 8x^2 - 6x + 1 = 0$$

$$x = \frac{1}{4} \quad x \neq \frac{1}{d}$$

$$y = \frac{1}{2} \quad [x > y]$$

$$\text{Now, } \frac{K_{p_1}}{K_{p_2}} = \frac{(1/4)(1/2)}{1(1/4)} = \frac{1}{8}$$

$$\Rightarrow \frac{K_{p_2}}{K_p} = 8$$

**Q.32** (A)

Given :- Heat of reaction (at constant V) = 1200 cal  
(at constant pressure)  $\Rightarrow T = 300\text{K}$

$$\frac{K_p}{K_c} = ?$$

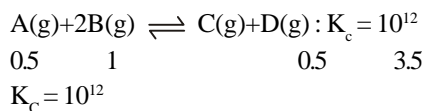
$$\text{Now, } \frac{K_p}{K_c} = e^{\frac{-\Delta H}{RT}}$$

$$= e^{\frac{-1200}{2 \times 300}} \Rightarrow e^{-2}$$

$$\Rightarrow \frac{1}{e^2} \Rightarrow 1.648 \times 10^{-3}$$

**Q.34** (B)

Given rxn -

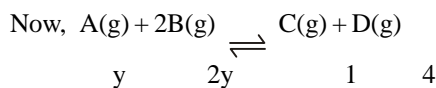


$$Q_c = \frac{[A][C]}{[A][B]^2} \Rightarrow \frac{0.5 \times 3.5}{0.5}$$

$$Q_c = 3.5$$

$$\Rightarrow Q_c < K_c$$

Forward shift



Let

$K_c$  is very high

$$\therefore x \sim 0.5$$

$$\text{as } \Rightarrow y = 0.5 - x \quad \text{and } 1 - 2x = 2y$$

$$K_c = \frac{[C][D]}{[A][B]^2} \Rightarrow \frac{1 \times 4}{4 \times 4y^2}$$

$$\Rightarrow \frac{4}{4y^3}$$

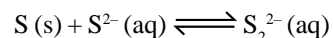
where  $K_c = 10^{12}$

$$\therefore 10^{12} = \frac{4}{4y^3}$$

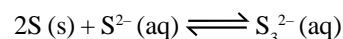
$$y = 10^{-4}$$

$$\text{conc}^n \text{ of B} = 2y \Rightarrow 2 \times 10^{-4}$$

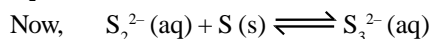
**Q.36** (A)



$$K_1 = 12$$

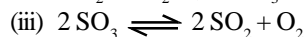
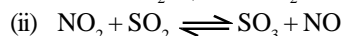
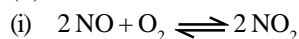


$$K_2 = 132$$



$$K_{eq} = \frac{K_2}{K_1} = \frac{132}{12} = 11$$

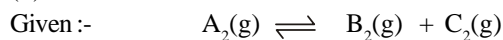
**Q.37** (B)



Now,  $-2(ii) = (i) + (iii)$

$$\text{so, } K_{C_3} \times K_{C_1} = 1/K_{C_2}^2$$

**Q.46** (C)



At eq.  $P-x \quad x \quad x$   
 Total pressure =  $P-x+x+x=P+x$   
 $\Rightarrow P+x=7$  [as total pressure = 7] ... (1)

$$\text{Now, } K_p = \frac{[P_{B_2}][P_{C_2}]}{[P_{A_2}]}$$

$$9 = \frac{x^2}{(P-x)} \quad (\text{as } K_p = 9)$$

$$\Rightarrow 9(7-x-x) = x^2 \quad [\text{from eq. (1)}]$$

$$\Rightarrow x^2 + 18x - 63 = 0$$

$$x = 3$$

$$\text{then } p+x=7$$

$$p=4$$

as we know

P.M. = dRT (volume cont.)

$$\Rightarrow P \times \frac{1}{M} \text{ \& initially only } A_2 \text{ is present}$$

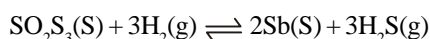
$$\Rightarrow \frac{P_i}{P_{eq}} = \frac{M_{eq}}{M_i}$$

$$\Rightarrow \frac{4}{7} = \frac{M_{eq}}{70}$$

$$\Rightarrow M_{eq} = 40$$

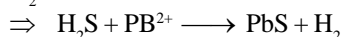
**Q.53** (A)

Given :-  $V = 250$  lit



After equilibrium

$H_2S$  treated with excess of  $Pb^{2+}$



$$\therefore \text{mole of PbS} = \frac{1.195}{239} = 5 \times 10^{-3}$$

$$\text{mole of } H_2S = 5 \times 10^{-3}$$

$$\text{mole of } H_2 \text{ remaining} = 0.01 - 0.005 = 0.005$$

$$K_c = \frac{[H_2S]^3}{[H_2]^3} = \left( \frac{0.005}{0.005} \right)^3$$

$$\Rightarrow K_c = 1$$

**Q.54** (A)

Given :-



$$K_p = 7 \times 10^{-2}$$

as given - .50 mole of  $H_2$

1.0 mole of S



$$0.5$$

$$1.0$$

$$0.5-x$$

$$1-x$$

$$x$$

$$\text{as } K_c = K_p = \frac{x}{(0.5-x)}$$

$$7 \times 10^{-2} = \frac{x}{(0.5-x)} \quad (\text{as } k_p = 7 \times 10^{-2})$$

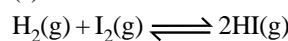
$$x = 0.035 - 0.07x$$

$$\Rightarrow x = \frac{0.035}{1.07}$$

$$P_{H_2S} = \frac{\left( \frac{0.035}{1.07} \right) \times 0.0821 \times 360}{1} \quad (\text{as } PV = nRT)$$

$$= 0.966 \text{ atm.}$$

**Q.55** (2)

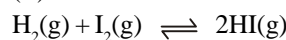


$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{50}{66.9} = \frac{\Delta H}{2.303R} \left[ \frac{1}{623} - \frac{1}{721} \right]$$

After calculation negative value of  $\Delta H$  is obtained.

**Q.58** (D)



$$\text{If } \Delta n_g = 0 \Rightarrow (2-2) = 0$$

then no effect of Pressure change

**Q.60** (D)



$ClF_3$  will be increased when reaction shifted forward.

$\Rightarrow$  Exothermic low temperature

$\therefore$  Addition of reactant

$$\Delta n_g < 0$$

$\Rightarrow$  Increase in pressure

lower the volume.

**Q.61** (C)



It is exothermic reaction

so it favours low temperature

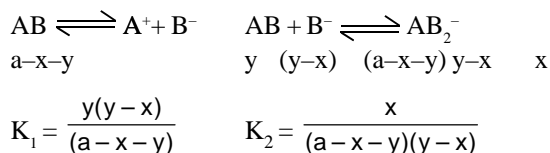
density of graphite is less than diamond  $\Rightarrow$  low pressure.

but for formation of diamond Reverse condition high temperature & high pressure

**Q.69** (B)

Addition of inert gas at constant volume has no effect on equilibrium concentrations.

**Q.70** (A)



$$\frac{K_1}{K_2} = \frac{\frac{y(y-x)}{(a-x-y)}}{\frac{x}{(a-x-y)(y-x)}} \Rightarrow \frac{K_1}{K_2} = \frac{y}{x} (y-x)^2$$

Q.71 (1)

$$\ln k_p = \frac{-\Delta H}{RT} + \ln A$$

Exothermic  $\Delta H < 0$   
slope +Ve

Q.73 (D)



$$K_1 = \frac{[A^+][B^-]}{[AB]} \quad K_2 = \frac{[AB_2^-]}{[AB][B^-]}$$

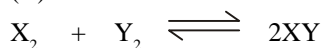
$$K_1/K_2 = \frac{[A^+][B^-]}{[AB]} \cdot \frac{[AB][B^-]}{[AB_2^-]} = \frac{[A^+]}{[AB_2^-]} \cdot [B^-]^2$$

$$\Rightarrow \frac{[A^+]}{[AB_2^-]} = \frac{K_1}{K_2} \cdot \frac{1}{[B^-]^2}$$

Therefore, (D) option is correct.

### JEE-ADVANCED OBJECTIVE QUESTIONS

Q.1 (A)



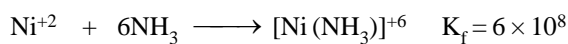
$$\frac{1}{3} - x \quad \frac{2}{3} - x \quad 2x \quad 2x = 0.6$$

$$\Rightarrow x = 0.3$$

$$[x_2] = \frac{1}{3} - 0.3 \quad [y_2] = \frac{2}{3} - 0.3$$

Therefore, (A) option is correct.

Q.2 (D)

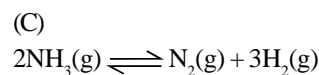


$$t=0 \quad 0.01 \text{ mole} \quad 0.1 \text{ mole} \quad 0$$

$$K_c = \frac{[Ni(NH_3)_6]^{+6}}{[Ni^{+2}][NH_3]^6} = \frac{(0.1)}{[Ni^{+2}](0.4)^6}$$

$$= 6 \times 10^8 \quad [Ni^{+2}] = 4 \times 10^{-8}$$

Q.3



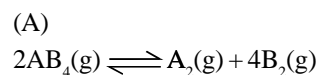
$$K_p = \frac{\frac{\alpha P_o}{2(1+\alpha)} \left\{ \frac{3\alpha P_o}{2(1+\alpha)} \right\}^3}{\left\{ \frac{1-\alpha}{1+\alpha} P_o \right\}^2}$$

$$1 - \alpha \quad \frac{\alpha}{2} \quad \frac{3\alpha}{2}$$

$$1 - \alpha \approx 1 \text{ and } 1 + \alpha \approx 1 \Rightarrow 27 \times 10^{-8} P_o^2 = \frac{27}{16}$$

$$P_o^2 \times \alpha^4 \\
 \alpha = 2 \times 10^{-2}$$

Q.4

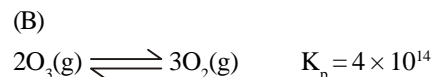


$$\sum n = 1 + \frac{3\alpha}{2} \approx 1$$

$$1 - \alpha \quad \frac{\alpha}{2} \quad 2\alpha \quad 1 - \alpha \approx 1$$

$$K_p = \frac{\left(\frac{\alpha P}{2}\right) \left(\frac{2\alpha}{1} \times P\right)^4}{(P)^2} = 8P^3\alpha^5$$

Q.5



$$P_{O_2} \gg P_{O_3}$$

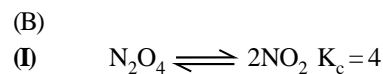
$$K_p = \frac{P_{O_2}^3}{P_{O_3}^2} \quad P_{O_2} + P_{O_3} = 8$$

$$\Rightarrow P_{O_2} \approx 8 \text{ atm.}$$

$$4 \times 10^{14} = \frac{8^3}{P_{O_3}^2} \quad P_{O_3}^2 = 11.3 \times 10^{-7} \quad \text{Therefore,}$$

(B) option is correct.

Q.6



at point — A

$$Q = \frac{[\text{Product}]}{[\text{Reactant}]} = 0$$

So, Q have minimum value at point A.

(II) at point  $[\text{N}_2\text{O}_4] = [\text{NO}_2] = 0.1\text{m}$

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.1 \times 0.1}{0.1} = 0.1$$

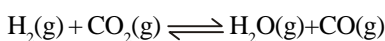
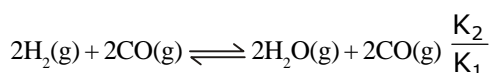
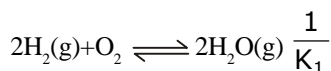
$$Q < K_c$$

So, reaction proceeds left to right

(III)  $K_c = Q$  at point [D & F].

Q.7 (B)

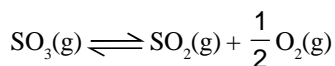
Given :



$$\Rightarrow K = \sqrt{\frac{K_2}{K_1}}$$

$$K = 2.58$$

Q.8 (B)



$$M_{\text{mix}} = \frac{0.9 \times 0.082 \times 1000}{1.23} = 60$$

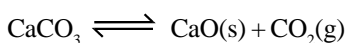
$$1 - \alpha \propto \frac{\alpha}{2}$$

$$M_{\text{mix}} = \frac{\alpha \cdot M_{\text{SO}_2} + \frac{\alpha}{2} \cdot M_{\text{O}_2} + (1 - \alpha)M_{\text{SO}_3}}{1 + \frac{\alpha}{2}}$$

$$1 + \frac{\alpha}{2} = \frac{80}{60} \quad \frac{\alpha}{2} = \frac{20}{60}$$

$$\alpha = \frac{2}{3}$$

Q.9 (D)



$$K_p = (P_{\text{CO}_2})$$

$(P_{\text{CO}_2})$  is equal to equilibrium constant which only change with changing only  $K_p$

But equilibrium constant only depends on temperature so.

Q.10 (B)

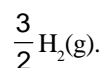
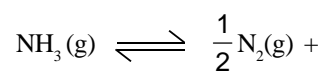
$$P_1 = 15 \text{ atm}; T_1 = 300 \text{ K.}$$

Equilibrium temperature is  $300^\circ\text{C}$  that is  $573 \text{ K}$ .

So first of all we have to calculate pressure of  $\text{NH}_3$  at  $573 \text{ K}$ .

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{15}{300} = \frac{P_2}{573}$$

$$P_2 = 28.65 \text{ atm at } 300^\circ\text{C.}$$



$$t = 0 \quad 28.65 \text{ atm} \quad 0 \quad 0$$

$$t = t_{\text{eq.}} \quad [28.65 - x] \quad \frac{x}{2} \text{ atm} \quad \frac{3}{2}x$$

But according to question.

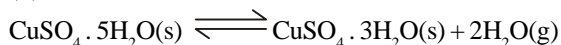
$$P_{\text{total}} = 28.65 - x + \frac{x}{2} + \frac{3}{2}x$$

$$= 28.65 - x = 40.11.$$

$$x = 11.46.$$

$$\text{Degree of dissociation of } \text{NH}_3 = \frac{11.46}{28.65} = 0.4.$$

Q.11 (B)



$$K_p = 2.25 \times 10^{-4}$$

$$K_p = p_{\text{H}_2\text{O}}^2 = 2.25 \times 10^{-4}$$

$$p_{\text{H}_2\text{O}} = 1.5 \times 10^{-2}$$

$$\text{Vapour Pr} = \frac{22.8}{760} = 3 \times 10^{-2}$$

$$\text{R.H.} = \frac{p_{\text{H}_2\text{O}}}{\text{V.P.}} \times 100 = 50\%$$

Therefore, (B) option is correct.

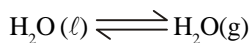
Q.12 (A)



$$K_p = 16 \times 10^{-12}$$

$$(P_{\text{H}_2\text{O}})^4 = K_p$$

$$P_{\text{H}_2\text{O}} = (K_p)^{1/4} = 2 \times 10^{-3} \text{ atm}$$



$$P_{\text{H}_2\text{O}} = \frac{7.6}{760} = 1.0 \times 10^{-2}$$

$$n_{\text{H}_2\text{O}} = \frac{PV}{RT} = \frac{10^{-2} \times 1}{0.082 \times 274} = 4.45 \times 10^{-4}$$

$$n_{\text{H}_2\text{O}} = \frac{2 \times 10^{-3}}{0.082 \times 274} = 8.9 \times 10^{-5} \quad \therefore n_{\text{H}_2\text{O}} \text{ absorbed}$$

$$= 3.56 \times 10^{-4}$$

$\therefore$  wt absorbed = 6.4 mg. Therefore, (A) option is correct.

**Q.13** (D)

As we know

$$\ln \left( \frac{K_{p_2}}{K_{p_1}} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln 4 = \frac{\Delta H^\circ}{8.314} \left( \frac{1}{298} - \frac{1}{313} \right)$$

$$\Delta H^\circ = 71.6 \text{ kJ}$$

**Q.14** (A)



$$4(1-\alpha) \quad 4\alpha \quad 2\alpha \quad \sum n = 4 + 2\alpha$$

$$K_p = \frac{\left( \frac{4\alpha}{4+2\alpha} \times P \right)^2 \left( \frac{2\alpha}{4+2\alpha} \times P \right)}{\left( \frac{4(1-\alpha)}{4+2\alpha} \times P \right)^2} = P$$

$$\Rightarrow 2\alpha^3 = (1-\alpha)^2 (4+2\alpha)$$

$$2\alpha^3 = (1+\alpha^2-2\alpha)(4+2\alpha)$$

$$2\alpha^3 = 4 + 2\alpha + 4\alpha^2 + 2\alpha^3 - 8\alpha - 4\alpha^2$$

$$\alpha = \frac{2}{3}$$

**Q.15** (D)

On increasing temperature though reaction equilibrium shifts in the backward direction but for rate of reaction to be higher, higher temperature is required and particle  $500^\circ\text{C}$  is found to be optimum temperature.

**Q.16** (C)

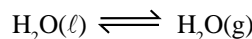


reaction is endothermic

$\Delta H > 0 \Rightarrow$  High temperature

$\Delta n_g > 0$  low pressure

**Q.17** (B)



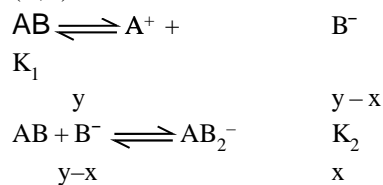
$$K_p = (P_{\text{H}_2\text{O}})$$

When neon is added at constant pressure, we have to increase volume of the container. So more water will evaporate to maintain equilibrium.

### JEE-ADVANCED

#### MCQ/COMPREHENSION/COLUMN MATCHING

**Q.1** (A,C)



$$\Rightarrow K_1 = (y-x)y \quad K_2 = \frac{x}{y-x}$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{y}{x} (y-x)^2$$

**Q.2** (A,C)

**Q.3** (A,B)

$$\log \frac{k_c}{k_p} = \log \frac{1}{(RT)}$$

$$\Rightarrow k_p = k_c (RT) \quad \Rightarrow \Delta n = 1$$

**Q.4** (A,B,C)

From given reactions.

$$(i) = -(iii);$$

$$\frac{1}{2} (i) = -(iv);$$

$$\frac{1}{2} (iii) = -(ii)$$

**Q.5** (C,D)

**Q.6** (B,C)

**Q.7** (A,C,D)



- Q.8** (C,D)  
Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as  $\Delta n_g$  is +ve.
- Q.9** (A,C)  
Given :  

$$\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$$

$$\begin{matrix} 2x & & x \end{matrix}$$

$$(2x)^2(x) = 2.92 \times 10^{-5}$$

$$x^3 = \frac{2.92}{4} \times 10^{-5}$$

$$P_{\text{total}} = 3x = 0.0582$$
- Q.10** (C,D)
- Q.11** (B,C)  
Exothermic  $\Rightarrow$  low temp  
 $\therefore$  forward reaction favoured  
High temp backward
- Q.12** (C,D)  
As given :  

$$\text{HgO}(\text{s}) + 4\text{I}^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HgI}_4^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq}),$$

$$K = \frac{[\text{HgI}_4^{2-}][\text{OH}^-]^2}{[\text{I}^-]^4}$$
as,  $\text{OH}^\ominus \uparrow$   $\text{HgI}_4^{2-} \downarrow$   
 $\text{H}_2\text{O}(\ell) \uparrow$   $\text{OH}^\ominus \uparrow$
- Q.13** (B,D)  

$$\Delta G = \Delta H^\ominus + \Delta ST \quad \dots(1)$$

$$\Delta G = RT \ln k \quad \dots(2)$$
from (1) & (2)  

$$\ln k = \frac{\Delta H^\ominus}{RT} + \frac{\Delta S}{R}$$
slope of the line equal to  $\Delta H^\ominus/R$
- Q.14** (A,C)  
As given :  

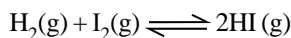
$$\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\ell)$$
At  $0^\circ\text{C}$  density of  $\text{H}_2\text{O}(\text{s}) < \text{H}_2\text{O}(\ell)$   
As  $P \downarrow$  &  $V \uparrow$   
 $\therefore$  formation of more  $\text{H}_2\text{O}(\text{s})$   
and increase in melting point of  $\text{H}_2\text{O}(\text{s})$
- Q.15** (C,D)  
Introduction of inert gas at constant Pressure will increase  $\uparrow$  & volume  $\downarrow$  the Pressure of gases of equilibrium  
 $\Rightarrow$  equilibrium shifted forward
- Q.16** (C,D)  

$$\text{NaNO}_3(\text{s}) \rightleftharpoons \text{NaNO}_2(\text{s}) + \text{O}_2(\text{g})$$
 $\Delta H > 0$  endothermic  
High temperature  
 $\therefore$  forward reaction favoured  
1000 pressure  
High pressure  $\rightarrow$  Reverse reaction
- Q.17** (A,C,D)  
(A) As reaction is endothermic therefore it will go in the forward direction hence moles of  $\text{CaO}$  will increase.  
(B) With the increase or decrease of volume particle pressure of the gases will remain same.  
(C) Due to the addition of inert gas at constant pressure reaction will proceed in the direct in which more number of gaseous moles are formed.
- Q.18** (B,C,D)  
According to  $K_p = \frac{P_{\text{PCl}_3(\text{g})} \times P_{\text{Cl}_2(\text{g})}}{P_{\text{PCl}_5(\text{g})}}$   

$$= \frac{(n_{\text{PCl}_3(\text{g})})_{\text{eq.}} \times (n_{\text{Cl}_2(\text{g})})_{\text{eq.}}}{V \times (n_{\text{PCl}_5(\text{g})})_{\text{eq.}}}$$
and on adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.
- Q.19** (A,D)  
For endothermic reaction,  $\Delta H^\ominus$  is positive so, if  $T_2 > T_1$  then  $K_2 > K_1$ .  
For exothermic reaction,  $\Delta H^\ominus$  is negative so, if  $T_2 > T_1$  then  $K_2 < K_1$ .
- Q.20** (C,D)  
As few moles of  $\text{CO}(\text{g})$  are introduced into the vessel

second equilibrium shifts backward, decreasing the concentration of  $\text{Cl}_2$ . So, first equilibrium will go forward.

**Q.21** (A,B,C,D,E)



(A) For changing pressure volume has to be changed, though number of moles of  $\text{HI}(\text{g})$  do not get changed but its concentration will get changed.

(B) Temperature change will change  $K_p$  and hence concentration.

(C) Volume change will change concentration, not the number of moles.

(D) Same equilibrium will be attained from either direction.

(E) Catalyst does not change equilibrium concentrations.

**Q.22** (B,D)

(A) Backward shifting will take place.

(B) Forward shifting will take place.

(C) Backward shifting will take place.

(D) Forward shifting will take place.

**Q.23** (A,B,C,D)

Addition of inert gas at constant volume has no effect on equilibrium concentrations.

**Q.24** (A,C)

Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as  $\Delta n_g$  is +ve.

**Q.25** (A,B,C)

Addition of inert gas at constant volume has no effect on equilibrium concentrations.

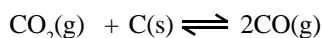
**Q.26** (B,C,D)

$$\text{From } K_p = (P_{\text{NH}_3(\text{g})})^2 (P_{\text{CO}_2(\text{g})})$$

and since reaction is exothermic.

### Comprehension # 1

**Q.27** (B)



$$t = 0, 0.1 \quad t = t_{\text{eq.}} \quad 0.1 - x \quad 2x$$

$$\frac{(0.1 - x)44 + (2x \times 28)}{0.1 + x} = 36$$

$$\Rightarrow x = \frac{1}{30}$$

$$\text{Total moles} = 0.1 + \frac{1}{30} = \frac{2}{15}$$

**Q.28** (A)

$$\text{Moles of } \text{CO}_2 \text{ at eq.} = 0.1 - x = \frac{1}{15}$$

$$\text{Moles of } \text{CO} \text{ at eq.} = 2x = \frac{2}{30} = \frac{1}{15}$$

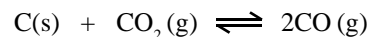
$$P_{\text{CO}_2} = \frac{0.082 \times 900}{15 \times 0.82} = 6 \text{ atm}$$

$$P_{\text{CO}} = \frac{1}{15} \times \frac{0.082}{0.82} \times 900 = 6 \text{ atm}$$

$$\therefore K_p = \frac{6 \times 6}{6} = 6 \text{ atm}$$

**Q.29** (B)

$$n_c = 0.1$$



$$\begin{array}{cccc} t = 0 & 0.1 & n & \\ t = t_{\text{eq.}} & - & n - 0.1 & 0.2 \end{array}$$

$$P_{\text{CO}} = \frac{0.2 \times 0.082 \times 900}{0.82} = 18 \text{ atm}$$

$$K_p = 6 = \frac{(18)^2}{P_{\text{CO}_2}}; P_{\text{CO}_2} = 54 \text{ atm}$$

$$\therefore \frac{(n - 0.1)(0.082)(900)}{0.82} = 54$$

$$n = 0.7$$

### Comprehension # 2

**Q.30** (B)

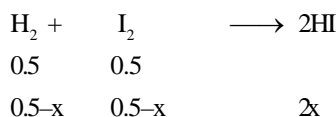
As we know,  $K_p = K_c (RT)^{\Delta n_g}$

$$\Delta n_g = 2 - 2 \Rightarrow 0$$

$$\Rightarrow 49 \times (.0802 \times 700)^0$$

$$K_p \Rightarrow 49$$

Q.31 (C)



Total number of moles

$$0.5 - x + 0.5 - x + 2x = 1$$

$$P = \frac{1 \times 0.0821 \times 700}{7}$$

$$P = 8.21 \text{ atm}$$

Q.32 (B)

from above question

$$K_c = \frac{4x^2}{(0.5 - x)^2}$$

$$\frac{\left(\frac{2x}{7}\right)^2}{\left(\frac{0.5-x}{7}\right)\left(\frac{0.5-x}{7}\right)} = 49$$

$$\frac{2x}{0.5-x} = 7 \Rightarrow x = 0.388$$

$$\text{remaining I}_2 = 0.5 - 0.388 = 0.112$$

Q.33 (A)

At equilibrium mole of HI = 2x

$$= 2 \times 0.388$$

$$P_{\text{HI}} = \frac{(2 \times 0.388) \times 0.082 \times 700}{7}$$

$$= 6.38$$

$$P_{\text{HI}} < P_{\text{total}}$$

$$P_{\text{HI}} < 8.21 \text{ only case } P_{\text{HI}} = 6.385$$

**Comprehension # 3**

Q.34 (D)

Solubility of gas is favourable at high pressure and this process is exothermic hence solubility will be more at low temperature.

Q.35 (C)

Since density of gold decreases after melting therefore it is favourable at low pressure and high temperature.

Q.36 (A,B)

Number of moles will remain unchanged but due to decreased volume pressure will get increased and also the concentrations.

**Comprehension # 4**

Q.37 (A)

Best drying agent reduces the moisture more effectively means reduces the

$P_{\text{H}_2\text{O}}$  to the minimum

$$\text{for SrCl}_2 \cdot 2\text{H}_2\text{O } P_{\text{H}_2\text{O}} = (K_p)^{1/4}$$

$$\Rightarrow (5 \times 10^{-12})^{1/4} = 1.49 \times 10^{-3}$$

for  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$

$$P_{\text{H}_2\text{O}} = (2.43 \times 10^{-13})^{1/5} = 3 \times 10^{-3}$$

for  $\text{Na}_2\text{SO}_4$

$$P_{\text{H}_2\text{O}} = (1.02 \times 10^{-27})^{1/10} = 2 \times 10^{-3}$$

Q.38 (B)

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  will release moisture

when  $P_{\text{H}_2\text{O}} < 2 \times 10^{-3}$

$$V.P_{\text{H}_2\text{O}} = 6 \times 10^{-3} \text{ atm}$$

$$\text{Relative humidity} = \frac{P_{\text{H}_2\text{O}}}{VP_{\text{H}_2\text{O}}} = \frac{2 \times 10^{-3}}{6 \times 10^{-3}} = 33.33\%$$

if relative humidity < 33.33%

$$\Rightarrow P_{\text{H}_2\text{O}} < 2 \times 10^{-3}$$

it will release the moles

Q.39 (A)

above 33.33%

from previous question

**Comprehension # 5**

Q.40 (B)

$$\text{Slope} = \frac{-\Delta H^\circ}{2.3R} = -\frac{230}{2.3 \times 2} = -50$$

Q.41 (B)

$$\text{Using equation, } \log K = -\frac{\Delta H^\circ}{2.3RT} + \frac{\Delta S^\circ}{2.3R}$$

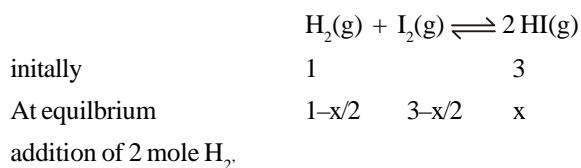
**Q.42** (B)

$$\text{Using equation, } \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.30R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

### Comprehension # 6

**Q.43** (C)

Given as :



$$\begin{array}{ccc} 3 - \frac{x}{2} - \frac{x}{2} & 3 - \frac{x}{2} - \frac{x}{2} & x+x \\ = 3-x & 3-x & 2x \end{array}$$

$$\Rightarrow \frac{(x)^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} = \frac{(2x)^2}{(3-x)(3-x)}$$

$$\Rightarrow 2x=3 \Rightarrow x = \frac{3}{2}$$

$x=1.5$

**Q.44** (C)

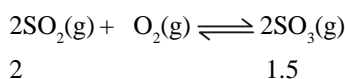
$$K_C = \frac{(2x)^2}{(3-x)(3-x)} = \frac{9}{\left(\frac{9}{4}\right)} = 4$$

$$K_C = K_p \text{ because } \Delta n_g = 0$$

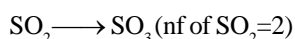
$$K_C = K_p = 4$$

**Q.45** (B)

Given :



$$\text{conc.} = \frac{2-2x}{5} \quad \frac{1.5-x}{5} \quad \frac{2x}{5}$$



$$\text{m.eq of KMnO}_4 = \text{m.eq of SO}_2$$

$$0.4 \times 5 = (2.2x) \times 2$$

$$2 = 2(1-x) \times 2$$

$$\Rightarrow 1-x = 1/2 \Rightarrow x = \frac{1}{2}$$

$$[\text{SO}_2] = \frac{1}{5}; [\text{O}_2] = \frac{1}{5}$$

$$[\text{SO}_3] = \frac{1}{5}$$

$$K_C = 5$$

**Q.46** (A) q, s; (B) p; (C) p; (D) r

$$(A) \Delta n_g = 2 - 4 = -2 \text{ and } K_p = K_C (RT)^{\Delta n_g}$$

$$(B) \Delta n_g = 2 - 1 = 1 \text{ and } K_p = K_C (RT)^{\Delta n_g}$$

$$(C) \Delta n_g = 2 - 1 = 1 \text{ and } K_p = K_C (RT)^{\Delta n_g}$$

(D)  $K_p$  is not defined.

**Q.47**  $A \rightarrow p; B \rightarrow q; C \rightarrow s; D \rightarrow r$

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

**Q.48** (A - r); (B - r); (C - q); (D - p)

(A)  $\Delta n_g$  is +ve so as P is increased, backward shifting will take place. Total pressure even after shifting will remain same.

(B)  $\Delta n_g$  is -ve so as V is increased, backward shifting will take place. But  $P_{\text{final}} < P_{\text{initial}}$ .

(C) No change but  $P_{\text{final}} < P_{\text{initial}}$  as volume has increased.

(D) Forward shifting will take place and  $P_{\text{final}} < P_{\text{initial}}$ .

**Q.49** A-p, t; B-q, r; C-q, s

$$(A) \Delta n_g = 0$$

$$(B) \Delta n_g = -1$$

$$(C) \Delta n_g = 2$$

**Q.50** (A)  $\rightarrow P, R, S$ ; (B)  $\rightarrow P, Q, R, S$ ; (C)  $\rightarrow P, Q, R, S$ ; (D)  $\rightarrow Q$

As we know

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

$K_p$  &  $K_C$  ratio depend on T &  $\Delta n_g$

if we take  $T=0^\circ\text{C}$  than

$$(RT) > 1$$

(A) if  $\Delta n_g < 0$   $\frac{K_p}{K_c} < 1 \Rightarrow K_p < K_c$

if  $\Delta n_g > 0$   $\frac{K_p}{K_c} > 1 \Rightarrow K_p > K_c$

if we take  $T = 0^\circ\text{C}$  then

P, R, S

(B) Addition of inert gas at const pressure means pressure of equilibrium gases will decrease equilibrium shift where mole of gases are high due to the conc of reactant means equilibrium shifted to forward

$\Rightarrow \Delta n_g > 0$

But pressure is constant  $\Rightarrow$  volume  $\uparrow$

$\Rightarrow$  conc. of reactants  $\downarrow$

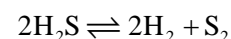
P, Q, R, S

(C)  $K_p^\circ$  always dimensionless P, Q, R, S

(D)  $T \downarrow$  forward shift  $\Rightarrow \Delta H > 0$

Molar conc. of  $\text{H}_2\text{S} = \frac{0.1}{0.4} \text{ mol L}^{-1} = 0.25 \text{ mol L}^{-1}$

Suppose degree of dissociation of  $\text{H}_2\text{S} = \alpha$  then



0.25 M

$0.25(1 - \alpha), 0.25 \alpha, \frac{0.25}{2} \alpha$

$= 0.125\alpha = 0.125\alpha$

$$K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

$$10^{-6} = \frac{(0.25\alpha)^2(0.125\alpha)}{[0.25(1 - \alpha)]^2}$$

Neglecting in comparison to 1 we get

$$10^{-6} = \frac{(0.25\alpha)^2(0.125\alpha)}{(0.25)^2} = 0.02$$

% age dissociation =  $0.02 \times 100 = 2\%$

### NUMERICAL VALUE BASED

Q.1 [2]

Q.2 [7]

Q.3 [3]

Q.4 [2]

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(1.59)^2}{1.26} = 2.00$$

Q.5 [1]

$$K_p = \frac{{}^n\text{Cl}_2 \times {}^n\text{PCl}_3}{{}^n\text{PCl}_5} \times \left[ \frac{P}{\Sigma n} \right]^1$$

$$= 2 \times \frac{2}{2} \times \left[ \frac{3}{6} \right]^1$$

1 atm

Q.6 [3]

Q.7 [0]

$$\Delta G^\circ = -2.303RT \log K_p$$

If  $K_p = 1, \Delta G^\circ = 0$

Q.8 [2]

Q.9 [2]

Q.10 [7]

As NaCl is salt of strong base + strong acid, it does not undergo salt hydrolysis

### KVPY

#### PREVIOUS YEAR'S

Q.1 (A)

Reaction quotient

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.4 \times 0.4}{0.1 \times 0.2}$$

$Q = 8$

$Q < K$

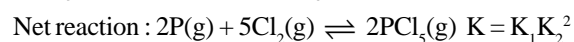
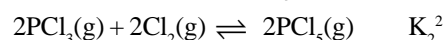
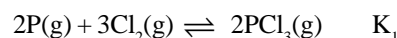
So reaction will proceed in forward direction.

Hence amount of HI increases

Q.2 (B)

Reaction move in forward direction

Q.3 (B)



Q.4 (D)

$$K_c = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$$

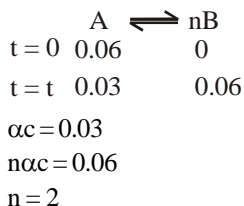
$$4 = \frac{0.5}{[\text{C}_2\text{H}_2]^3} \quad [\text{C}_2\text{H}_2]^3 = \frac{0.5}{4}$$

$$[\text{C}_2\text{H}_2]^3 = \frac{1}{8}$$

$$[\text{C}_2\text{H}_2] = \frac{1}{2}$$

$$[\text{C}_2\text{H}_2] = 0.5$$

**Q.5** (A)



$$K_c = \frac{(0.06)^2}{0.03} = \frac{(0.06)^2}{0.03} = 0.12$$

**Q.6** (B)

$$K_1 = \frac{[\text{SO}_3]}{[\text{O}_2]^{1/2}[\text{SO}_2]}$$

$$K_2 = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}$$

$$\text{Hence: } K_2 = \frac{1}{K_1^2}$$

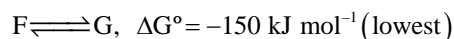
$$K_1^2 = \frac{1}{K_2}$$

**Q.7** (C)

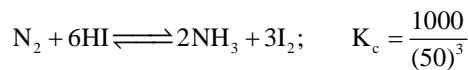
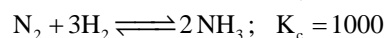
$$\Delta G^\circ = -2.303RT \log_{10} K$$

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

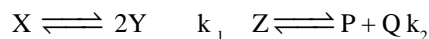
So lower value of  $\Delta G^\circ$  higher will be  $\log K$



**Q.8** (C)



**Q.9** (A)



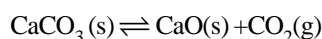
$$\begin{array}{cccccc} 1 & 0 & 1 & 0 & 0 \\ 1 - \alpha & 2 - \alpha & 1 - \alpha & \alpha & \alpha \end{array}$$

$$\frac{k_1}{k_2} = \frac{\frac{(2\alpha)^2}{(1+\alpha)}}{\frac{\alpha^2}{(1+\alpha)}} = \frac{4\alpha^2}{\alpha^2} = 4$$

**Q.10** (D)

According to Lechatelier principal on increasing volume of closed vessel equilibrium will shift towards right.

**Q.11** (A)



$$\Delta_f G^\circ = \Delta_f G^\circ(\text{CaO}) + \Delta_f G^\circ(\text{CO}_2) - \Delta_f G^\circ(\text{CaCO}_3)$$

$$= -603.501 - 394.389 + 1128.79 = 130.9 \text{ kJmol}^{-1}$$

$$\Delta_r G^\circ = -2.303 RT \log K_p$$

$$\log K_p = \frac{130.9 \times 1000}{-2.303 \times 298 \times 8.314} = -22.94$$

$$K_p = \text{antilog}(-22.94) = 1.13 \times 10^{-23}$$

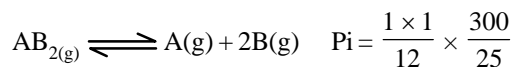
**Q.12** (D)

- Equilibrium constant is dependent on temperature.
- Equilibrium constant do not tell us about the rate of reaction.
- At equilibrium, the forward and backward reactions do not stop but they have same rate.

### JEE-MAIN

#### PREVIOUS YEAR'S

**Q.1** [7]



$$\begin{array}{ccc} 1 & - & - \\ 1 - x & x & 2x \end{array} = 1$$

$$1 + 2x = 19 \quad KP = \frac{P_A \times (P_B)^2}{P_{\text{AB}_2}}$$

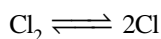
$$2x = 0.9 \quad KP = \frac{9 \times 9 \times 9 \times 20}{20 \times 100 \times 11}$$

$$x = 0.45$$

$$K_p = \frac{9 \times 9 \times 9}{100 \times 11} = 0.6627 \times 10^{-1}$$

Q.2

(5)



Moles x x

at eq<sup>n</sup>

$$\text{P.P.} \quad \frac{1}{2} \quad \frac{1}{2}$$

$$K_p = \frac{P_{\text{Cl}}^2}{P_{\text{Cl}_2}}$$

$$P = \frac{\left(\frac{1}{2}\right)^2}{\frac{1}{2}} = \frac{1}{2} = 0.5$$

$$= 5 \times 10^{-1}$$

$$x = 5$$

Q.3 (2)

Using formula

$$\Delta_r G^0 = -RT \ln K_p$$

$$25200 = -2.3 \times 8.3 \times 400 \log(K_p)$$

$$K_p = 10^{-3.3} = 10^{-3} \times 0.501$$

$$= 5.01 \times 10^{-4} \text{ Bar}^{-1}$$

$$= 5.01 \times 10^{-9} \text{ Pa}^{-1}$$

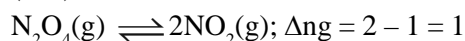
$$= \frac{K_c}{8.3 \times 400}$$

$$K_c = 1.66 \times 10^{-5} \text{ m}^3/\text{mole}$$

$$= 1.66 \times 10^{-2} \text{ L/mol}$$

$$\text{Ans} = 2$$

Q.4 (354)



$$\text{Now, } K_p = K_c \cdot (RT)^{\Delta n_g}$$

$$\text{or, } 600.1 = 20.4 \times (0.0831 \times T)^1$$

$$\therefore T = 353.99 \text{ K} = 354 \text{ K}$$

Q.5 (20)

$$\Delta G^0 = -RT \ln K_{\text{eq}}$$

$$\text{Given } \Delta G^0 = -9.478 \text{ KJ/mole}$$

$$T = 495 \text{ K} \quad R = 8.314 \text{ J mol}^{-1}$$

$$\text{So } -9.478 \times 10^3 = -495 \times 8.314 \times \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = 2.303$$

$$= \ln 10$$

$$\text{So } K_{\text{eq}} = 10$$

Now A(g) – B(g)

$$t = 0 \quad 22 \quad 0$$

$$t = t \quad 22-x \quad x$$

$$K_{\text{eq}} = \frac{[\text{B}]}{[\text{C}]} = \frac{x}{22-x} = 10$$

$$\text{or } x = 20$$

So millmoles of B = 20

Q.6 (875)

Q.7 (16)

Q.8 (1400)

Q.10 (25)

Q.11 (2)

Q.12 (172)

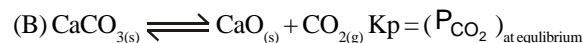
Q.13 [182]

Q.14 (6)

### JEE-ADVANCED PREVIOUS YEAR'S

Q.1 (A,B,D)

(A)  $\Delta H_2 - \Delta H_1 = C_{p(\text{rxn})}(T_2 - T_1)$  and  $C_p$  depends on temperature. Hence enthalpy also depends on temperature.



For a given reaction.

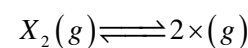
 $K_{\text{eq}}$  depends only on temperature.(C)  $K_{\text{eq}}$  depends only on temperature.

(D) Enthalpy of reaction is independent of the catalyst.

Catalyst generally changes activation energy.

### Paragraph for Question no. 2 to 3

Q.2 (B)



$$1 - \frac{\beta}{2} \quad \beta$$

$$K_p = \frac{\left[ \frac{\beta}{1 + \frac{\beta}{2}} \right]^2 \times 2^2}{\frac{1 - \frac{\beta}{2}}{1 + \frac{\beta}{2}} \times 2} = \frac{\beta^2}{1 - \frac{\beta^2}{4}} \times 2$$

$$K_p = \frac{8\beta^2}{4 - \beta^2}$$

**Q.3** (C)

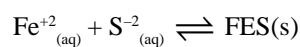
$$\Delta G^0 = (+)ve$$

$$\therefore -RT \ln K_p = \Delta G^0 = (+)ve$$

$$K_p < 1$$

Also  $\beta$  cant be 0.7 otherwise  $K_p$  will have to be (+)ve

**Q.4** (8.92 or 8.93)



$$0.03 \text{ M} \qquad \qquad 0.1 \text{ M}$$

$$(0.03 - x)(0.1 - x)$$

$$\approx y \qquad \approx 0.07$$

$$K_c \gg 10^3 \Rightarrow 0.03 - x \approx 0 \approx y$$

$$\Rightarrow x = 0.03$$

$$K_c = 1.6 \times 10^{17} = \frac{1}{y \times 0.07}$$

$$y = \frac{10^{-17}}{1.6 \times 0.07} = 8.928 \times 10^{-17} = Y \times 10^{-17}$$

$$y = 8.93$$

**Q.5** [0.25]

$$K_{eq} = \frac{[B]}{[A]}$$

$$K_{1000} = \frac{10}{1} = 10 \text{ and } K_{2000} = \frac{100}{1} = 100$$

$$\text{Now, } \frac{\Delta G^0_{1000}}{\Delta G^0_{2000}} = \frac{(-RT \ln k_{eq})_{1000}}{(-RT \ln k_{eq})_{2000}} = \frac{1000 \times \ln 10}{2000 \times \ln 100}$$

$$= 0.25$$



# Ionic Equilibrium

## ELEMENTRY

**Q.1** (4)

**Q.2** (3)

Because it is a electron pair acceptor it's central atom have a vacant d-orbital

**Q.3** (2)

The basic character of hydride decreases down the group.

**Q.4** (4)

**Q.5** (1)

$\text{BF}_3$  is a Lewis acid because 'B' has incomplete octet.

**Q.6** (2)

According to Bronsted principle  $\text{HNO}_3$  is acid they give  $\text{H}^+$  in aqueous solution and form  $\text{NO}_3^-$ .

**Q.7** (4)

$10^{-3} \text{ N KOH}$  will give  $[\text{OH}^-] = 10^{-2} \text{ M}$

$$\text{pOH} = 2$$

$\therefore \text{pH} + \text{pOH} = 14$ ,  $\text{pH} = 14 - 2 = 12$

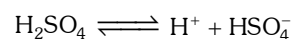
**Q.8** (2)

For pure water  $[\text{H}^+] = [\text{OH}^-]$ ,  $\therefore K_w = 10^{-12} \text{ s}$

**Q.9** (1)

Because pure water has a 7 pH.

**Q.10** (3)



**Q.11** (3)

It is a conjugate base of the strong acid.

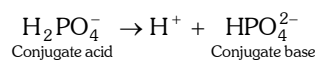
**Q.12** (1)

Conjugate acid is obtained from the base by gain of  $\text{H}^+$ .

**Q.13** (4)

$\text{HCl}$  is a strong acid its conjugate base means  $\text{Cl}^-$  is a weak base

**Q.14** (4)



**Q.15** (3)

$\text{pH} = 4$  means;  $[\text{H}^+] = 10^{-4} \text{ mol}$

**Q.16** (3)

$\text{H}_2\text{SO}_4$  ionized in two step

**Q.17** (2)

$$[\text{H}^+] = 2 \times 10^{-2} \text{ M}$$

$$\therefore \text{pH} = -\log [2 \times 10^{-2}];$$

$\text{pH} = 1.7$  i.e. in between 1 and 2.

**Q.18** (2)

**Q.19** (3)

$0.01 \text{ M HCl} = 10^{-2} \text{ M } [\text{H}^+]$ ,  $\text{pH} = 2$ .

**Q.20** (2)

Because the degree of dissociation is inversely proportional to the concentration of the electrolyte

**Q.21** (1)

$$K = \frac{\alpha^2 C}{1 - \alpha}; \alpha = \frac{0.01}{100} \approx 1 \therefore K = \alpha^2 C = \left[ \frac{0.01}{100} \right]^2 \times 1 = 1 \times 10^{-8}.$$

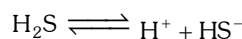
**Q.22** (3)

**Q.23** (1)

In weak electrolyte the degree of dissociation is very small. So it increases with increasing dilution

**Q.24** (4)

In aqueous solution following equilibrium is exist.



While adding the dilute  $\text{HCl}$  solution

$(\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-)$  equilibrium is shift to the left

side in  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$

**Q.25** (1)

$$[\text{H}^+] = c \times \alpha = 0.1 \times \frac{30}{100} = 0.03 \text{ M}$$

- Q.26** (1)  
 $[H^+] = \sqrt{Kc} = \sqrt{10^{-5} \times 0.1} = 10^{-3}$ , pH = 3
- Q.27** (4)  
 Salt of a strong base with a weak acid
- Q.28** (3)  
 (3)  $Fe^{3+}$  ions are hydrolysed to develop acidic nature
- Q.29** (3)  
 0.001 M of NaOH means  $[OH^-] = .001$   
 $= 10^{-3} M \Rightarrow pOH = 3$   
 $pH + pOH = 14 \Rightarrow pH = 14 - 3 = 11$
- Q.30** (1)  
 $MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl$
- Q.31** (2)  
 It contains replacable H atom.
- Q.32** (3)  
 $CH_3COONH_4$  is a simple buffer and called salt of weak acid.
- Q.33** (4)  
 $NH_4OH$  is a weak acid and  $NH_4Cl$  is a strong base salt.
- Q.34** (1)  
 $pH = pK_a + \log \frac{[Salt]}{[Acid]} = -\log 2 \times 10^{-5} + \log \frac{10 \times 1}{50 \times 2} = 4$ .
- Q.35** (2)  
 $CaF_2 \rightleftharpoons Ca_{(s)}^{++} + 2F_{(2S)}^- ; K_{sp} = 4S^3$
- Q.36** (2)  
 Due to common ion effect.
- Q.37** (4)  
 $K_{sp}$  for  $CaF_2 = 4s^3 = 4 \times [2 \times 10^{-4}]^3 = 3.2 \times 10^{-11}$ .

## JEE-MAIN

## OBJECTIVE QUESTIONS

- Q.1** (4)  
 $HCl(aq) + CH_3COOH(aq) \longrightarrow Cl^-(aq) + CH_3COOH_2^+(aq)$   
 Acid-1 base-2 base-1 acid-2
- Q.2** (4)  
 $HC_2O_4^-(aq) + PO_4^{3-}(aq) \longrightarrow HPO_4^{2-}(aq) + C_2O_4^{2-}(aq)$   
 Acid-1 base-2 base-1 acid-2
- Q.3** (1)  
 $NH_2^- + H^+ \longrightarrow$
- Q.4** (3)  
 Amphiprotic : can accept and Release  $H^+$   
 Only  $H_2PO_4^-$  &  $HCO_3^-$
- Q.5** (4)  
 Fact based
- Q.6** (1)  
 $[OH^-] =$  in pure water.  
 So as temperature increases  $K_w$  decreases  $[OH^-]$  decreases.
- Q.7** (2)  
 $[H^+] = 5.5 \times 10^{-2} M$   
 $\therefore pH = 2 - 0.74 = 1.26$
- Q.8** (3)  
 Factual.
- Q.9** (2)  
 In this solution, source of  $OH^-$  is water  
 $\therefore \alpha = [OH^-]$   
 $\alpha = 1.8 \times 10^{-11} M$   
 % ionisation =  $1.8 \times 10^{-9} M$
- Q.10** (4)  
 $[H^+]_1 = 10^{-2}$ ;  $[H^+]_2 = 10^{-6} = 10^4$
- Q.11** (2)  
 (1) At  $25^\circ C$ ,  $[H^+]$  in a solution of  $10^{-8} M HCl > 10^{-7} M$ .  
 (2)  $[H^+] = 10^{-8} M$ .  
 (3)  $[OH^-] = 4 \times 10^{-6} M \Rightarrow [H^+] = 2.5 \times 10^{-9} M$ .

(4)  $[H^+] = 10^{-9} \text{ M}$ .

$\Rightarrow \text{pH} = \text{pK}_a = 4.5$

$\Rightarrow \text{pOH} = 9.5$

**Q.12** (3)

$[H^+] = 0.016 \text{ M}$

$[H^+][OH^-] = 10^{-14} \Rightarrow [OH^-] = 6.25 \times 10^{-13} \text{ M}$

**Q.13** (1)

Initial

$\text{pH} = 12$

$[H^+] = 10^{-12} \text{ M}$

$[OH^-] = 10^{-2} \text{ M}$

Initial No. of mole of  $OH^- = 10^{-2}$  Final No. of mole of  $OH^- = 10^{-3}$ 

So no. of mole of  $OH^-$  removed =  $[.01 - 0.001] = 0.009$

**Q.14** (4)

(1) HClNaOH

No. of mili eq. =  $\times 100 = 10 \times 100 = 10$

So solution is Neutral

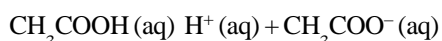
(2)  $\times 55 = 5.5 \times 45 = 4.5$

$[H^+] = 10^{-2} \text{ M}, \text{pH} = 2$

(3)  $\times 10 = 1 \times 90 = 9$  Basic

(4)  $\times 75 = 15 \times 25 = 5$

$[H^+] = 0.1 \text{ M}, \text{pH} = 1$

**Q.15** (3)As  $V \rightarrow$ , effect of water dominates so pH become 7.**Q.16** (3)

$t = 0 \quad 0.01$

$t = \text{eq } 0.01 - xx \quad x$

$[H^+] = x + 0.01 \approx 0.01 \text{ M}$

$\therefore K_a \Rightarrow 1.69 \times 10^{-5} =$

$\therefore [CH_3COO^-] = 1.69 \times 10^{-5} \text{ M}$

So, degree of dissociation of  $CH_3COOH = 1.69 \times 10^{-3}$

**Q.17** (4)

$0.01 - x \quad x \quad 10^{-4}$

$= 2 \times 10^{-6}$  (Neglect  $x$ )

$x^2 + 10^{-4}x - 2 \times 10^{-8} = 0$

$x = 10^{-4}$

$[OH^-] = x + 10^{-4} = 2 \times 10^{-4}$

**Q.18**

$\text{pH} = \text{pK}_a + \log \left[ \frac{\text{salt}}{\text{acid}} \right]$

50% ionised  $\Rightarrow [\text{Salt}] = [\text{Acid}]$

**Q.19** (1)

$M$  of HCl =  $25 \times 0.5 = 12.5$

$M^{\text{eq}}$  of NaOH =  $10 \times 0.5 = 5$

$M^{\text{eq}}$  of HCl remaining  $12.5 - 5 = 7.5$

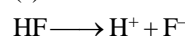
$[H^+] = 0.15$

$\text{pH} = -\log 0.15$

$= 0.8239$

**Q.20** (1)**Q.21** (4)

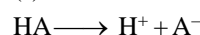
As concentration of solution decreases, degree of dissociation of weak electrolyte increases.

**Q.22** (3)

$\text{pK}_w = \text{pK}_a + \text{pK}_b$  [For conjugate Acid-Base]

$\Rightarrow \text{pK}_a = 14 - 10.87 = 3.17$

$K_a = 6.76 \times 10^{-4}$

**Q.23** (2)

$1 - x \quad x \quad x$

$x = 1\%$

$\Rightarrow [H^+] = 0.01$

$\Rightarrow \text{pH} = 2$

**Q.24** (3)Ostwald dilution law is valid for weak acid and  $CH_3COOH$  is the weak acid.**Q.25** (3)

NaCl Solution : pH is the, pH of water.

As  $T \uparrow$ ,  $K_w \uparrow$ , &  $[H^+] \uparrow$ pH at  $25^\circ\text{C} < 7$ **Q.26** (2)

Volume of resulting solution = 100 ml

$[H^+] = 10^{-3}$

$\Rightarrow \text{pH} = 3$ .

**Q.27** (3)

HCl

$N = 0.4$

$V = 50 \text{ ml}$

No. of milieq =

$[H^+] = 0.1 \text{ M}, \text{pH} = 1$

NaOH

$N = 0.2$

$V = 50 \text{ ml}$

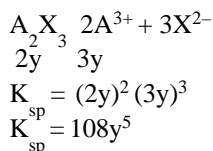
$0.4 \times 50 = 200.2 \times 50 = 10$

- Q.28** (2)  
 % Hydrolysis does not depend on the conc. in case of "Weak acid + weak base : Salt"
- Q.29** (1)  
 Weak acid + Strong base : Salt  
 $CN^- + H_2O \rightleftharpoons HCN + OH^-$   
 $-x \quad x \quad x \quad 2x$   
 X can be neglected  
 $\Rightarrow X = 3.1 \times 10^{-4}$   
 % Hydrolysis =  $\times 100$   
 = 2.48 %
- Q.30** (4)  
 Salt of weak acid & strong Base  
 $CH_3COONa \longrightarrow CH_3COO^- + Na^+$   
 $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$   
 Basic Solution
- Q.31** (4)  
 Factual
- Q.32** (1)  
 $h = .03 \quad C = 0.1 \text{ M}$   
 $K_h = Ch^2 = 9 \times 10^{-5}$   
 $K_h = \frac{9 \times 10^{-5}}{\times 10^{-10}} \quad K_a = 1.11 \times 10^{-10} \text{ l}$
- Q.33** (2)  
 Solution of HCl &  $NH_4Cl$  will be acidic, solution of NaCl neutral whereas solution of NaCN will be basic.
- Q.34** (1)  
 NaCl + HCl : Not the Buffer and Solution is acidic due to HCl.  
 $\Rightarrow pH < 7$ .
- Q.35** (4)  
 m. equivalent of KOH = 8  
 m. equivalent of HCOOH = 16  
 Remaining m. eq. (HCOOH) = 8  
 Formed m. eq. (HCOOK) = 8  
 $\Rightarrow$  Acidic Buffer  
 $pH = pK_a = 4 - \log 2$   
 = 3.7  
 $pOH = 10.3$
- Q.36** (2)  
 $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$   
 $t = 0 \quad \quad \quad 20 \quad \quad \quad 20$   
 $t = eq - \quad - 20$   
 So,  $[CH_3COO^-] = 0.1 \text{ M}$   
 $pH = 7 + pK_a + \log C = 7 + 2.37 + \log 10^{-1} = 7 + 2.37 - 0.5 = 8.87$
- Q.37** (3)  
 $pH = 8.7 \Rightarrow pOH = 5.3$   
 Basic Buffer  
 $\Rightarrow pOH = pK_b + \log$   
 $\Rightarrow = 4$   
 If volume of salt = V ml  
 $\Rightarrow = 4$
- Q.38** (4)  
 Factual
- Q.39** (3)  
 $K_b = 5 \times 10^{-10} \quad pK_a = 10 \log 5 = 9.3$   
 $pH = pK_b + \log$   
 $9 = 9.3 + \log - 0.3 = \log$   
 $0.3 = \log = 2 \quad V_{ml} = 2 \text{ ml}$
- Q.40** (1)  
 $pH = pK_a + \log$   
 $\Rightarrow 5.5 = 5 + \log$   
 $\Rightarrow = 3.16$   
 Suppose x m. mole NaOH was added  
 Acid + Base  $\longrightarrow$  Salt  
 $10x \quad 10$   
 $10 - x \quad 0 \quad 10 + x$   
 $\Rightarrow = 3.16 \Rightarrow x = 5.2 \text{ m.mole}$   
 $\Rightarrow \text{NaOH (mass)} = \times 40 = 0.208 \text{ g}$
- Q.41** (1)  
 $HCOOH + KOH \rightleftharpoons HCOOK + H_2O$   
 milimole 20 - 10  
 $10 - \quad \quad \quad 10$   
 $pH = pK_a + \log = 3.74 + \log \quad pH = 3.74$
- Q.42** (2)  
 $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$   
 time t = 0  
 $40 \text{ mmole} \quad 20 \text{ mmole}$   
 time t = t  
 $20 \text{ mmole} \quad -20 \text{ mmole}$   
 $pH = pK_a + \log \Rightarrow pH = pK_a \Rightarrow [H^+] = K_a = 1.8 \times 10^{-5} \text{ M}$

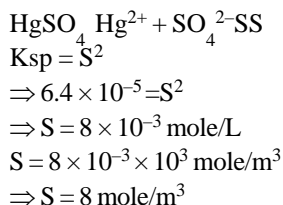
Q.43 (3)

Mole of NaOH is required for 1 lit solution = x  
 $\therefore$  Mole of NaOH is required for 100 ml of solution = 0.1x  
 Now,  $0.1x = 1 \times V$ ,  $V = 0.1x \text{ Lt} = 100x \text{ ml}$ .

Q.44 (4)



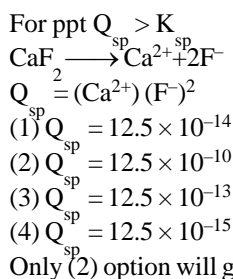
Q.45 (4)



Q.46 (4)

Calculate the solubility 's' for each option,  
 Higher the value of 's' Higher the solubility.

Q.47 (2)



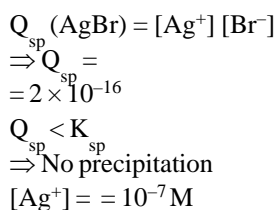
Q.48 (4)

WA Vs SB end point  $> 7$  Phenolphthalein

Q.49 (1)

Same as problem Number = 28

Q.50 (3)

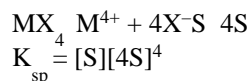


Q.51 (3)

$$pH = pK_a + \log \Rightarrow 6 = 5 + \log \Rightarrow 1 = \log$$

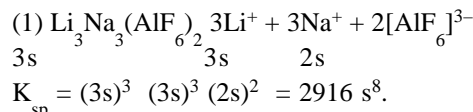
$$= 10$$

Q.52 (1)



$$\Rightarrow K_{sp} = 256S^5 \Rightarrow S = \left( \frac{K_{sp}}{256} \right)^{1/5}$$

Q.53 (4)



Q.54 (2)

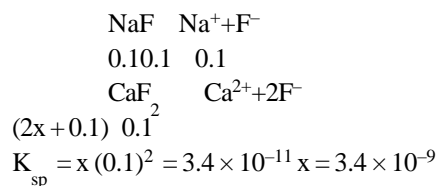
$$K_{sp} \text{ of } Mg(OH)_2 = 2.56 \times 10^{-13}$$

$$4s_1^3 = 2.56 \times 10^{-13} \quad s_1 = 4 \times 10^{-5} \text{ M}$$

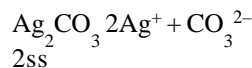
$$K_{sp} \text{ of } Al(OH)_3 = K_{sp} = 4.32 \times 10^{-34}$$

$$27s_2^4 = 4.32 \times 10^{-34} \quad s_2 = 2 \times 10^{-9} \text{ M} = 2 \times 10^4$$

Q.55 (3)



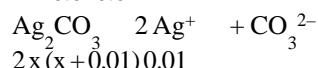
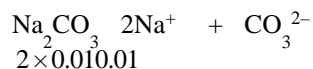
Q.56 (1)



$$\text{Here } [Ag^+] = 2s = 2 \times 10^{-4} \text{ M} \Rightarrow s = 1 \times 10^{-4}$$

$$\therefore K_{sp} = 4s^3 = 4(1 \times 10^{-4})^3 = 4 \times 10^{-12}$$

Q.57 (3)



$$K_{sp} = 4x^2(0.01)$$

$$K_{sp} = 4s^3 = 4 \times 10^{-12} = 4x^2(0.01) \quad x = 10^{-5}$$

Q.58 (3)

$$\text{Let } K_{sp} \text{ of } AgCl = x$$

(1) solubility of AgCl in pure water =  $s_1 = (2)$   
 solubility of AgCl in 0.01 M  $\text{CaCl}_2 = s_2 =$

(3) solubility of AgCl in 0.01 M NaCl =  $s_3 = (4)$   
 solubility of AgCl in 0.05 M  $\text{AgNO}_3 = s_4 =$

So  $s_1 > s_3 > s_2 > s_4$

**Q.59**

(1)

$K_{\text{sp}}(\text{BaCrO}_4) = 2.4 \times 10^{-10} \text{ M}^2$   
 $[\text{CrO}_4^{2-}] = 6 \times 10^{-4} K_{\text{sp}}(\text{BaCrO}_4) = [\text{Ba}^{2+}] [\text{CrO}_4^{2-}]$   
 $2.4 \times 10^{-10}$   
 $\Rightarrow [\text{Ba}^{2+}] \times 6 \times 10^{-4} = 2.4 \times 10^{-10}$   
 $[\text{Ba}^{2+}] = 4 \times 10^{-7} \text{ M}$  **Ans.**

**Q.60**

(1)

$\text{pH} = 4 \Rightarrow [\text{H}^+] = 10^{-4} \text{ M} \Rightarrow [\text{OH}^-] = 10^{-10} \text{ M}$   
 $\text{Al}(\text{OH})_3 \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^-$   
 $K_{\text{sp}}(\text{Al}(\text{OH})_3) = [\text{Al}^{3+}] [\text{OH}^-]^3$   
 $[\text{Al}^{3+}] [\text{OH}^-]^3 = 1 \times 10^{-33}$   
 $[\text{Al}^{3+}] (10^{-10})^3 = 1 \times 10^{-33} \Rightarrow [\text{Al}^{3+}] = 10^{-3} \text{ M}$

**Q.61**

(4)

Higher the concentration of  $\text{H}^+$ , higher is the solubility of  $\text{Fe}(\text{OH})_3$ .  
 solubility of  $\text{Fe}(\text{OH})_3$  is maximum in 0.1 M  $\text{H}_2\text{SO}_4$

**Q.62**

(4)

$\text{MnS(s)} \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ ;  $\text{S}^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{S}(\text{aq})$

**Q.63**

(1)

order of solubility : Complex formation > Pure water > Common ion effect.  
 $\text{AgBr}$  form complex  $[\text{Ag}(\text{NH}_3)_2]^+$  in  $\text{NH}_3$  so solubility is maximum in  $\text{NH}_3(\text{aq})$ .

**Q.64**

(1)

pH of 0.1 M  $\text{H}_2\text{S}$  solution can be derived by :  
 $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ ;  $K_1 = 1 \times 10^{-7}$

$\therefore [\text{H}^+] = C\alpha = C = 10^{-4} \therefore \text{pH} = 4$

**Q.65**

(3)

$\text{H}_2\text{A} \rightleftharpoons \text{H}^+ + \text{HA}^-$   
 $10^{-5} =$   
 $\text{HA}^- \rightleftharpoons \text{H}^+ + \text{A}^{2-}$   
 $5 \times 10^{-10} =$   
 $\text{H}_2\text{A} \rightleftharpoons 2\text{H}^+ + \text{A}^{2-}$   
 $K_{\text{overall}}^2 = 5 \times 10^{-10} \times 10^{-5}$   
 $= 5 \times 10^{-15}$

**JEE-ADVANCED**

**OBJECTIVE QUESTIONS**

**Q.1** (D)

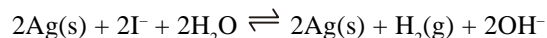
$$\log \frac{(K_w)_{50^\circ\text{C}}}{(K_w)_{25^\circ\text{C}}} = \frac{\Delta H}{2.303} \left[ -\frac{1}{323} + \frac{1}{298} \right]$$

$$\Rightarrow \log \frac{5.474}{1.08} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{25}{323 \times 290}$$

$(\Delta H)_{\text{ionization}}$  of  $\text{H}_2\text{O} = 51.963 \text{ KJ/mol}$

$\therefore (\Delta H)_{\text{Neutralization}} = -51.963 \text{ KJ/mol}$

**Q.2** (C)



$$K_{\text{eq}} = \frac{[\text{H}_2][\text{OH}^-]^2}{[\text{I}^-]^2} \dots\dots\dots(1)$$

For  $\text{H}_2(\text{s})$

$$PV = nRT,$$

$$P = CRT$$

$$C = \frac{P}{RT} = \frac{0.6}{0.082 \times 298} = 0.0245$$

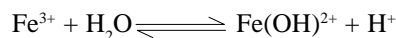
From eq<sup>n</sup>(1)

$$[\text{OH}^-]^2 = \frac{1.2 \times 10^{-2} \times (0.1)^2}{0.0245}$$

$$[\text{OH}^-] = 0.0699$$

$$[\text{OH}^-]^2 = \frac{1.2 \times 10^{-2} \times (0.1)^2}{0.6} = 1.650$$

**Q.3** (D)



$$\text{conc at eq}^n \frac{1-0.05}{V} \frac{0.05}{V} \frac{0.05}{V} \frac{0.05}{V}$$

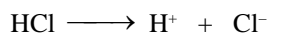
$$\text{we have } K_{\text{eq}} = 6.5 \times 10^{-3} = \frac{(0.05/V)^2}{(1-0.05/V)}$$

$$\Rightarrow V = \frac{100}{19 \times 13}$$

$$\therefore (\text{H}^+) = \frac{0.05}{V} = 0.1235$$

$$P_{\text{H}} = -\log(\text{H}^+) = 0.908$$

Q.4 (B)



$$(x+x) \quad (x)$$



$$(x+x) \quad (x)$$

$$\text{Ionic product} = K_w = (2x)(x) = 10^{-14}$$

$$\Rightarrow 2x^2 = 10^{-14} \Rightarrow x = \sqrt{50} \times 10^{-8}$$

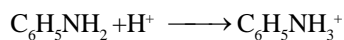
Q.5 (A)

Order of basic strength  $\text{O}^{2-} > \text{S}^{2-} > \text{Se}^{2-} > \text{Te}^{2-}$ 

Q.6 (A)

pH of amphiprotic salts and weak acid-weak base salt is independent of its concentration.

Q.7 (C)



$$t=0 \quad 5 \qquad 2.5t_{\text{eq}} \quad 2.5-2.5$$

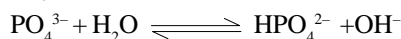
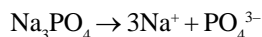
$$\text{pOH} = \text{p}K_a = 14 - 8 = 6$$

$$\therefore \text{p}K_a = 6$$

Now for the solution of  $[\text{C}_6\text{H}_5\text{NH}_3^+] = 0.01 \text{ M}$ 

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C = 7 - \frac{6}{2} - \frac{1}{2} \log(0.01) = 5$$

Q.8 (A)



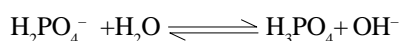
$$K'_3 = \frac{K_w}{K_3} = \frac{10^{-14}}{4.5 \times 10^{-13}}$$

$$0.1(1-\alpha_1)0.1\alpha_1(1-\alpha)0.1\alpha_1 + 0.1\alpha_1\alpha_2 + 0.1\alpha_1\alpha_2\alpha_3$$



$$K'_2 = \frac{K_w}{K_2} = \frac{10^{-14}}{6.3 \times 10^{-8}}$$

$$0.1(1-\alpha_2)0.1\alpha_1\alpha_2(1-\alpha_3)0.1\alpha_1\alpha_2 + 0.1\alpha_1 + 0.1\alpha_1\alpha_2\alpha_3$$



$$K'_1 = \frac{K_w}{K_1} = \frac{10^{-14}}{7.1 \times 10^{-3}}$$

$$0.1\alpha_1\alpha_2(1-\alpha_3) \quad 0.1\alpha_1\alpha_2\alpha_3 \quad 0.1\alpha_1\alpha_2\alpha_3 + 0.1\alpha_1 + 0.1\alpha_1\alpha_2$$

$$\text{Now } 1 - \alpha_2 \approx 1$$

$$1 - \alpha_3 \approx 1$$

$$\text{or } [\text{OH}^-] = 0.1\alpha_1$$

$$\text{We have } K'_3 = \frac{[\text{OH}^-][\text{HPO}_4^{2-}]}{[\text{PO}_4^{3-}]} = \frac{0.1\alpha_1 \times 0.1\alpha_1}{0.1(1-\alpha_1)}$$

$$= 0.022$$

$$0.1\alpha_1^2 = 0.022 - 0.022\alpha_1$$

$$0.1\alpha_1^2 + 0.022\alpha_1 - 0.022 = 0$$

$$\alpha_1 = 3.73 \times 10^{-2} \text{ M}$$

$$[\text{OH}^-] = 0.1\alpha_1 = 3.73 \times 10^{-2} \text{ M}$$

$$K'_2 = \frac{[\text{OH}^-][\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}$$

$$\text{As, } [\text{OH}^-] \approx [\text{HPO}_4^{2-}]$$

$$\text{We have, } [\text{H}_2\text{PO}_4^-] = K_2^{-1} = 1.587 \times 10^{-7} \text{ M}$$

$$\text{So, } K'_1 = \frac{[\text{OH}^-][\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]}$$

$$[\text{H}_3\text{PO}_4] = \frac{10^{-14}}{7.1 \times 10^{-3}} \times \frac{1.587 \times 10^{-7}}{3.73 \times 10^{-2}} = 6 \times 10^{-18} \text{ M}$$

Q.9 (C)

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\Rightarrow 4.5 = 4.2 + \log \left( \frac{V_2}{V_1} \right) \Rightarrow \frac{V_2}{V_1} = 2$$

$$\therefore \text{ volume of } \text{C}_6\text{H}_5\text{COONa} \text{ required} = V_2 = 200 \text{ ml}$$

$$\text{ volume of } \text{C}_6\text{H}_5\text{COOH} \text{ required} = V_1 = 100 \text{ ml.}$$

Q.10 (B)

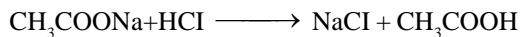
For the buffer solution of  $\text{NH}_3$  &  $\text{NH}_4^+$ 

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow 8.26 = 9.26 + \log$$

$$\frac{(500 \times 0.01)}{\text{m. moles of } \text{NH}_4^+}$$

$\Rightarrow$  m. moles of  $\text{NH}_4^+ = 50 \therefore$  moles of  $(\text{NH}_4)_2 \text{SO}_4$  required = **0.025**.

**Q.11** (A)



$t = 0$  20 m eq.                      20 meq.  $t_{\text{eq}}$  — 20 meq.

$$[\text{CH}_3\text{COOH}] = \frac{20}{200} = 0.1 \text{ M}$$

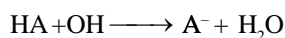
$$\text{pH} = \frac{1}{2} [\text{pK}_a - \log C] = \frac{1}{2} [5 - \log 2 + 1]$$

$$= \frac{1}{2} [6 - \log 2] = 3 - \log \sqrt{2}$$

**Q.12** (C)

meq. of acid = meq of base  $\Rightarrow 20 \times M = 20 \times 0.2 = 4$

Molarity of HA = 0.2 M



5                      2m. mole

3—                      2 m. mole

$$\therefore \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow 5.8 = \text{pK}_a + \log \left( \frac{2}{3} \right) \Rightarrow \text{pK}_a$$

= **5.98**

**Q.13** (D)



Difference in pH between  $\frac{1}{3}$  &  $\frac{2}{3}$  stages of

$$\text{neutralisation} = \left[ \text{pK}_a + \log \left( \frac{2/3}{1/3} \right) \right] -$$

$$\left[ \text{pK}_a + \log \left( \frac{1/3}{2/3} \right) \right] = 2 \log 2.$$

**Q.14** (B)

m. moles of HA taken =  $27 \times 0.1 = 2.7$



$t=0$  2.71.2

$t_{\text{eq}}$  1.5 — 1.2

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow 5 = \text{pK}_a + \log \left( \frac{1.2}{1.5} \right)$$

$$= \text{pK}_a + \log \frac{4}{5}$$

$$\therefore \text{pK}_a = 5.1 \Rightarrow \text{K}_a = 8 \times 10^{-6}.$$

**Q.15** (B)

m. moles of HCl =  $0.1 \times 20 = 2$

m. moles of  $\text{CH}_3\text{COOH} = 0.1 \times 20 = 2$

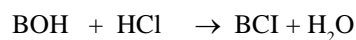
After titration of HCl by NaOH

$$[\text{CH}_3\text{COOH}] = \frac{2}{40} = \frac{1}{20} \text{ M}$$

$$\therefore \text{pH} = \frac{1}{2} (\text{pK}_a - \log C)$$

$$= \frac{1}{2} [5 - \log 2 - \log \left( \frac{1}{20} \right)] = 3.$$

**Q.16** (B)



Initially 4 0.16  $\times$  V 0

no. of milli moles

After R $\times$ n 0 0 4

$$\Rightarrow 0.16 \times V = 4$$

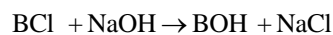
$$\therefore \text{Concentration of BCl} = \frac{4}{25 + 40}$$

$$= \frac{4}{65} 6.15 \times 10^{-2} \text{ M}$$

$$\therefore \text{pH} = \frac{1}{2} [\text{pk}_2 - \text{pk}_b - \log C] = 5.23$$

$$\Rightarrow \text{pk}_b = 4.75$$

Now,



Initially 4 1.800

no. of milli moles

After R $\times$ n 4 — 1.801.81.8

$$= 2, 2 = 0 = 1.8$$

The mixture is buffer of BOH and BCl



$$\therefore P_{OH} = pK_b + \log \frac{[BCl]}{[BOH]}$$

$$= 4.75 + \log \frac{2.2}{1.8}$$

$$P_{OH} = \mathbf{9.16}$$

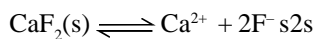
**Q.17** (B)

(A) pH of  $\text{NaHCO}_3$  is independent of dilution.

(C) pH of buffer solution is approximately remains constant with dilution.

(D) pH of salt of WA & WB is independent of dilution.

**Q.18** (C)



$$4s^3 = K_{sp} = 4 \times 10^{-11} \Rightarrow s = 2.15 \times 10^{-4} \text{ M}$$

So, amount of  $\text{F}^-$  in 20000 lt of water

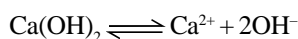
$$= 2s \times 20000 = \mathbf{8.6 \text{ mol.}}$$

**Q.19** (C)

$$[\text{Fe}^{3+}][\text{OH}^-]^3 \geq K_{sp}$$

$$[\text{OH}^-] \geq 3.7 \Rightarrow pOH \leq 3.7 \Rightarrow pH \geq \mathbf{10.3.}$$

**Q.20** (B)

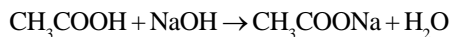


$$t = 0 \quad \frac{1.48}{74} = 0.02 \quad \text{0.02} \quad \text{0.04}$$

$$\text{so, } pOH = 2 - \log 4 = 1.4$$

$$\text{so } pH = 12.6$$

**Q.21** (D)



Initially

no. of milli moles 20.10

After  $r \times n$  1.900 0.1

$$(P_H)_1 = PKa + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

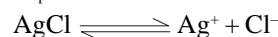
$$= PKa + \log \frac{0.1}{1.9}$$

$$\text{Similarly } (P_H)_2 = PKa + \log \frac{1.9}{0.1}$$

$$= p_H = (P_H)_2 - (P_H)_1 = \log \frac{(1.9)^2}{(0.1)^2} = \mathbf{2.558}$$

**Q.22** (A)

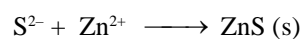
$$K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}$$



$$2.8 \times 10^{-10} = (s + 0.1)s$$

$$s = 2.8 \times 10^{-9}$$

**Q.23** (A)



m.moles 0.40.20.2-so in solution,

$$[\text{S}^{2-}] = \frac{0.2}{20} = 0.01 \text{ M}$$

$$\therefore [\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{S}^{2-}]} = \frac{4 \times 10^{-24}}{0.01} = 4 \times 10^{-22} \text{ M}$$

$\therefore$  mass of  $\text{Zn}^{2+}$  remain unprecipitated in 20 ml of

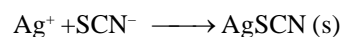
$$\text{solution} = \frac{4 \times 10^{-24}}{1000} \times 20 \times 65 = \mathbf{5.2 \times 10^{-22} \text{ gm.}}$$

**Q.24** (A)

m.moles of  $\text{Ag}^+$  in 100 ml of saturated solution of  $\text{AgCl}$

$$= \sqrt{K_{sp}} \times 100 = 1.4 \times 10^{-3}$$

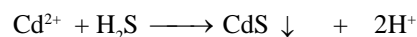
Now



m.moles of  $\text{SCN}^-$  = m.moles of  $\text{Ag}^+$

$$1 \times 10^{-5} \times V = 1.4 \times 10^{-3} \Rightarrow \text{volume} = \mathbf{140 \text{ mL.}}$$

**Q.25** (A)



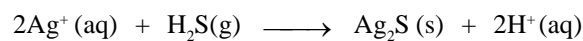
m.moles 0.10.2

Total m.moles of  $\text{H}^+$  in solution after the reaction

$$= 0.2 + 0.8 = 1$$

$$\therefore [\text{H}^+] = \frac{1}{100} = 0.01 \text{ M} \Rightarrow pH = \mathbf{2.}$$

**Q.26** (A)



;

$$K = 10^{29}$$

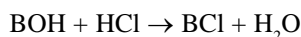
moles of  $\text{H}_2\text{S}$  dissolved =  $1.5 \times 10^{-4}$

$\therefore$  moles of  $\text{Ag}^+$  precipitated =  $3 \times 10^{-4}$

$$\therefore K_{sp}(\text{AgBrO}_3) = \left( \frac{3 \times 10^{-4}}{0.25} \right) \left( \frac{3 \times 10^{-4}}{0.25} \right) = 1.44 \times 10^{-6}$$

**Q.27** (B)

**Q.28** (A)



$$a - \frac{a}{4} = 6$$

$$= 24 \times \frac{3}{4} = 18 \text{ meq} \quad \text{Now, } \frac{a}{4} = 6 \text{ meq}$$

$$P_{\text{OH}} + \log \frac{[\text{salt}]}{[\text{basic}]} = 24 \text{ meq}$$

$$= PK_b + \log \frac{4}{4 \times 3} = 14 - 9.24 = 4.76$$

$$\Rightarrow PK_b = 5.237$$



$$\begin{array}{r} 6 - 6 \\ = 0 \end{array} \quad \begin{array}{r} 6 - 6 \\ = 0 = 6 = 6 \end{array}$$

Total BOH =  $6 + 18 = 24 \text{ meq}$

$$\therefore (\text{BOH}) = \frac{24}{50} \text{ M}$$

$$P_{\text{OH}} = \frac{1}{2} [PK_b - \log C]$$

$$= \frac{1}{2} [5.237 - \log \frac{24}{50}] = 2.774$$

$$\therefore P_{\text{H}} = 11.22$$

**Q.29** (C)

If  $x$  be the concentration of  $\text{AgCl}$  in the solution, then  $[\text{Cl}^-] = x$

From the  $K_{sp}$  for  $\text{AgCl}$ , we derive

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.7 \times 10^{-10}}{x}$$

If we answer that the majority of the dissolved  $\text{Ag}^+$  goes into solution as  $\text{Ag}(\text{NH}_3)_2^+$  then  $\text{Ag}(\text{NH}_3)_2^+$  then  $\text{Ag}(\text{NH}_3)_2^+ = x$

Since two molecules of  $\text{NH}_3$  are required for every  $\text{Ag}(\text{NH}_3)_2^+$  ion formed, we have  $[\text{NH}_3] = 0.2 - 2x$

$$\therefore K_{\text{inst}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

$$= \frac{\left( \frac{1.7 \times 10^{-10}}{x} \right) (0.2 - 2x)^2}{x} = 6 \times 10^{-8}$$

$\therefore x = [\text{Ag}(\text{NH}_3)_2^+] = 9.6 \times 10^{-3} \text{ M}$ , which is the solubility of  $\text{AgCl}$  in  $0.2 \text{ M NH}_3$

## JEE-ADVANCED

### MCQ/COMPREHENSION/COLUMN MATCHING

**Q.1** (B, D)

$$pK_a(\text{H}_3\text{O}^+) = -1.74 = pK_b \text{ of } \text{OH}^-$$

$pK_a + pK_b = 14$  only for conjugate acid base pair.

$$\alpha = 1.8 \times 10^{-9} \text{ or } 1.8 \times 10^{-7} \% \text{ for } \text{H}_2\text{O}.$$

**Q.2** (A, B, C)

$$pK_w = -\log K_w = -\log 1 \times 10^{-12} = 12.$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-12}.$$

$$[\text{H}^+] = [\text{OH}^-]$$

$$\Rightarrow [\text{H}^+]^2 = 10^{-12}; [\text{H}^+] = 10^{-6}; \text{pH} = -\log[\text{H}^+] = -\log 10^{-6} = 6.$$

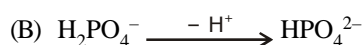
$\text{H}_2\text{O}$  is neutral because  $[\text{H}^+] = [\text{OH}^-]$  at  $373 \text{ K}$  even when  $\text{pH} = 6$ .

(D) is not correct at  $373 \text{ K}$ . Water cannot become acidic.

**Q.3** (B, C)

(A) pH of  $10^{-8} \text{ M}$  sol. of  $\text{HCl}$  is  $6.97$

(consider the  $\text{H}^+$  from  $\text{H}_2\text{O}$  also)



$$\text{(C) } K_w = [\text{H}^+][\text{OH}^-]$$

On  $\uparrow$  temp  $[\text{H}^+][\text{OH}^-]$

both  $\uparrow \Rightarrow K_w \uparrow$



$$\text{pH} = \text{pK}_a + \log \frac{\text{salt}}{\text{acid}}$$

**Q.4** (B, C)

(B) is correct because  $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Base}]}$  for acidic buffer.

If  $[\text{Salt}]$  increases, pH of acidic buffer will increase.

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Acid}]} \text{ for basic buffer.}$$

If [Salt] increases, pOH will increase, pH will decrease as  $\text{pH} = 14 - \text{pOH}$ .

Therefore (C) is correct but (D) is wrong.

(A) is not correct  $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

If [Salt] increase, pH will increase.

**Q.5** (B, C, D)

(B), (C) and (D) are the mixtures of conjugate acid-base pairs.

**Q.6** (A, B)

(A) is buffer because it contains weak acid and its salt and they will also show common ion effect.

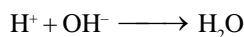
(B) is also a buffer because it contains a weak acid and its salt. They will not show common ion effect.

(C) is not buffer solution because they contains strong acids and its salt. They will not show common ion effect.

(D) is not a buffer solution because it contains strong acids and its salt. They will not show common ion effect.

**Q.7** (A, D)

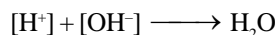
(A)  $[\text{H}^+] = 10^{-2}$  and  $[\text{OH}^-] = 10^{-2}$



This leads complete neutralisation

$$\text{so, } \text{pH} = 7 = \frac{2+12}{2}$$

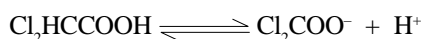
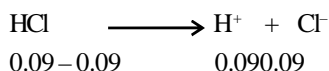
(D)  $[\text{H}^+] = 10^{-5}$  and  $[\text{OH}^-] = 10^{-5}$



This leads complete neutralisation

$$\text{so, } \text{pH} = 7 = \frac{5+9}{2}$$

**Q.8** (A,B,C)



$$0.1 - y \quad y \quad + 0.09 + x$$

$$\text{We have, } y + 0.09 + x = 10^{-1} = 0.10$$

$$x + y = 0.01$$

$$\text{Also, } K_{\text{CH}_3\text{COOH}} = 10^{-5} = \frac{0.1 \times y}{0.01 - y} \approx \frac{0.01}{0.1}$$

$$\therefore x \approx 0.01$$

$$\therefore K_{\text{Cl}_2\text{HCCOOH}} = \frac{x \times 0.1}{0.09 - 0.01} = \frac{0.01 \times 0.1}{0.08}$$

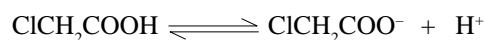
$$= 1.25 \times 10^{-2}$$

**Q.9** (A,B,C)

MW of  $\text{ClCH}_2\text{COOH} = 44.5$

$$\text{No. of Moles of acid} = \frac{9.45}{94.5} = 0.1$$

$$\therefore [\text{acid}] = 0.1 \times 2 = 0.2 \text{ M}$$



$$0.2(1 - \alpha) \quad 0.1 \alpha \quad 10^{-2} = 0.2 \alpha$$

$$\alpha = \frac{10^{-2} \times 10^5}{2} = 0.05$$

**Q.10** (A, C, D)

(A) In 0.6 m M HCOOH solution

$$K_a = \frac{[\text{H}^+]^2}{\text{C} - [\text{H}^+]} \Rightarrow 8 \times 10^{-4} = \frac{[\text{H}^+]^2}{6 \times 10^{-4} - [\text{H}^+]}$$

$$\therefore [\text{H}^+] = 4 \times 10^{-4} \text{ M.}$$

So solution in (A), (C) & (D) are ISOHYDRIC.

**Q.11** (A, B)

$$\text{Total } [\text{H}^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{\left(3.6 \times 10^{-4} \times \frac{0.5}{500} \times 100\right) + \left(8 \times 10^{-4} \times \frac{0.1}{500} \times 400\right)}$$

$$\therefore [\text{H}^+] = 10^{-2} \text{ M.}$$

$$\text{For } \text{HN}_3, [\text{N}_3^-] = \frac{K_a[\text{HN}_3]}{[\text{H}^+]} = \frac{3.6 \times 10^{-4} \times 0.5}{0.01 \times 500} \times 100 =$$

$$3.6 \times 10^{-3} \text{ M.}$$

$$\text{For } \text{HOCN}, [\text{OCN}^-] = \frac{K_a[\text{HOCN}]}{[\text{H}^+]}$$

$$= \frac{8 \times 10^{-4} \times 0.1 \times 400}{0.01 \times 500} = 6.4 \times 10^{-3} \text{ M.}$$

**Q.12** (A, C)

As  $K_a$  of acid increases,  $K_b$  of its conjugate base decreases.

**Q.13** (B, C)

On the basis of ostwald dilution law, number of  $\text{H}^+$  ions will increase but increase in volume will be more. Therefore,  $[\text{H}^+]$  decreases, pH increases.

**Q.14** (B, C, D)

Let BA be this salt  $BA \rightarrow B^+ + A^-$

$A^-$  does not undergo hydrolysis because HA is strong acid.  $B^+$  undergoes hydrolysis

$h = h =$  degree of hydrolysis where  $K_h =$  Hydrolysis constant = .

$h \propto$  greater the hydrolysis constant greater the  $h$  (degree of hydrolysis).

$h \propto$  greater the  $K_b$  lesser the  $h$ .

Hydrolysis is endothermic,  $K_h$  increases with temperature and  $h$  also increase with temperature.

$h \propto V =$  volume of salt solution hence  $h$  increases with dilution.  $K_h =$

Both  $K_w$  and  $K_b$  change with temperature, hence  $K_h$  changes with temperature.

Hence, statement(B) is correct.  $h$  increases if  $K_b$  decreases, statement(C) correct.

It is found that as temperature increase,  $K_w$  and  $K_b$  increase but increase in  $K_w$  is greater than increase in  $K_b$ .

Hence,  $h$  increases with increase in temperature. or  $h$  decrease in temperature., hence statement.

(D) is correct.

(D) is not correct from explanation of (B).

**Q.15** (A, B, C)

At eq. point  $pH = 4.5$

$pOH = 9.5$

$pOH = 1/2 [pK_b + pK_w + hc]$

$9.5 = 1/2 [5.6 + 14 + hc] \Rightarrow C = 0.25$

(C) Total volume be  $(100 + V)$

$0.25 \times (100 + V) = 0.5 \times C \Rightarrow V = 100 \text{ ml}$

(D)  $100 \text{ M} = 0.5 \text{ V}$

$100 \times M = 0.5 \times 100$

$M = 0.5$

100 ml \_\_\_\_\_ 0.5 mole

100 ml \_\_\_\_\_ 0.055 mole of base

$0.05 = \frac{\text{wt.}}{45} \Rightarrow \text{wt.} = 2.25 \text{ gm}$

% of base =  $\frac{2.25}{2.5} \times 100 = 90\%$

**Q.16** (A, D)

(A)  $\frac{[H_3AsO_4]}{[H_2AsO_4^-]} = \frac{[H^+]}{K_1} = \frac{10^{-8}}{2.5 \times 10^{-4}} = \frac{1}{25000}$

$\therefore [H_3AsO_4] \ll [H_2AsO_4^-]$ .

(B)  $\frac{[H_2AsO_4^-]}{[HAsO_4^{2-}]} = \frac{[H^+]}{K_2} = \frac{10^{-8}}{5 \times 10^{-8}} = \frac{1}{5}$

(C)  $\frac{[AsO_4^{3-}]}{[HAsO_4^{2-}]} = \frac{K_3}{[H^+]} = \frac{2 \times 10^{-13}}{10^{-8}} = \frac{1}{50000}$

$\therefore [AsO_4^{3-}] \ll [HAsO_4^{2-}]$ .

**Q.17** (A, B, C)

(A)  $H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$

moles 1.5 1  
0.5 -1

so it is a buffer solution.

(B)  $H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$

moles 1.5 2-0.5 1.5

$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$

moles 1.5 0.5- -0.5

so it is a buffer solution.

(C)  $NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$

moles 5 4 1 -4

so it is a buffer solution.

**Q.18** (A, B, C)

(A)  $CH_3COOH/CH_3COONa$

(B)  $CH_3COONa/HCl \rightarrow CH_3COOH + NaCl$   $CH_3COONa/CH_3COOH$  (Buffer)

(C)  $NH_3/NH_4Cl$  (Buffer)

(D)  $NH_3 + NaOH$  (not Buffer)

**Q.19** (A, B)

(A) A buffer solution is a solution which contains weak acid and its conjugate base. it is acidic buffer.

(B) Basic buffer contains weak base and its conjugate acid.

(C) is wrong because it does not show change in pH on adding small amount of acid or base.

(D) is wrong ; all the above statements are not correct.

**Q.20** (A, C)

Sodium acetate and acetic acid solution and ammonia and ammonium chloride solution are the examples of acidic buffer.

**Q.21** (C, D)

Higher the  $K_a$  of acid lower is the pH of acid for same concentration.

**Q.22** (A, D)

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{10^{-9}}{10^{-9.6}} =$$

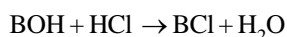
$$10^{0.6} = 4$$

$$\therefore \% \text{ of } [\text{In}^-] \text{ in solution} = \frac{4}{5} \times 100 = 80\%$$

so pink colour will be visible.

**Q.23** (B,C,D)

Initial decrement is due to consumption of free  $\text{OH}^-$  ions, then slow decrement in pH is due to basic buffer solution and minimum slope will be there when there is best buffer action ( $[\text{salt}] / [\text{base}] = 1$ )

**Q.24** (B, C)

$$100 \text{ m} 0.5 \text{ V } 20 \text{ M}$$

$$100 \text{ M} - 0.5 \text{ V } 0 = 80 \text{ M } 14\text{-a}$$

$$\text{pOH} = \text{pKb} + \log \frac{\text{salt}}{\text{base}}$$

$$5 = \text{pKb} + \log \frac{20 \text{ M}}{80 \text{ M}}$$

$$\Rightarrow \text{pKb} = 5 - \log 0.25 \Rightarrow \text{pKb} = 5.6$$

$$\Rightarrow \text{Kb} = 2.5 \times 10^{-6}$$

greater than  $10^{-6}$

**Q.25** (A, B, C, D)

Factual

**Q.26** (C, D)

In  $\text{AgNO}_3$  solution, the solubility of  $\text{AgCN}$  will decrease as compared to pure water because of common ion effect of  $\text{Ag}^+$  ion.

In  $\text{NH}_3$  solution and buffer of  $\text{pH} = 5$ , the solubility of  $\text{AgCN}$  will increase due to complex formation in case of  $\text{NH}_3$  solution and hydrolysis of  $\text{CN}^-$  ions in case of buffer of  $\text{pH} = 5$ .

**Q.27** (A, B)

$$K_{\text{sp}} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^{x+y} x^x \cdot y^y$$

so we have  $x + y = 3$  (by comparing values)

$$\text{so, } x^x \cdot y^y = \frac{1.1 \times 10^{-11}}{1.4 \times 1.4 \times 1.4 \times 10^{-12}} = \frac{110}{1.96 \times 1.4} =$$

4

Hence  $x = 1, y = 2$  or  $y = 1, x = 2$

**Q.28** (B, D)

Factual

**Q.29** (C, D)

Given graph is plotted for the titration of weak diprotic acid with base.

**Q.30** (A, B, D)

$[\text{Ag}^+]$  ion required to precipitate  $\text{Cl}^-$  ion = = =  $2 \times 10^{-9}$  mol/L.

$[\text{Ag}^+]$  ion required to precipitate  $\text{I}^-$  ion = = =  $8 \times 10^{-15}$  mol/L.

Since  $[\text{Ag}^+]$  ion conc. required to precipitate  $\text{AgI}$  is less than the  $[\text{Ag}^+]$  ion conc. required to precipitate  $\text{AgCl}$ ,  $\text{AgI}$  precipitates first.

Hence choices (A), (B) and (D) are correct while (C) is incorrect.

**Q.31** (A, B)

$\text{H}_2\text{SO}_4$  is a strong acid and it completely dissociated in  $\text{H}_2\text{O}$ . Hence its  $K_{a1}$  and  $K_{a2}$  are determined in  $\text{CH}_3\text{COOH}$ .

Also  $\text{H}_2\text{SO}_4$  is neutral while  $\text{HSO}_4^-$  because the -ve charge has more affinity towards  $\text{H}^+$  ion. Hence choices (A) and (B) are correct while (C) is incorrect. As  $\text{H}_2\text{SO}_4$  is completely dissociated in water so a 0.01 M  $\text{H}_2\text{SO}_4$  is completely dissociated and its  $[\text{H}^+]$  ion conc. will be equal to 0.02 M.

Hence choice (D) will be incorrect.

**Q.32** (A, B, C)

$$[\text{A}^{2-}] = K_{a2} = 10^{-5}$$

$$\text{pH} = 1 \quad \text{pH} = 3$$

$$[\text{H}^+]_1 = 10^{-1} \quad [\text{H}^+]_2 = 10^{-3}$$

$$\frac{[\text{H}^+]_1}{[\text{H}^+]_2} = 100$$

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

pH is independent of dilution with in a limit since no concentration term in pH expression.

**Comprehension # 1 (Q. No. 33 to 35)**
**Q.33** (D)

Facutal

**Q.34** (A)

Since  $K_a$  of  $\text{CH}_3\text{COOH}$  &  $K_b$  of  $\text{NH}_4\text{OH}$  are same so degree of hydrolysis of  $\text{CH}_3\text{COO}^-$  &  $\text{NH}_4^+$  are exactly same.

**Q.35** (C)

Facutal

**Comprehension # 2 (Q. No. 36 to 39)**
**Q.36** (A)

$$\text{Mole of Potash Alum} = \frac{11.85}{474}$$

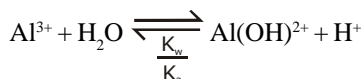
$$= 0.025$$

$$\text{Mole } [\text{Al}^{3+}] = 0.025$$

$$\text{Mole } [\text{K}^+] = 0.025$$

If none of the Ion Hydrolysed

$$\Rightarrow [\text{H}^+] = 10^{-7}$$

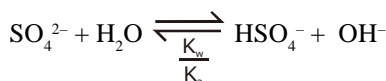
**Q.37** (A)


$$\text{C-x} \quad x \quad \quad \quad x$$

$$C = \frac{0.025}{100} \times 1000 = 0.25$$

$$\Rightarrow \frac{x^2}{0.25 - x} = 1.4 \times 10^{-5} \Rightarrow x^2 = 1.4 \times 0.25 \times 10^{-5}$$

$$\Rightarrow x = 1.87 \times 10^{-3}$$

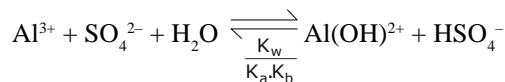
**Q.38** (C)


$$0.5-x \quad x \quad \quad \quad x$$

$$\frac{x^2}{0.5 - x} = \frac{10^{-14}}{1.25 \times 10^{-2}} \text{ (Neglect } x)$$

$$\Rightarrow [\text{OH}^-] = x = 6.32 \times 10^{-7}$$

$$\Rightarrow [\text{H}^+] = \frac{10^{-14}}{6.25 \times 10^{-7}} = 1.58 \times 10^{-8}$$

**Q.39** (A)


$$0.25-x \quad 0.5-x \quad \quad \quad x \quad \quad \quad x$$

$$\frac{\text{K}_w}{\text{K}_a \cdot \text{K}_b} = \frac{1.4 \times 10^{-5}}{1.25 \times 10^{-2}} = 1.12 \times 10^{-3}$$

$$\Rightarrow \frac{x^2}{(0.25 - x)(0.5 - x)} = 1.12 \times 10^{-3}$$

$$\Rightarrow x = [\text{HSO}_4^-] = 0.0114$$

$$\Rightarrow \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \text{K}_a = 1.25 \times 10^{-2}$$

$$\Rightarrow \frac{[\text{H}^+][0.5 - 0.0114]}{[0.0114]} = 1.25 \times 10^{-2}$$

$$\Rightarrow [\text{H}^+] = 2.92 \times 10^{-4} \text{ } 10^{-2}$$

$$\Rightarrow [\text{H}^+] = 2.92 \times 10^{-4}$$

**Comprehension # 3 (Q. No.40 to 42)**
**Q.40** (C)

From the Graph 19 ml

**Q.41** (C)

 From the Graph pH  $\approx$  8.5

**Q.42** (C)

$$\frac{1.2}{\text{Mol. mass}} = \frac{0.222 \times 19}{1000}$$

$$\Rightarrow \text{Mol. mass} = 284.5$$

**Comprehension # 4 (Q. No. 43 to 45)**
**Q.43** (A)

 For  $\text{SrF}_2$  in pure water

$$4s_1^3 = \text{K}_{sp}$$

 For  $\text{SrF}_2$  in 0.1 M NaF solution

$$s_2 (0.1)^2 = \text{K}_{sp}$$

$$\Rightarrow 4s_1^3 = s_2 (0.01)$$

$$\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6} \quad (0.01)$$

$$\Rightarrow s_1 = 8 \times 10^{-4} \text{ M}$$

$$\therefore K_{sp} = 4s_1^3 = 2.048 \times 10^{-9}$$

**Q.44** (C)

$$[\text{Sr}^{2+}]_i = 0.0011 = 11 \times 10^{-4} \text{ M}$$

$$[\text{Sr}^{2+}]_f = 2 \times 10^{-4} \text{ M}$$

$$\therefore [\text{Sr}^{2+}] \text{ precipitated} = (11 - 2) \times 10^{-4} \text{ M} \\ = 9 \times 10^{-4} \text{ M}$$

[F<sup>-</sup>] needed for this precipitation

$$= 2 \times 9 \times 10^{-4} = 18 \times 10^{-4} \text{ M}$$

$$\text{Also, } [\text{Sr}^{2+}]_f [\text{F}^-]_f^2 = K_{sp} = 2.048 \times 10^{-9}$$

$$\text{But, } [\text{Sr}^{2+}]_f = 2 \times 10^{-4} \text{ M}$$

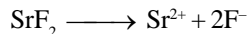
$$\therefore [\text{F}^-]_f = 3.2 \times 10^{-3} \text{ M}$$

$$\therefore \text{Total } [\text{F}^-] \text{ needed} = 3.2 \times 10^{-3} + 18 \times 10^{-4} = 5 \times 10^{-3} \text{ M}$$

$$\therefore \text{NaF needed for 100 ml solution} = \frac{5 \times 10^{-3} \times 42}{10}$$

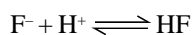
$$= 0.021 \text{ g}$$

**Q.45** (B)



$$s \qquad \qquad 2s$$

F<sup>-</sup> will react with H<sup>+</sup> to produce HF



$$K = \frac{1}{K_a} = \frac{[\text{HF}]}{[\text{H}^+][\text{F}^-]} = \frac{7}{10^{-5}}$$

$$\therefore [\text{HF}] = 7 \times 10^5 [\text{F}^-] [\text{H}^+] \quad (\because [\text{H}^+] = 10^{-5}; \text{pH}=5) \\ = 7 \times 10^5 [\text{F}^-] \times 10^{-5} = 7 [\text{F}^-]$$

$$\text{Here} \qquad \qquad \qquad [\text{F}^-] + [\text{HF}] = 2s$$

$$\therefore [\text{F}^-] = \frac{s}{4}$$

$$K_{sp} = s \left( \frac{s}{4} \right)^2 = 2.048 \times 10^{-9}$$

$$\therefore s = 3.2 \times 10^{-3} \text{ mol/L}$$

**Q.46** A-S, B-S, C-Q

$$(A) [\text{H}^+] = \frac{200 \times 1.225 \times \frac{25}{100} \times 2}{98}$$

$$= 1.25$$

$$[\text{OH}^-] = 0.525 \times \frac{800}{1000} \times 3 = 1.26$$

$$\text{Remaining } [\text{OH}^-] = 10^{-2}$$

$$\Rightarrow \text{pOH} = 2$$

$$\Rightarrow \text{pH} = 12$$

Indicator having range 11.4 to 13.

$$(B) \text{pH} = 11 - \log 2 + \log \frac{0.8}{0.1}$$

$$= 11 + 2 \log 2$$

$$= 11.6$$

Indicator having range 11.4 to 13.

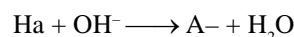
$$(C) \text{HCl m.eq} = 5$$

$$\text{NaOH m.eq} = 13$$

↓

$$\text{Remaining NaOH} = 8$$

$$\text{m.eq of HA} = 10$$



$$10$$

$$8$$

$$2$$

$$08$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= 5 + \log 4$$

$$\Rightarrow 5.6$$

Indicator having range 4.6 to 6.4

**Q.47** (A-p, q, r, s); (B-p, r); (C-r); (D-p, q, s)

$$(A) [\text{H}^+] \text{ in HCl solution} = 10^{-5} \text{ M}$$

$$[\text{H}^+] \text{ in H}_2\text{S solution} = \sqrt{K_a \times C} = 10^{-4} \text{ M}$$

so  $[\text{H}^+] \text{ in HCl solution} < [\text{H}^+] \text{ in H}_2\text{S solution}$

&  $[\text{OH}^-] \text{ in HCl solution} > [\text{OH}^-] \text{ in H}_2\text{S solution}$

& degree of dissociation of water in HCl solution > degree of dissociation of water in H<sub>2</sub>S solution

pH of HCl solution > pH of H<sub>2</sub>S solution.

$$(B) \text{ At pH} = 4.74 \text{ in CH}_3\text{COOH solution, } [\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$$

$$\therefore \text{degree of dissociation of CH}_3\text{COOH} = \frac{1}{2}$$

At pH = 9.26 i.e. pOH = 4.74 in NH<sub>4</sub>OH solution,  $[\text{NH}_4^+] = [\text{NH}_4\text{OH}]$

∴ degree of dissociation of  $\text{CH}_3\text{COOH}$  = degree of dissociation of  $\text{NH}_4\text{OH}$

degree of dissociation of water in  $\text{CH}_3\text{COOH}$  solution > degree of dissociation of water in  $\text{NH}_4\text{OH}$  solution.

$$(C) [\text{H}^+] \text{ in } \text{CH}_3\text{COOH} \text{ solution} = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8} \times 10^{-3} \text{ M}$$

$$[\text{H}^+] \text{ in } \text{HCOOH} \text{ solution} = \sqrt{1.8 \times 10^{-4} \times 1} = \sqrt{1.8} \times 10^{-2} \text{ M}$$

so, degree of dissociation of  $\text{CH}_3\text{COOH}$  = degree of dissociation of  $\text{HCOOH}$ .

$$(D) [\text{H}^+] \text{ in } \text{HA}_1 \text{ solution} = \sqrt{10^{-5} \times 0.1} = 10^{-3} \text{ M}$$

$$[\text{H}^+] \text{ in } \text{HA}_2 \text{ solution} = \sqrt{10^{-6} \times 0.01} = 10^{-4} \text{ M}$$

so  $[\text{OH}^-]$  in solution of  $\text{HA}_1 < [\text{OH}^-]$  in solution of  $\text{HA}_2$

pH in solution of  $\text{HA}_1 < \text{pH}$  in solution of  $\text{HA}_2$

& degree of dissociation of water  $\text{HA}_1 < \text{degree}$  of dissociation of water  $\text{HA}_2$ .

**Q.48** A-P, B-Q, C-S, D-R

$$(A) [\text{OH}^-] = \frac{10 \times 0.03}{500} = 6 \times 10^{-4}$$

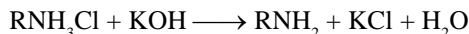
$$[\text{OH}^-] = \frac{0.08 \times 5}{500} = 8 \times 10^{-4}$$

Remaining  $[\text{H}^+] = 2 \times 10^{-4}$

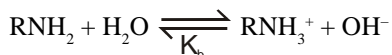
$$\text{pH} = 4 - \log 2 = 3.7$$

$$(B) [\text{RNH}_3\text{Cl}] = \frac{0.5 \times 10}{50} = 0.1$$

$$[\text{KOH}] = 0.1$$



$$0.1 \quad 0.1 \quad 0.1 \quad 0.1$$



$$0.1 - x \quad \quad \quad xx$$

$$x^2 / 0.1 - x = K_b = \frac{K_w}{K_x} = 10^{-5}$$

$$\Rightarrow x = 10^{-3} \Rightarrow \text{pOH} = 3 ; \text{pH} = 11$$

(C) Buffer :  $\text{HCO}_3^- / \text{CO}_3^{2-}$

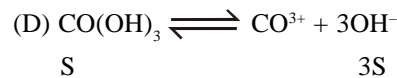
$$\text{pH} = \text{pKa} + \log \frac{\text{Salt}}{\text{Acid}}$$

$$= 11 - \log 4 + \log \frac{4}{8}$$

$$= 11 - \log 4 - \log 2$$

$$= 11 - 3 \log 2 = 11 - 0.9$$

$$= 10.1$$



$$S \quad \quad \quad 3S$$

$$\Rightarrow 27S^4 = 27 \times 10^{-44}$$

$$\Rightarrow S = 10^{-11} \text{ \&}$$

$$[\text{OH}^-] = [10^{-11} + x] : x \text{ from water}$$

$$[\text{H}^+] = x \text{ \& } x(10^{-11} + x) = 10^{-14}$$

$$\Rightarrow \text{pH} \approx 7$$

**Q.49** (A - p, q); (B - q, r); (C - p, q, s); (D - r, s)



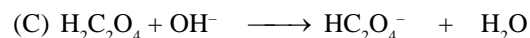
$$\text{m.moles } 5025 \quad \quad \quad 25-25$$

Buffer solution  $\text{pH} = \text{pKa}_1$

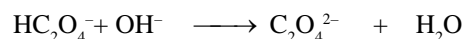


$$\text{m.moles } 5050 \text{ --- } \quad \quad \quad 50$$

$$\text{Amphiprotic, } \text{pH} = \frac{\text{pKa}_1 + \text{pKa}_2}{2} = \frac{13}{2} = 6.5.$$



$$\text{m.moles } 5075-2550$$



$$\text{m.moles } 502525-25$$

Buffer solution  $\text{pH} = \text{pKa}_2$ .



$$\text{m.moles } 50 \quad \quad \quad 100$$

$$-50 \quad \quad \quad 50$$



$$\text{m.moles } 50 \quad \quad \quad 50$$

$$\text{---} \quad \quad \quad 50$$

Salt hydrolysis,  $\text{pH} > 7$ .

**Q.50** (A - s); (B - p, q); (C - q, s); (D - q, r)



so on increase in  $[\text{Br}^-]$ , solubility of  $\text{AgBr}$  decreases.



(B) For AgCN,  $K_{sp} = [Ag^+][CN^-]$

CN<sup>-</sup> undergoes hydrolysis so solubility in water is more than expectation.

In acidic solution, CN<sup>-</sup> gets protonated so solubility of AgCN increases.

AgCN forms complex Ag(CN)<sub>2</sub><sup>-</sup> with excess of CN<sup>-</sup>.

(C) For Fe(OH)<sub>3</sub>,  $K_{sp} = [Fe^{3+}][OH^-]^3$ .

In acidic solution OH<sup>-</sup> decreases so solubility increases.

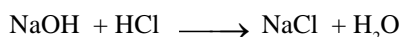
Solubility decreases in presence of OH<sup>-</sup>.

(D) For Zn(OH)<sub>2</sub>,  $K_{sp} = [Zn^{2+}][OH^-]^2$

Zn(OH)<sub>2</sub> is amphoteric in nature so its solubility increases in both acidic as well as strongly basic solution.

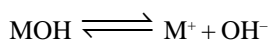
### NUMERICAL VALUE BASED

Q.1 [7]



NaCl is a salt of strong base and strong acid, hence it gives the neutral solution with pH = 7.

Q.2 [9]



$$[OH^-] \sqrt{K_{sp}} = \sqrt{1 \times 10^{-10}} = 10^{-5}$$

$$pH = 9.$$

Q.3 [7]

Q.4 [6]

$$s = \sqrt{K_{sp}} = \sqrt{36} = 6 \text{ M}$$

Q.5 [3]



Q.6 [4]

Q.7 [9]

Q.8 [0]

$$\Delta G^0 = -2.303RT \log K_c$$

Q.9 [2]

Phenolphthalein is used for titration of solution of

(i) strong acid and strong base and

(ii) weak acid and strong base

Q.10 [5 [(i) to (v)]]

Q.11 [31]

$$pH = pK_a + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$\Rightarrow 4.5 = 4.2 + \log \left( \frac{V_2}{V_1} \right) \Rightarrow \frac{V_2}{V_1} = 2$$

$$\therefore \text{volume of } C_6H_5COONa \text{ required} = V_2 = 62 \text{ mL}$$

$$\text{volume of } C_6H_5COOH \text{ required} = V_1 = 31 \text{ mL.}$$

### KVPY

#### PREVIOUS YEAR'S

Q.1 (D)

$$\text{Meq of } CH_3COOH = 100 \times 0.1 \times 1 = 10$$

$$\text{Meq of } CH_3COONa = 50 \times 0.2 \times 1 = 10$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = 4.76 + \log \frac{10}{10}$$

$$pH = 4.76 + \log 1$$

$$pH = 4.76$$

Q.2 (B)

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$\therefore [\text{Conjugate base}] = [\text{Acid}]$$

$$pH = pK_a = 5.85$$

Q.3 (A)

$$C = 0.1 \text{ M}$$

$$K_a = 10^{-5}$$

$$K_a = \alpha^2 C$$

$$10^{-5} = \alpha^2 \times 0.1$$

$$\alpha^2 = 10^{-4}$$

$$\alpha = 10^{-2}$$

Q.4 (B)

Order of pH

less than 7

pH=7

more than 7

NH<sub>4</sub>Cl <

NaCl <

CH<sub>3</sub>COONa

Salt of strong acid + weak base

Salt of strong acid + strong base

Salt of strong base + weak acid

**Q.5** (D)

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-]$$

$$= (5 \times 10^{-10})(10^{-3})$$

$$= 5 \times 10^{-3}$$

Now

$$5 \times 10^{-3} = (10^{-2})[\text{Br}]$$

$$[\text{Br}] = 5 \times 10^{-11} \text{ M}$$

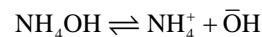
**Q.6** (C)

$$K_{sp} \text{Mg(OH)}_2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

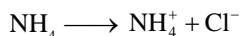
$$5.6 \times 10^{-12} = [10^{-10}][\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{5.6 \times 10^{-2}} = 0.25 \text{ M}$$

**Q.7** (A)

 Dil aqueous solution of  $\text{NH}_3$  is  $\text{NH}_4\text{OH}$  solution


On adding solid ammonium chloride



the reaction moves backward due to common ion effect.

 The concentration of  $\text{OH}^-$  decreases and pH decreases

**Q.8** (D)

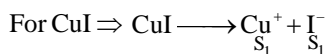
Given  $K_{sp} = 10^{-10}$

For  $\text{BaSO}_4$ ,  $K_{sp} = S^2$ .

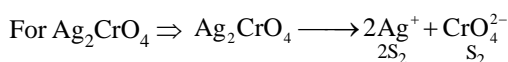
$$S = 10^{-5} \text{ mol/L} \Rightarrow 2.33 \times 10^{-3} \text{ g/L}$$

**Q.9** (A)

 Mixing equal volume of  $\text{NH}_4\text{OH}$  (0.2 M) and  $\text{HCl}$  (0.1 M) result in formation of  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  basic buffer mixture

**Q.10** (B)


$$K_{sp}(\text{CuI}) = S_1^2 = 4 \times 10^{-12} \Rightarrow S_1 = 2 \times 10^{-6}$$



$$K_{sp}(\text{Ag}_2\text{CrO}_4) = 4S_2^3 = 4 \times 10^{-2} \Rightarrow S_2 = 10^{-4}$$

$$\text{So, } \frac{S_1}{S_2} = \frac{2 \times 10^{-6}}{10^{-4}} = 0.02$$

**JEE-MAIN**
**PREVIOUS YEAR'S**
**Q.1** [6.76]

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

$$= \frac{1}{2} (14 + 4.75 - 5.23)$$

$$= 6.76$$

**Q.2** (1)

 For  $\text{Ca(OH)}_2$ 

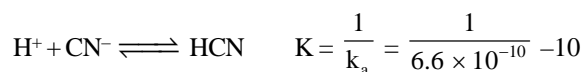
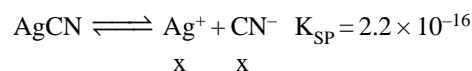
$$K_{sp} = 4s^3$$

$$5.5 \times 10^{-6} = 4s^3$$

$$s = \sqrt[3]{\frac{5.5}{4} \times 10^{-6}} = 1.11 \times 10^{-2} \text{ M}$$

**Q.3** (1)

Lets solubility is x



$$K_{sp} \times \frac{1}{k_a} = [\text{Ag}^+][\text{CN}^-] \times \frac{[\text{HCN}]}{[\text{H}^+][\text{CN}^-]}$$

$$2.2 \times 10^{-16} \times \frac{1}{6.6 \times 10^{-10}} = \frac{[S] \times [S]}{10^{-3}}$$

$$S^2 = \frac{2.2}{6.6} \times 10^{-9}$$

$$S^2 = \frac{1}{30} \times 10^{-8}$$

$$S = \sqrt{\frac{1}{30}} \times 10^{-4} = 1.9 \times 10^{-5}$$

**Q.4** (50)

 Most precise volume of  $\text{HCl} = 5 \text{ ml}$ 

at equivalence point

 Meq. of  $\text{Na}_2\text{CO}_3 = \text{meq. of HCl}$ .

 Let molarity of  $\text{Na}_2\text{CO}_3$ 

solution = M, then

$$M \times 10 \times 2 = 0.2 \times 5 \times 1$$

$$M = 0.05 \text{ mol / L}$$

$$= 0.05 \times 1000$$

$$= 50 \text{ mM}$$

**Q.5** (78)

$$\text{Moles of Benzoic acid} = \frac{6.1}{122}$$

= moles of m-bromobenzoic acid

So, weight of m-bromobenzoic acid

$$= \frac{6.1}{122} \times 201 \text{ gm}$$

$$= 10.05 \text{ gm}$$

$$\% \text{ yield} = \frac{\text{Actual weight}}{\text{Theoretical weight}} \times 100$$

$$= \frac{7.8}{10.05} \times 100$$

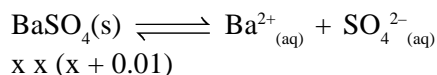
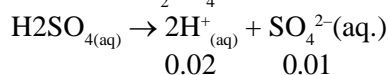
$$= 77.61\%$$

**Q.6** (64)

In pure water,

$$K_{sp} = S_2 = (8 \times 10^{-4})^2$$

$$= 64 \times 10^{-8}$$

In 0.01 M  $\text{H}_2\text{SO}_4$ 

$$K_{sp} = x(x + 0.01)$$

$$= 64 \times 10^{-8}$$

$$x + 0.01 \cong 0.01 \text{ M}$$

$$\text{So, } x(0.01) = 64 \times 10^{-8}$$

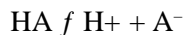
$$x = 64 \times 10^{-6} \text{ M}$$

**Q.7** (10)

$$\text{pH} = \text{pKa} + \log \frac{[\text{CB}]}{[\text{WA}]}$$

$$5.74 = 4.74 + \log \frac{[\text{CB}]}{1}$$

$$\Rightarrow [\text{CB}] = 10 \text{ M}$$

**Q.8** (2)

Initial conc. 0.01M 0.1M 0

Equ. conc. (0.01 - x) (0.1 + x) xM

 $\approx 0.01\text{M} \approx 0.1\text{M}$ 

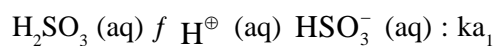
$$\text{Now, } K_a = \frac{[\text{x}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow 2 \times 10^{-6} = \frac{0.1 \times x}{0.01}$$

$$\therefore x = 2 \times 10^{-7}$$

$$\text{Now, } \alpha = \frac{x}{0.01} = \frac{2 \times 10^{-7}}{0.01} = 2 \times 10^{-5}$$

**Q.9** (1) $\text{H}_2\text{SO}_3$  [Dibasic acid]

$$c = 0.588 \text{ M}$$

 $\Rightarrow$  pH of solution  $\Rightarrow$  due to First dissociation onlysince  $K_a \gg K_{a2}$  $\Rightarrow$  First dissociation of  $\text{H}_2\text{SO}_3$ 

$$= 1.7 \times 10^{-2}$$

$$t = 0 \text{ C}$$

$$t \quad \text{C-x} \qquad \qquad \qquad x \qquad \qquad \qquad x$$

$$\Rightarrow K_{a1} = \frac{1.7}{100} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$\Rightarrow \frac{1.7}{100} = \frac{x^2}{(0.588 - x)}$$

$$\Rightarrow 1.7 \times 0.588 - 1.7x = 100 x^2$$

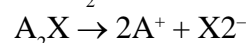
$$\Rightarrow 100x^2 + 1.7x - 1 = 0$$

$$[\text{H}^+] = x = \frac{-1.7 + \sqrt{(1.7)^2 + 4 \times 100 \times 1}}{2 \times 100}$$

$$= 0.09186$$

Therefore pH of sol. is :  $\text{pH} = -\log [\text{H}^+]$ 

$$\Rightarrow \text{pH} = -\log (0.09186) = 1.036 ; 1$$

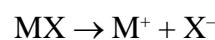
**Q.10** (50)For  $\text{A}_2\text{X}$ 

$$2\text{S}_1 \quad \text{S}_1$$

$$K_{sp} = 4\text{S}_1^3 = 4 \times 10^{-12}$$

$$\text{S}_1 = 10^{-4}$$

for MX



$$\text{S}_2 \quad \text{S}_2$$

$$K_{sp} = \text{S}_2^2 = 4 \times 10^{-12}$$

$$\text{S}_2 = 2 \times 10^{-6}$$

$$\text{so } \frac{\text{S}_{\text{A}_2\text{X}}}{\text{S}_{\text{MX}}} = \frac{10^{-4}}{2 \times 10^{-6}} = 50$$

**Q.11** (1)**Q.12** (4)**Q.13** (3)**Q.14** (108)

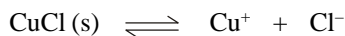
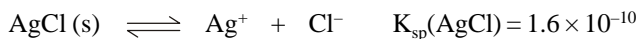
Q.15 (6021)

$$[\text{BH}^+] = \frac{0.1V}{2V} = 0.5M$$

Q.16 (2)

**JEE-ADVANCED  
PREVIOUS YEAR'S**

Q.1 [7]



$$K_{sp}(\text{CuCl}) = 10^{-6}$$



$$Z(Z + Y) = 1.6 \times 10^{-10}$$

$$\text{and } Y(Z + Y) = 10^{-6}$$

$$\Rightarrow (Z + Y)^2 = 1.6 \times 10^{-10} + 10^{-6} \quad \Rightarrow (Z + Y)^2 \approx 10^{-6}$$

$$\Rightarrow Z + Y = 10^{-3}$$

We know

$$\Rightarrow Z(Z + Y) = 1.6 \times 10^{-10} \quad \Rightarrow Z \times 10^{-3} = 1.6 \times 10^{-10}$$

$$\Rightarrow Z = 1.6 \times 10^{-7} \quad \Rightarrow 1.6 \times 10^{-x} = 1.6 \times 10^{-7}$$

$$\Rightarrow x = 7$$

Q.2 (4.47)

$$S = \sqrt{K_{sp} \left( \frac{[\text{H}^+]}{K_a} + 1 \right)} = \sqrt{2 \times 10^{-10} \left( \frac{10^{-3}}{10^{-8}} + 1 \right)}$$

$$= \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3}$$

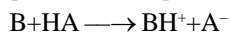
Q.3 [0.11]

No. of eq. of oxalic acid = No. of eq. of NaOH

$$\text{or } \frac{5.00 \times 0.10}{1000} \times 2 = \frac{9.0 \times M}{1000} \times 1$$

$$\therefore \text{Molarity of NaOH solution} = \frac{1}{9} = 0.11M$$

Q.4 [2.30 TO 3.00]



0.1M, V ml

0.1V mmol      0.1 V mmol      0.1 V 0.1V

pH at eq. pt=6 to 6.28

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b + \log 0.05]$$

$$\text{So } \text{p}K_b = 2.30 - 2.80$$

Possible

**Solution 2**

at V=6 ml      rxn is complete

So V=3ml      is half of eq. pt

at which      pH=11

$$\text{pOH} = (14 - 11) = \text{p}K_b + \log 1$$

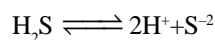
$$\text{p}K_b = 3$$

Q.5 [0.20]

 For ppt,  $[\text{Zn}^{2+}][\text{S}^{2-}] = K_{sp}$ 

$$[\text{S}^{2-}] = \frac{1.25 \times 10^{-22}}{0.05}$$

$$= 2.5 \times 10^{-21} \text{ M}$$



$$K_{\text{Net}} = 10^{-21} = \frac{[\text{H}^+]^2 \times 2.5 \times 10^{-21}}{0.1}$$

$$[\text{H}^+]^2 = \frac{1}{25}$$

$$[\text{H}^+]^2 = \frac{1}{5} \text{ M} = 0.2 \text{ M}$$

# Thermodynamics

## ELEMENTARY

Q.1 (2)

Q.2 (4)

Q.3 (3)

Surface tension is an intensive property which do not depend upon the quantity of matter present in the system.

Q.4 (3)

Q.5 (2)

$$W = 2.303 nRT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$$

$$= 298 \times 10^7 \times 8.314 \times 2.303 \log 2.$$

Q.6 (3)

$$W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$$

$$= -1 \times 10^5 \times 9 \times 10^{-3} = -900 \text{ J}$$

Q.7 A

We have,

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15}$$

$$= -1426.87 \text{ calories.}$$

Q.8 (2)

$$\Delta H = \Delta E + P\Delta V.$$

Q.9 (3)

At constant  $P$  or  $T$

$$\Delta H = \Delta U + \Delta nRT \Rightarrow \Delta n = n_p - n_R = 2 - 4 = -2$$

$$\therefore \Delta H < \Delta U.$$

Q.10 (3)

Here  $\Delta n = 0$  so,  $\Delta E = \Delta H$ .

Q.11 (3)

Q.12 (4)

Heat is always flow from the higher to lower temperature.

Q.13 (2)

(2) Solid  $\longrightarrow$  Gas,  $\Delta S$  is maximum.

Q.14 (1)

Q.15 (3)

Q.16 (2)

Q.17 (1)

When  $\Delta H = -ve$ ,  $\Delta S = +ve$  and  $\Delta G = -ve$  than reaction is spontaneous .

Q.18 (2)

For spontaneous change  $\Delta G = -ve$  .

Q.19 (4)

At equilibrium  $\Delta G = 0$  .

Q.20 (2)

Q.21 (4)

Heat of neutralisation between strong acid and a strong base is about  $-13.7 \text{ Kcal}$ .

Q.22 (4)

Q.23 (2)

Effect of temperature in heat of reaction is given by Kirchoff's equation.

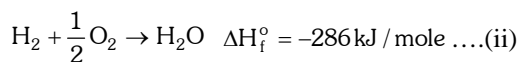
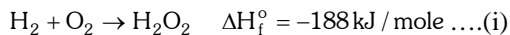
Q.24 (2)

78g of benzene on combustion produces heat  $= -3264.6 \text{ kJ}$

$$\therefore 39\text{g will produce} = \frac{-3264.6}{2} = -1632.3 \text{ kJ}.$$

Q.25 (1)

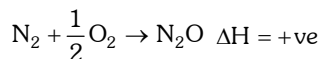
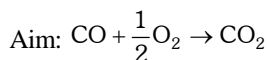
eq. (i) + eq. (ii) gives the required result.

**Q.26** (1)

eq. (i) – eq. (ii)  $\times 2$  gives the required result.

**Q.27** (3)

Heats of combustions are always exothermic except oxidation of *N* as,

**Q.28** (2)

$$\Delta H = \Delta H_f^\circ(\text{CO}_2) - \left[ \Delta H_f^\circ(\text{CO}) + \frac{1}{2} \Delta H_f^\circ(\text{O}_2) \right]$$

$$= -94.0 - (-26.4) = -67.6 \text{ kcal.}$$

**Q.29** (3)

$\text{NH}_4\text{OH}$  is a weak base. Heat of neutralisation < 13.7 kcal.

**Q.30** (1)

$$\Delta H - \Delta E = \Delta nRT = 3 \times 8.314 \times 298$$

$$= -7432 \text{ J} = -7.43 \text{ kJ.}$$

**Q.31** (2)

$\Delta H = +ve$  for endothermic reaction.

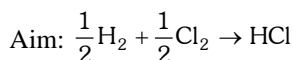
**Q.32** (4)

Standard molar heat enthalpy ( $H^\circ$ ) of a compound is equal to its standard heat of formation from most stable states of initial components.

**Q.33** (1)

4g  $\text{H}_2 = 2 \text{ moles}$ . Bond energy for 1 mole of

$$\text{H}_2 = 208 / 2 = 104 \text{ kcal.}$$

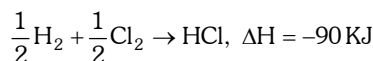
**Q.34** (3)

$$\Delta H = \sum \text{B.E.}_{(\text{Products})} - \sum \text{B.E.}_{(\text{Reactants})}$$

$$= \text{B.E.}(\text{HCl}) - \left[ \frac{1}{2} \text{B.E.}(\text{H}_2) + \frac{1}{2} \text{B.E.}(\text{Cl}_2) \right]$$

$$= -103 - \left[ \frac{1}{2}(-104) + \frac{1}{2}(-58) \right]$$

$$= -103 - (-52 - 29) = -22 \text{ kcal.}$$

**Q.35** (4)

$$\therefore \Delta H = \frac{1}{2} E_{\text{H-H}} + \frac{1}{2} E_{\text{Cl-Cl}}$$

$$\text{or } -90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - E_{\text{HCl}}$$

$$\therefore E_{\text{H-Cl}} = 425 \text{ kJ mol}^{-1}.$$

**Q.36** (2)

When strong acid and strong base neutralize each other than the value of heat generated is about 13.7 kcal.

**JEE-MAIN****OBJECTIVE QUESTIONS****Q.1** (3)

Boiling point, pH & density are intensive properties. Entropy is an extensive property.

**Q.2** (2)**Q.3** (4)

For isothermal process involving ideal gas  
 $\Delta T = \Delta E = \Delta H = 0$

**Q.4**  $w = -n C_v (T_2 - T_1)$ 

$$T_2 = 150 \text{ K}$$

**Q.5** (2)

$$C_p = \frac{q}{n \Delta T}$$

$$\Delta T = 0$$

$$C_p = \infty$$

**Q.6** (2)**Q.7** (2)

$$\Delta H = \Delta E + \Delta n RT$$

Given

$$\Delta H = -651 \times 10^3 \text{ cal.}, R = 2 \text{ cal.}$$

$$T = 290 \text{ K and } \Delta n = 6 + 6 - 6 = 6$$

$$\therefore \Delta E = -651 \times 10^3 - 6 \times 2 \times 290$$

$$= -654480 \text{ cal} = -654.5 \text{ Kcal}$$

**Q.8** (1)

**Q.9** (2)

**Q.10** (2)

**Q.11** (4)

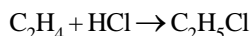
$$\Delta n_g = 0$$

$$\Delta H = \Delta U$$

$$\Delta U = -185 \text{ kJ/Mole}$$

$$\text{For three moles} = -185 \times 3 = -555$$

**Q.12** (4)



$$\Delta n_g = -1$$

HCl is limiting reagent

$$\Delta U = \Delta H - \Delta n_g RT$$

$$= -185 + (1 \times 8.314 \times 10^{-3} \times 300)$$

$$= -69.8 \text{ kJ}$$

$$\text{For two mole of HCl} = -69.8 \times 2 = -139.6 \text{ kJ}$$

**Q.13** (2)

$$W = -100 \text{ J}, q = 150 \text{ J}$$

$$\therefore q = \Delta E - W$$

$$\therefore 150 = \Delta E - (-100)$$

$$= 150 - 100$$

$$\Delta E = 50 \text{ J}$$

**Q.14** (1)

$$W = -P\Delta V$$

$$= -1.5(1-0.5)$$

$$= -0.75 \text{ atm-litre} = -0.75 \times 101 \text{ Joule}$$

$$q = 200 \text{ J}$$

$$\therefore q = \Delta E - W$$

$$200 = \Delta E - (-0.75 \times 101)$$

$$\Delta E = 124.25 \text{ Joule}$$

**Q.15** (2)

$$\Delta S_f = \frac{\Delta H_f}{T} = \frac{6025}{273}$$

$$= 22.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

**Q.16** (3)

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

$$= 2 \times \frac{3}{2} R \ln \frac{573}{473}$$

**Q.17** (3)

$$\Delta S_{\text{vap}} = + \frac{300 \times 30}{300} = -30 \text{ J/mol.K}$$

$$\Delta S_{\text{cond}} = -30 \text{ J/mol.K}$$

**Q.18** (1)

$$\Delta H = -3600 \text{ cal}$$

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

$$\Delta G = -600 \text{ cal}$$

**Q.19** (1)

$$\Delta G^\circ = -RT \ln k$$

**Q.20** (4)

$$\Delta H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{Reactants})$$

$$= [\Delta H_f^\circ (\text{H}_2\text{O}) + \Delta H_f^\circ (\text{CO})] - [\Delta H_f^\circ (\text{CO}_2) + \Delta H_f^\circ (\text{H}_2)]$$

$$\Delta H^\circ = [-241.8 - 110.5] - [-393.5 + 0]$$

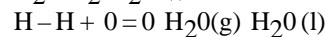
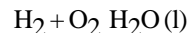
$$= -352.3 + 393.5 = +41.2 \text{ KJ}$$

**Q.21** (4)

$$\Delta_r H = 0;$$

If all the reactants & products have zero  $\Delta_f H$ .

**Q.22** (2)



$$X = X_1 + -2X_3 - X_4$$

**Q.23** (1)

$$\text{H}^+ = 1 \text{ Mole}; \text{OH}^- = 0.75 \text{ Mole}$$

$$\Delta H = 0.75 (-57)$$

$$\text{Heat evolved} = 57 \frac{3}{4}$$

Q.24 (2)

Q.25 (3)

Q.26 (4)

$$-25 = (4x + y) - (3x + 84 + 103)$$

$$x + y = 162$$

$$y = 57.85$$

Q.27 (4)

Q.28 (2)

Q.29 (3)

Q.30 (3)

Q.31 (1)

Q.32 (4)

Q.33 (2)

Q.34 (2)

Q.35 (3)

Q.36 (1)

Q.37 (3)

Q.38 (4)

Q.39 (2)

Q.40 (2)

Q.41 (1)

Q.42 (2)

Q.43 (1)

Q.44 (1)

**JEE-ADVANCED**
**OBJECTIVE QUESTIONS**

Q.1 (C)

Work done in the cyclic process

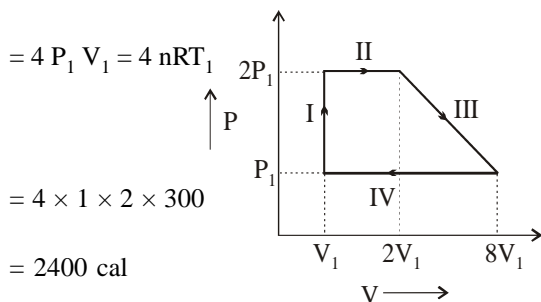
= Area bounded (ABCA)

$$= \frac{1}{2} \times AC \times AB$$

$$= \frac{1}{2} \times 2V_1 \times 3P_1 = 3P_1V_1$$

Q.2 (A)

$$\text{Magnitude of work} = A = P_1 V_1 + \frac{1}{2} \times P_1 \times 6V_1$$



Q.3 (C)

Equation of process

$$\frac{\log P - 2.38}{\log V - 1.10} = \frac{2.10 - 2.38}{1.30 - 1.10} = \frac{-0.28}{0.20} = \frac{-7}{5}$$

$$\Rightarrow (\log P - 2.38) \times 5 = -7 (\log V - 1.1)$$

$$\Rightarrow 5 \log P + 7 \log V = 19.60$$

$$\Rightarrow \log P^5 + \log V^7 = 19.60$$

$$P^5 V^7 = \text{antilog}(19.60) = \text{constant}$$

$$\text{or } PV^{1.4} = \text{constant}$$

$$\therefore \gamma = 1.4 - \text{diatomic \& adiabatic}$$

Q.4 (A)

$$|w| = \pi ab = \frac{22}{7} \times 7 \times 5 = 110 \text{ bar lit.} = 11000 \text{ J} = 11 \text{ kJ}$$

$$\text{Final Answer} = -11$$

Q.5 (A)

 $w = \text{zero}$ 

Since the area of both triangle is equal. Also work done in one is positive while in other is negative.

Q.6 (C)

$$W = -P_{\text{ext}} [V_2 - V_1]$$

$$W_1 = -2 [16 - 4] \times 100 = -2400 \text{ J}$$

$$W_2 = -[32 - 16] = -16 \times 100 = -1600 \text{ J}$$

$$-4000$$

$$q = -W = 4000 \text{ J}$$

Q.7 (D)

$$nC_V (T_2 - T_1) = -P_{\text{ext}} \times nR \left[ \frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

$$T_2 = \frac{9}{7} T_1$$

$$w = 2 \times \frac{5}{2} \times R \left[ \frac{9}{7} T_1 - T_1 \right]$$

$$= 500 \text{ R}$$

Q.8 (D)

$$C_V = \frac{\Delta U}{n\Delta T}, n = \frac{4.48}{22.4} = 0.2$$

$$= \frac{12}{0.2 \times 15} = 4 \text{ cal}$$

$$C_P = C_V + R = 4 + 2 = 6 \text{ cal}$$



**Q.9** (C)

Total cubes = n

$$\text{Moles of H}_2\text{O} = n \times \frac{9}{18} = 0.5n$$

Heat released by liquid = Heat absorbed by ice

$$n \times 0.5 \times 6 = \frac{500}{18} \times 75.6 \times 20 \times 10^{-3}$$

$$3n = 42$$

$$n = 14$$

**Q.10** (A)

As container is insulated

$$q = 0$$

$$q_1 + q_2 = 0$$

$$n_1 C_m (T - T_1) + n_2 C_m (T - T_2) = 0$$

$$T = \frac{n_1 T_1 + n_2 T_2}{(n_1 + n_2)} = \frac{(P_1 V_1 + P_2 V_2) T_1 T_2}{(P_1 V_1 T_2 + P_2 V_2 T_1)}$$

**Q.11** (D)

$$\Delta U = 100 - \frac{209}{4.18} = 50 \text{ cal}$$

$$\Delta U = n C_v dT$$

$$C_{v,m} = \frac{5}{2} R$$

$$n dT = \frac{20}{R}$$

$$q = n C_m dT$$

$$C_m = \frac{100R}{20} = 5R$$

**Q.12** (B)

Heat released to cool 500 g water from 20°C to 0°C,

$$q = ms \Delta T$$

$$= 500 \times 4.18 \times 20 = 41800 \text{ J} = 41.8 \text{ kJ}$$

Number of moles of water (ice) that will melt to absorb 41.8 kJ

$$= \frac{41.8}{6.02} \approx 7$$

∴ Number of cubes of ice that will melt = 7

**Q.13** (B)

$$\Delta n = 2 - (5 + 2) = -5 \text{ mol.}$$

$$\Delta H = \Delta E + (\Delta n) RT$$

$$-50160 = \Delta E + (\Delta n) RT$$

$$\Delta E = -50160 - (-5)(8.314)(300)$$

$$= -50160 + 12471 = -37689 \text{ J}$$

**Q.14** (B)

$$\Delta U = q + w$$

$$= (40 \times 200) + (-2 \times 10 \times 100)$$

$$= 6000 \text{ J Ans.}$$

**Q.15** (B)

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vap}}}{T} = \frac{-540 \times 18}{373}$$

$$\Delta S_{\text{cooling}} = +n C_p \ln \left( \frac{T_2}{T_1} \right) = 18 \ln \left( \frac{273}{373} \right)$$

$$\Delta S_{\text{fusion}} = \frac{-80 \times 18}{273}$$

$$= - \left[ 18 \left( \frac{80}{273} + \frac{540}{373} \right) + \left( 18 \ln \frac{273}{373} \right) \right]$$

$$= -18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right)$$

$$\Rightarrow 36.95 \text{ cal /}^\circ \text{ Ans.}$$

**Q.16** (C)

$$0.40 = aT_1^3 + bT_1 \Rightarrow 0.40 = a \times (1000) + b \times 10$$

$$\Rightarrow 0.4 = 1000a + 10b$$

$$\dots(1)$$

$$0.92 = aT_2^3 + bT_2 \Rightarrow 0.92 = a \times 8000 + 20b$$

$$\dots(2)$$

On solving

$$0.12 = 6000a \quad ; \quad a = 2 \times 10^{-5}$$

$$0.40 = 2 \times 10^{-5} \times 1000 + b \times 10$$

$$\therefore b = 0.038$$

$$S_m = \int \frac{aT^3 + bT}{T} \cdot dT$$

$$\Rightarrow \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

$$\Rightarrow \frac{2 \times 10^{-5} \times (8000 - 0)}{3} + b(20)$$

$$\Rightarrow \frac{2 \times 10^{-5} \times 8000}{3} + 0.038 \times (20)$$

$$\Rightarrow 0.053 + 0.76 \Rightarrow 0.813 \text{ J/K-mol}$$

**Q.17 (D)**

$$C_v(T_h - T) = C_v(T - T_c) \Rightarrow T = \frac{T_c + T_h}{2}$$

$$\therefore \Delta S = \int_{T_1}^{T_2} \frac{C_v \cdot dt}{T}$$

$$\Delta S_c = C_v \ln \frac{T}{T_c} \quad \& \quad \Delta S_h = C_v \ln \frac{T}{T_h}$$

$$\text{Total } \Delta S = C_v \ln \frac{(T_c + T_h)}{2T_c} + C_v \ln \frac{(T_c + T_h)}{2T_h} =$$

$$C_v \ln \frac{(T_c + T_h)^2}{4T_c \cdot T_h}$$

**Q.18 (B)**

$$\eta = 1 - \frac{300}{500}$$

$$= 1 - 0.6 = 0.4$$

$$\% \eta = 40 = \frac{|W|}{q} \times 100$$

$$w = \frac{40}{100} \times 2 = 0.8 \text{ Kcal}$$

**Q.19 (D)**

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$V_2 = 40$$

$$V_1 = 20$$

$$\Delta S = 2 \times 2 \ln 2$$

$$= 4 \ln 2 = 2.77 \text{ cal.}$$

**Q.20 (C)**

$$\Delta S (\text{system}) = nR \ln \frac{P_1}{P_2} = 10 \times 8 \times \ln 2 = 80 \times 0.7 = 56$$

$$\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T} = \frac{w_{\text{irr}}}{T}$$

**Q.21 (C)**

$$\Delta G^\circ = 2 \times \Delta G^\circ_{\text{NH}_3} - \Delta G^\circ_{\text{N}_2} - (\Delta G^\circ_{\text{H}_2} \times 3)$$

$$= 2 \times (-16.66) - 0 - 0$$

$$= -33.32 \text{ KJ}$$

**Q.22 (A)**

$$\Delta G^\circ = -2.303 RT \log K_p$$

$$K_p = P = 10^{-5.44}$$

**Q.23 (D)**

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

$$Q = \frac{(0.02)^2}{1 \times 3^3}$$

$$= -60.5 \text{ kJ/Mol}$$

**Q.24 (C)**

$$\Delta G^\circ = -2.303 RT \log K_{\text{eq}}$$

$$= -RT \ln K_p$$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{x}{2} \text{ bar} = -RT \ln \left( \frac{x}{2} \right)^2 = -2RT (\ln$$

$$x - \ln 2)$$

**Q.25 (A)**

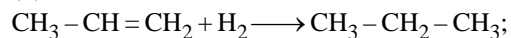
$$\Delta G^\circ = 2.303 RT \log K_c$$

$$460.6 = -2.303 \times 2 \times 900 \log K_c$$

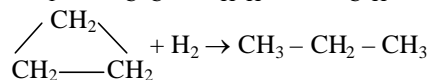
$$\log K_c = -\frac{1}{9}$$

$$\log \frac{[C]_{\text{eq}}^2}{[A]_{\text{eq}}^2} = \frac{1}{9} \quad \log \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}} = -\frac{1}{18} =$$

$$5.56 \times 10^{-2} \quad (\text{at equilibrium } [C]_{\text{eq}} = [D]_{\text{eq}} [A]_{\text{eq}} = [B]_{\text{eq}})$$

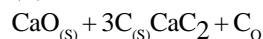
**Q.26 (B)**


$$\Delta H_1 = (\text{BE}_{\text{C-C}} + \text{BE}_{\text{H-H}}) - (2\text{BE}_{\text{C-H}} + \text{BE}_{\text{C-C}})$$



$$\Delta H_2 = (\text{BE}_{\text{C-C}} + \text{BE}_{\text{H-H}}) - (2 \times \text{BE}_{\text{C-H}})$$

$$\Delta H_2 - \Delta H_1 = 2\text{BE}_{\text{C-C}} - \text{BE}_{\text{C-C}}$$

**Q.27 (D)**


$$\Delta_r = -14 - 26 + 152 = 112 \text{ per mole}$$

$$\text{for } 1.28 \text{ Kg} = 112 \times 20 = 2240 \text{ Kcal}$$

Q.28 (A)

HCl = NaOH = 510 Mole  
 $q = 4.2 \times 3 = 1.26 \text{ KJ}$   
 per mole  
 $\text{KJ} = 2.5 \times 10^2 \text{ KJ/Mole}$

Q.29 (D)

C – E bond has highest bond energy ; it means that the covalent bond C – E will be strongest. Smaller is the size of atom, stronger is the covalent bond.]

Q.30 (D)

$\therefore$  58 g isobutane provides energy  
 $= 2658 \text{ kJ}$   
 $\therefore 11.2 \times 10^3 \text{ g isobutane provides energy}$   
 $= \frac{2658 \times 11.2 \times 10^3}{58} \text{ kJ} = 513268.9 \text{ KJ}$   
 The daily requirement of energy = 15000 kJ  
 $\therefore$  cylinder will last =  $\frac{513268.9}{15000} = 34 \text{ days}$

Q.31 (C)

HA BOH

$\text{H}^+ \text{A}^- + \text{B}^+ \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{BA}$   
 $-56.1 = \text{ionH} - 57.3$   
 $1.5 \alpha = 1.2 = 0.8$

Q.32 (C)

C (graphite) (diamond) ;  $\text{H}_1 - \text{H}_2$   
 $\text{H}_1 - \text{H}_2 = (6 \text{ g}^\circ \text{ Mole})$   
 $= 0.95$

Q.33 (A)

$\text{N}_2(\text{g}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{NCl}_3(\text{g})$ ;  $\text{fH}$   
 above eq<sup>n</sup> can become  
 $2 \text{Rx}^n + \text{Rx}^n - 3 \text{Rx}^n$   
 $\text{fH}(\text{NCl}_3, \text{g}) = \text{fH}$   
 $= [-2\text{H}_1 + \text{H}_2 - 3\text{H}_3]$   
 $= -\text{H}_1 + -\text{H}_3$

Q.34 (C)

By  $\text{Rx}^n \dots 1 - \text{Rx}^n \dots 2$   
 $4\text{AuBr}_4 + 4\text{HCl} \rightarrow \text{HA}_4\text{Cl}_4 + 4\text{HBr}$   
 $\Delta\text{H} = -28 + 36.8 = 8.8 \text{ Kcal/mol}$   
 But  $\Delta\text{H} = 0.44 \text{ Kcal}$   
 $= 0.05$   
 $\% \text{ dissociation} = 5\%$

Q.35 (A)

By  
 Eq ....2 – Eq....1  
 t – 2 – butene 1 – butene

 $\text{H}_2 - \text{H}_1 > 0$ 

By

Eq ....6 – Eq....7

t – 2 – butene 1 – butene

 $\text{H}_2 - \text{H}_1 > 0$  $\text{H} = -647 + 649.8 = 2.8$  $\text{H}_2 - \text{H}_1 = 2.8$  and $9\text{H}_1 + 5\text{H}_2 = 0$  $\text{H}_2 = 1.0$  and  $\text{H}_2 = 1.8$ 

Q.36 (D)

 $\text{H}_2 + \text{O}_2 \rightarrow \text{OH}(\text{g})$ ; 42 ....(1) $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ ; -242 ....(2) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$ ; 436 ....(3) $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$ ; 495 ....(4)

(a) Eq.....3 + Eq.....4 Eq 2

 $242 + 436 = 925.5$ ; True(b) Eq<sup>n</sup> 3 + Eq<sup>n</sup> 4 – Eq<sup>n</sup> 1 $\Delta\text{H} = -42$ , false(c)  $\text{H}_2 \rightarrow 2\text{H}$ ;  $\Delta\text{fH} = 2\text{fH}(\text{H}, \text{g})$  $\text{fH}(\text{H}, \text{g}) = 218$ ; False(d) First reaction is  $\Delta\text{rH} = \Delta\text{fH}(\text{OH}, \text{g})$  $= 42$ ; True

Q.37 (C)

 $+ 3\text{H}_2$  $\Delta\text{rH} = \Delta\text{fH}(\text{cyclohexane}) - \Delta\text{fH}(\text{Benzene})$  $= -156 - 49$  $\Delta\text{rH} = 3(-19) + \text{R.E}$  $\text{R.E} = -156 - 49 + (3 \times 119) = 152 \text{ KJ/Mole}$ 

Q.38 (B)

Q.39 (A)

Q.40 (B)

Q.41 (D)

Q.42 (B)

Q.43 (C)

Q.44 (C)

Q.45 (A)

Q.46 (D)

Q.47 (B)

## JEE-ADVANCED

## MCQ/COMPREHENSION/COLUMN MATCHING

Q.1 (A)

(a)  $y = mx + C$  $10 = m \times 300 + C$  $15 = m \times 600 + C$ 

-----

 $5 = 300 m$

$$m = \frac{1}{60}, \quad c = 5$$

$$V = \frac{1}{60} T + 5 \quad w = - \int P \Delta V$$

$$P = 60 R - \frac{300R}{V}$$

$$w = - \int_{10}^{15} \left( 60R - \frac{300R}{V} \right) dV = - 1496.52$$

J

$$(b) \quad \Delta U = q + w \quad \text{or} \quad q = \Delta U - w$$

$$\Delta U = C_v \Delta T = 374.13$$

$$q = 374.13 + 1496.525 = 5237.82 \text{ J}$$

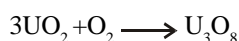
$$(c) \quad \Delta H = \frac{5}{2} \times R \times 300$$

$$(d) \quad \Delta S = +ve$$

**Q.2** (A,B,C)

G &lt; 0 for spontaneous

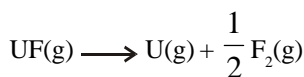
(D) Assumed to zero not unity

**Q.3** (B,C,D)**Q.4** (A,B,C) $P_{\text{white}} < P_{\text{red}}$  (Stability) $\Rightarrow$  Exothermic**Q.5** (A,C)

$$-76.01 = -853.5 - (3 \times \Delta_f H(\text{UO}_2))$$

$$\Rightarrow \Delta_f H = \frac{-853.5 + 76.01}{3}$$

$$= -259.16 \text{ Kcal / Mole}$$

**Q.6** (A, C)

$$\Delta_f H = \Delta_f H(\text{U,g}) - \Delta_f H(\text{UF}_6,\text{g})$$

$$= 128 - 22 = 106$$

or

$$\Delta_f H = E_{\text{U-F}} - \frac{1}{2} E_{\text{F-F}} = 106$$

$$\Rightarrow E_{\text{U-F}} = 106 + \frac{1}{2} \times 37$$

$$= 124.5 \text{ Kcal / Mole}$$

or

$$521 \text{ kJ/Mole}$$

**Q.7** (C,D)

Enthalpy of formation : follow the definition

**Q.8** (A, C, D)C (diamond);  $\Delta_f H \neq 0$ **Q.9** (A, B, C, D)Solid  $\longrightarrow$  liquidEndothermic ;  $\Delta H > 0$ **Q.10** (A, C, D)**Q.11** (C,D)Arrhenius equation ;  $K = Ae^{-E_a/RT}$ 

Kirchhoff's Equation ;

$$d(\Delta_f H) = \Delta_f C_p dT$$

**Comprehension # 01 (Q. No. 12 to 16)****Q.12** (A)**Q.13** (B)**Q.14** (B)**Q.15** (A)**Q.16** (A)**12** Stable state had zero standard molar enthalpy**13**  $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$ ;  $\Delta_f H > 0$  $\text{N}_2 + 2\text{O}_2 \longrightarrow 2\text{NO}_2$ ;  $\Delta_f H > 0$ 

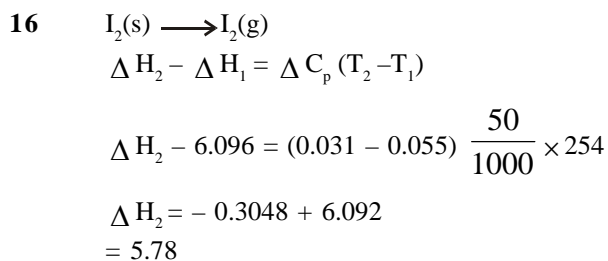
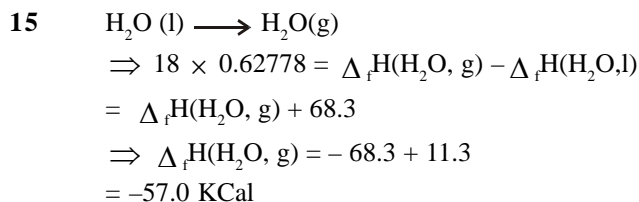
Endothermic reactions are favourable High temperature.

**14** (diamond) +  $\text{O}_2 \longrightarrow \text{CO}_2$ ; -94.3(Amorphous) +  $\text{O}_2 \longrightarrow \text{CO}_2$ ; -97.6(diamond)  $\longrightarrow$  (amorphous) ;

$$\Delta_f H = -94.3 + 97.6 = 3.3 \text{ KCal / Mole}$$

$$\text{for } 6\text{g C} \equiv \frac{1}{2} \text{ Mole C}$$

$$\Delta_r H = \frac{3.3}{2} = 1.65 \text{ KCal}$$



**Comprehension # 02 (Q. No. 17 to 20)**

Q.17 (B)

Q.18 (A)

Q.19 (A)

Q.20 (C)

**Comprehension # 3 (Q. No. 21 to 24)**

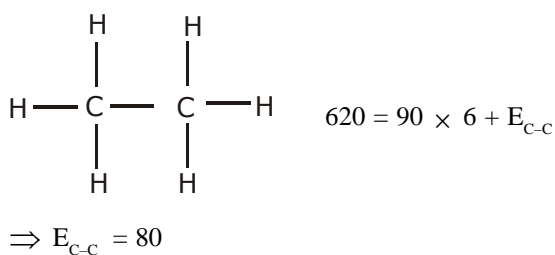
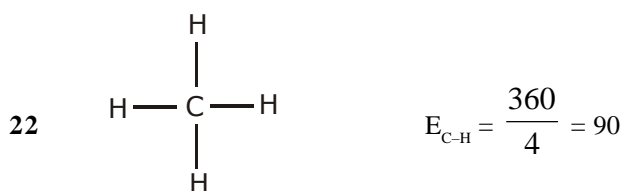
Q.21 (A)

Q.22 (B)

Q.23 (B)

Q.24 (A)

21 1 True 2 True 3 True 4 True 5 False



23 To Keep the temp. constant  $\Delta H$  overall = 0

Let x mole  $\text{O}_2$  and y mole steam

$$\Rightarrow 110 \times 2x = 132 y$$

$$\Rightarrow \frac{x}{y} = \frac{n_{\text{O}_2}}{n_{\text{steam}}} = 0.6$$

$$\Rightarrow \frac{n_{\text{O}_2}}{n_{\text{steam}}} = \frac{1}{0.6} = 1.666$$

24  $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l}); 1.44 \text{ KCal}$

$$\text{For } 27 \text{ g} \longrightarrow \frac{1.44}{18} \times 27 = 2.16$$

**Comprehension # 4 (Q. No. 25 to 27)**

Q.25 (A)

Q.26 (D)

Q.27 (B)

25 Acetic acid ; weak acid (Less than 13.7)

And HF is the exceptional case having larger value for Heat of neupralization than 13.7

26 (i) True

(ii) Due to cont. volume it measure  $\Delta U$

(iii)  $\Delta n_g = 0 \Rightarrow \Delta H = \Delta U$

(iv) False (due to involvement of R.E)

27 Case I ;  $\text{H}^+ = 0.1 \times 100 \times 2 = 20 \text{ m.eq.}$

$\text{OH}^- = 0.1 \times 100 \times 2 = 20 \text{ m.eq.}$

Case II ;  $\text{H}^+ = 50 \times 0.1 \times 2 = 10 \text{ m.eq.}$

$\text{OH}^- = 100 \times 0.1 = 10 \text{ m.eq.}$

$$\Rightarrow 2 \Delta H_{\text{II}} = \Delta H_{\text{I}}$$

$$\Delta H_{\text{I}} = 274 \text{ cal} ; \Delta H_{\text{II}} = 137$$

$\Delta T_{\text{I}} = \Delta T_{\text{II}}$  (Because amount of substasace in case I is double than case II)

Q.28  $\text{A} \rightarrow (\text{P,R}), \text{B} \rightarrow (\text{Q,S}), \text{C} \rightarrow (\text{Q,S}), \text{D} \rightarrow (\text{Q,S})$

If  $\Delta n_g > 0 : \Delta S > 0$

Q.29  $\text{A} \rightarrow (\text{P,S}), \text{B} \rightarrow (\text{Q}), \text{C} \rightarrow (\text{R})$

Kircaff's equation

$$d(\Delta_r H) = \Delta_r C_p dt$$

$$\Rightarrow \Delta H = \Delta U + \Delta n g R T$$

$$\Rightarrow \Delta S = \frac{q_{rev}}{T}$$

**NUMERICAL VALUE BASED****Q.1** [6]

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Rightarrow \Delta H = 40 + (P_2 V_2 - P_1 V_1) = 40 + (5 \times 6 - 2.5 \times 4) = 40 + 20 = 60 = 10x$$

$$\Rightarrow x = 6$$

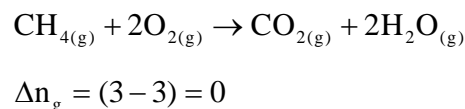
**Q.2** [9]

$$q = \Delta U - w$$

-w is work done by the system

$$\Delta U = q + w$$

$$= 5 + 4 = 9$$

**Q.3** [0]**Q.4** [4]

$$P V^3 = \text{constant} \Rightarrow (P/P') \times (V/V')^3 = 1 \Rightarrow (P/P') = (V'/V)^3$$

$$\Rightarrow (P/P') = (d'/d)^3 \text{ (Since } V \propto 1/d)$$

$$\Rightarrow (d'/d) = (1/32)^{-3} = (1/32)^{-1.4} = 128 = 32x$$

$$\Rightarrow x = 4$$

**Q.5** [8]

$$w = P dv$$

$$= 1 \times (2.5 - 2.0)$$

$$= -0.5 \text{ litre-atm}$$

$$= \frac{-0.5 \times 1.987 \times 4.184}{0.0821} = -50.63 \text{ J}$$

$\therefore$  work is carried out of constant P and thus irreversible

from 1<sup>st</sup> law of thermodynamics

$$q = \Delta U - w$$

$$58.63 = \Delta U + 50.63$$

$$\Delta U = 8 \text{ joule}$$

**Q.6** [2]

$$\Delta H_{\text{fusion}} = 6.025 \times 1000 \text{ J mol}^{-1}$$

$$= \frac{6025}{18} \text{ J/g}^{-1} = 334.72 \text{ Jg}^{-1}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{334.72}{167 \text{ K}} = 2 \text{ Jk}^{-1} \text{ g}^{-1}$$

**Q.7** [5]

$$\gamma = 1.4$$

$$C_v = \frac{5}{2} R \quad C_p = \frac{7}{2} R$$

$$\Delta H = 85 \text{ Joule at constant pressure}$$

$$\Delta T = \frac{85}{nC_p} = \frac{140 \times 2}{7n \times R} = \frac{40}{n}$$

$$\text{Now, } w = -nR\Delta T = -n \times 2 \times \frac{40}{n} = -80 \text{ J}$$

$$q_p = \Delta H = \Delta U + (-W), \quad \Delta U = \Delta H + W$$

$$= 85 - 80 = 5 \text{ J}$$

**Q.8** [2]

Reversible work is maximum work

$$w = -2.303nRT$$

$$\log_{10} \left( \frac{v_2}{v_1} \right) = 2.303 \times \frac{16}{32} \times 8.314 \times 300 \times \log \frac{25}{5}$$

$$= 2.01 \times 10^3 \text{ joule} = 2 \text{ kJ}$$

**Q.9** [0]

$$P_{\text{ext}} = 0, w = -p_{\text{ext}}(v_2 - v_1) = -0(v_2 - v_1) = 0$$

As temp is not given, assume it as constant and therefore  $\Delta E = 0$

$$\Delta E = q + w \Rightarrow 0 = q + 0 = 0, \Delta H = 0$$

**Q.10** [9]

In isothermal reversible process

$$\Delta S = \frac{q_{rev}}{T}$$

$$q = -W = 2.303RT \log(V_2/V_1)$$

$$= 2.303 \times 8.314 \times 300 \log 3 = 2740.6 \text{ J mol}^{-1}$$

$$\Delta S_{\text{system}} = \frac{q_{rev}}{T} = \frac{2740.6}{300} = 9.135 \text{ JK}^{-1} \text{ mol}^{-1} \cong 9$$

**Q.11** [1]

$$\rho_L = 0.075 \times 40 = 3 \text{ Cal}$$

$$\rho_P = 0.125 \times 40 = 5 \text{ Cal}$$

$$\frac{\rho_P}{\rho_L} = \frac{5}{3} = 1.66 \text{ gas is mono atomic}$$

**Q.12** [1]

Heat of neutralisation of a strong acid by strong base is -13.7 Kcal

1 mole of  $\text{H}_2\text{SO}_4$  furnishes 2 moles of  $\text{H}^+$

**Q.13** [6]

$$\Delta H = 12 \text{ Kcal}$$

$$\Delta H_f = \frac{12}{2} = 6 \text{ Kcal}$$

**Q.14** [6]

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta n = \frac{3.6}{2 \times 10^{-3} \times 300} = 6$$

**Q.15** [7]

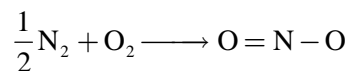
$$\text{Since } \Delta G = \Delta H - T\Delta S$$

$$\text{But at equilibrium, } \Delta G = 0 = \Delta H - T\Delta S$$

$$\therefore \Delta S = \frac{\Delta H}{T} = \frac{2000}{286} = 7 \text{ J / mole / K}$$

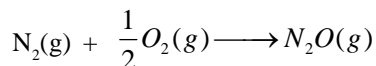
**Q.16** [8]

Theoretical heat of formation of  $\text{NO}_2$  142 KJ/mol

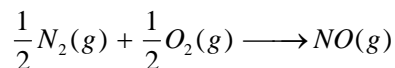


$$\Delta H_{(\text{Theoretical})} = \frac{1}{2} \times 946 + 498 - 222 - 607 = 142 \text{ kJ / mol}$$

**Q.17** [3]

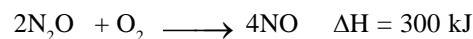


$$\Delta H = 30 \text{ kJ} \quad \dots \dots \text{(i)}$$



$$\Delta H = 90 \text{ kJ} \quad \dots \dots \text{(ii)}$$

$$\text{By eq [4} \times \text{(ii)} - 2 \times \text{(i)]}$$

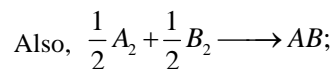


$$3 \times 10^2 \text{ kJ} \quad \therefore x = 3$$

**Q.18** [4]

$$e_{A-A} = a; \quad e_{A-B} = a;$$

$$e_{B-B} = 0.5a$$



$$\Delta H = -100 \text{ kJ mol}^{-1}$$

$$\therefore \Delta H = -[e_{A-B}] + \frac{1}{2} [e_{A-A} + e_{B-B}]$$

$$= -a + \frac{1}{2} [a + 0.5a]$$

$$-100 = -0.25a$$

$$\therefore a = 400 \text{ kJ mol}^{-1} = 4 \times 10^2$$

$$\therefore X = 4$$

$$\therefore \text{Resonance Energy} = 142 - 134 = 8 \text{ kJ / mol.}$$

**Q.19** [6]

$$x(100) = (10 - x)(150) \Rightarrow x = 6$$

### KVPY

#### PREVIOUS YEAR'S

**Q.1** (A)

According to KTG

Force of attraction and repulsion amongst molecules of ideal gas are negligible

So,  $\Delta H = 0$

and randomness increases due to increase in volume so  $\Delta S = + \text{ve}$ .

**Q.2** (D)

$$(\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}} > 0 \text{ (irreversible process)}$$

**Q.3** (D)

**Q.4** (C)

$$\Delta S = \frac{nRT}{T} \ln \frac{v_2}{v_1}$$

$$= nR \ln \frac{v_2}{v_1}$$

$$= 2.303 nR \log \frac{v_2}{v_1}$$

$$= 2.303 \times 2 \times 8.314 \times 1$$

$$= 38.3 \text{ J/k}$$

**Q.5** (C)

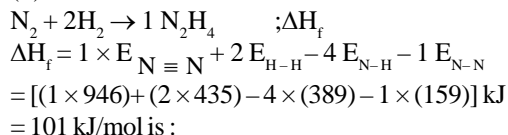
$$\Delta U = 0, \Delta H = 0$$

Q.6 (A)

$$\Delta S = \frac{\Delta H_{\text{Melting}}}{T_{\text{F.P}}} = \frac{6 \times 1000 \text{ J}}{273 \text{ K}}$$

$$= 21.978 \approx 22 \text{ J/k}$$

Q.7 (B)



Q.8 (D)

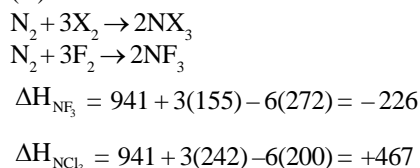
$$W = -nRT = -(1 \times 8.314 \times 10^{-3} \times 373) \text{ kJ}$$

$$= -3.10 \text{ kJ}$$

$$q = \Delta H = 41 \text{ kJ}$$

$$\& \Delta E = q + W = (41 - 3.1) \approx 37.9 \text{ kJ}$$

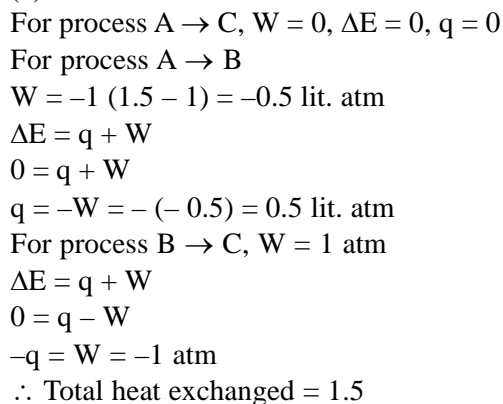
Q.9 (A)



Q.10 (D)

Use the concept of calorimetry and solve to get the answer.

Q.11 (C)



Q.12 (D)

$$q = mc\Delta t + \text{heat of vapourisation}$$

$$= 1000 \times 2.44 (351.45 - 293.45) + 855 \times 1000 \text{ J}$$

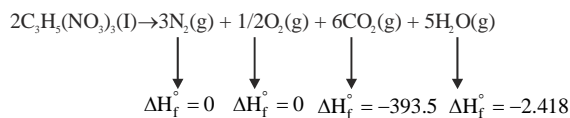
$$= 9.97 \times 10^5 \text{ J}$$

Q.13 (A)

Number of H-bond is A-T pair = 2, while no of H-bond in G-C pair is 3. therefore  
 (i) Total number of A-T. H-bond = number of A-T pair  $\times$  Number of H bond =  $5 \times 2 = 10$   
 (ii) Total number of G-C. H-bond = number of G-C pair  $\times$  Number of H bond =  $3 \times 3 = 9$

total energy required to dissociate the stand =  $10x + 9y \text{ Kcal mol}^{-1}$

Q.14 (B)



$$\Delta H_{\text{reaction}}^\circ = 3 \times 0 + \frac{1}{2} \times 0 + 6 \times (-393.5) + 5 \times (-2.418) - (2 \times -364)$$

$$= -2842 \text{ kJ} \rightarrow \text{for 2 mole of nitroglycerine}$$

$$\text{for 1 mole of for } 227.1 \text{ g} = \frac{2842}{2}$$

$$\text{for 1 g} = -\frac{2842}{2 \times 227.1} \times 10 = -62.5 \text{ KJ}$$

Q.15 (D)

For a spontaneous process entropy change of the system plus surrounding must be positive.

Q.16 (A)

Free expansion of gas when a gas expands in vacuum work done by it is = 0

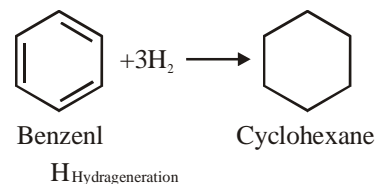
$$\text{As } P_{\text{ext}} = 0$$

As no heat is supplied to the system  $q = 0$  &

$$\Delta E = \Delta H = \Delta T = 0$$

So, internal energy remains constant.

Q.17 (B)



Q.18 (B)

$$\text{Entropy change } \Delta S = nC_v \ln \left( \frac{T_2}{T_1} \right) + mR \ln \left( \frac{V_2}{V_1} \right)$$

Since temperature is constant throughout process.

$$\text{He : } \Delta S = n_1 R \ln \frac{V_1 + V_2}{V_1}$$

$$\text{Ne : } \Delta S = n_1 R \ln \frac{V_1 + V_2}{V_2}$$



$$\text{Total change in } (\Delta S) = n_1 R \ln \left( \frac{V_1 + V_2}{V_1} \right)$$

$$+ n_1 R \ln \left( \frac{V_1 + V_2}{V_2} \right)$$

**Q.19 (B)**

Since products are formed in the chemical reaction taking place at constant temperature and pressure, we can say that the reaction is spontaneous.

$$\text{Hence, } \begin{aligned} \Delta G_{\text{reaction}} &< 0 \\ \Delta S_{\text{total}} &> 0 \end{aligned}$$

**Q.20 (A)**

Specific heat capacity of substance

$$= 0.86 \text{ J g}^{-1} \text{ K}^{-1}$$

1 molal aqueous solution

⇒ 1000 gm water has 58 gm solute

(total mass of solution = 1058 gm)

If we take 10 gm solution it would have

$$\text{water} = \frac{1000}{1058} \times 10 \text{ gm}$$

$$\text{substance} = \frac{58}{1058} \times 10 \text{ gm}$$

$$\text{Heat required} = \frac{1000}{1058} \times 10 \times 4.2 \times 10$$

$$\text{(for water)} = 396.975$$

$$\frac{58}{1058} \times 10 \times 0.86 \times 10 \text{ (for substance)} = 4.715$$

$$= 396.975 + 4.715 = 401.69 \approx 401.7$$

**Q.21 (A)**

AB is isothermal reversible expansion process i.e.

$\Delta T = 0$  and  $S$  increases as there is increase in volume.

BC is adiabatic reversible expansion process

( $q_{\text{rev}} = 0$ ) i.e. temperature decreases and

$\Delta S = 0$ .

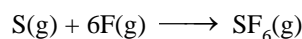
CD is isothermal reversible compression process i.e.

$\Delta T = 0$  and  $S$  decreases as there is decrease in volume.

DA is adiabatic reversible compression process

( $q_{\text{rev}} = 0$ ) i.e. temperature decreases and

$\Delta S = 0$ .

**JEE-MAIN****PREVIOUS YEAR'S****Q.1** [309.16]

$$\begin{aligned} \Delta H_{\text{R}}^{\circ} &= \Delta H_{\text{f}}^{\circ}(\text{SF}_6) - \Delta H_{\text{f}}^{\circ}(\text{S}) - 6\Delta H_{\text{f}}^{\circ}(\text{F}) \\ &= (-1100) - (275) - 6(80) = -1855 \end{aligned}$$

$$\Delta H_{\text{R}}^{\circ} = -1855 = 0 - 6 \times (\Delta H_{\text{S-F}}^{\circ})$$

$$\Rightarrow \Delta H_{\text{S-F}}^{\circ} = \frac{1855}{6} = 309.16 \frac{\text{kJ}}{\text{mole}}$$

**Q.2** [200]

For spontaneous reaction  $\Delta G < 0$

$$\Delta H - T\Delta S < 0$$

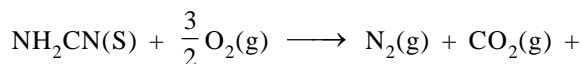
$$80,000 - (T)(2T) < 0$$

$$2T^2 > 80,000$$

$$T^2 > 40,000$$

$$T > 200 \text{ K}$$

∴ Ans. 200 K

**Q.3** [15]**Q.4** [743]

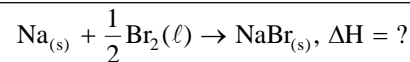
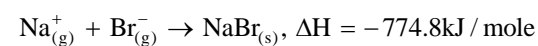
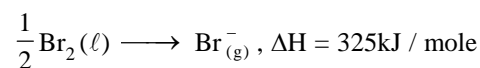
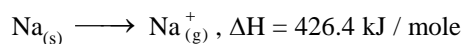
$$\text{H}_2\text{O}(\ell) \quad \Delta n_{\text{g}} = (1 + 1) - \frac{3}{2} = \frac{1}{2}$$

$$\Delta H = \Delta U + \Delta n_{\text{g}} RT$$

$$= -744.24 + \frac{1}{2} \times \frac{8.314 \times 298}{1000}$$

$$= -744.24 + 1.24$$

$$\approx -743 \text{ kJ/mole}$$

**Q.5** [673.4]

$$\Rightarrow \Delta H = 426.4 - 325 - 774.8$$

$$= -673.4 \text{ kJ/mole}$$

**Q.6** [1380]

$$\Delta_{\text{r}} G^{\circ} = -RT \ln K_{\text{eq}}$$

$$= -R \times 300 \times 2 \times 2.3$$

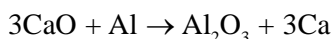
$$= -1380 \text{ R}$$

Q.7 [150.72]

$$\begin{aligned}\Delta G^\circ &= \left(G_m^\circ\right)_{C_6H_6} - 3\left(G_m^\circ\right)_{C_2H_6} \\ &= -1.4 \times 10^5 - 3 \times 2.4 \times 10^5 \\ &= -8.6 \times 10^5 \text{ Joule} \\ -2.303RT \log_{10} k &= -8.6 \times 10^5 \\ -2.303 \times 8.314 \times 298 \log_{10} k &= -8.6 \times 10^5 \\ \log_{10} k &= 150.72\end{aligned}$$

Q.8 [230]

Given reaction:

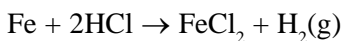


$$\begin{aligned}\text{Now, } D_f H^\circ &= S D_f H^\circ_{\text{Products}} - S D_f H^\circ_{\text{Reactants}} \\ &= [1 \times (-1675) + 3 \times 0] - [3 \times (-635) + 2 \times 0] \\ &= +230 \text{ kJ mol}^{-1}\end{aligned}$$

Q.9 [2218]

$$T = 298 \text{ K}, R = 8.314 \frac{\text{J}}{\text{molK}}$$

→ Chemical reaction is



50g P = 1 bar

$$= \frac{50}{50.85} \text{ mol}$$

$$\frac{50}{50.85} \text{ mol}$$

→ Work done for 1 mol gas

$$= -P_{\text{ext}} \times DV$$

$$= Dng RT$$

$$= -1 \times 8.314 \times 298 \text{ J}$$

→ Work done for  $\frac{50}{50.85}$  mol of gas

$$= -1.8314 \times 298 \times \frac{50}{50.85} \text{ J}$$

$$= -2218.059 \text{ J}$$

$$; -2218 \text{ J}$$

Q.10 (1)

(A) Water  $\xrightarrow{0^\circ\text{C}}$  ice;  $\Delta S = -ve$ (B) Water  $\xrightarrow{-10^\circ\text{C}}$  ice;  $\Delta S = -ve$ (C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ;  $\Delta S = -ve$ (D) Adsorption;  $\Delta S = -ve$ (E)  $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ ;  $\Delta S = +ve$ 

Q.11 [128]

$$\Delta_r H = [\epsilon_{C-C} + 2\epsilon_{C-H}] - [\epsilon_{C=C} + \epsilon_{H-H}]$$

$$= [347 + 2 \times 414] - [611 + 436]$$

$$= 128$$

Q.12 [31]

Q.13 [50]

Q.14 [101]

Q.15 [26]

Q.16 [21]

Q.17 [336]

Q.18 [38]

Q.19 [718]

Q.20 [964]

Q.21 [82]

Q.22 (2)

Q.23 [5]

**JEE-ADVANCED****PREVIOUS YEAR'S**

Q.1 (A - p, r, s); (B - r, s); (C - t); (D - p, q, t)

(A)  $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$ 

It is phase transition. The process is endothermic (sublimation).

Gas is produced, so entropy increases.

(B) On heating  $\text{CaCO}_3$  decomposes. So, process is endothermic.

The entropy increases as gaseous product is formed.

(C)  $2\text{H}\bullet \longrightarrow \text{H}_2(\text{g})$ 

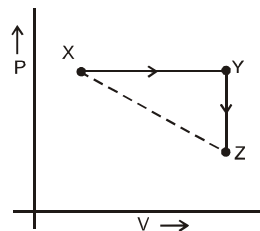
Entropy decreases as number of gaseous particles decreases.

(D) It is phase transition.

White and red P are allotopes.

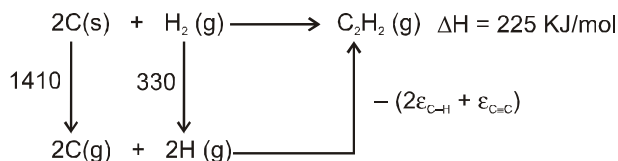
Red P is more stable than white. So  $\Delta H$  is -ve.

Q.2 (A, C)



- (A)  $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$  (Correct)  
 (B)  $W_{x \rightarrow y} = W_{x \rightarrow z} + W_{y \rightarrow z}$  (Incorrect)  
 (C)  $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$  (Correct)  
 (D)  $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$  (Incorrect)

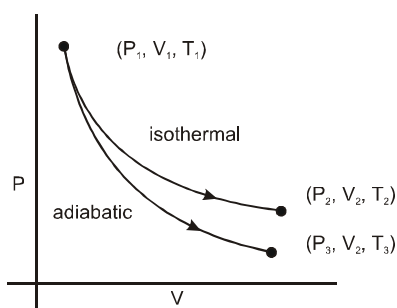
Q.3 (D)



$$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{C=C} = +225$$

$$\therefore \varepsilon_{C=C} = 1740 - 700 - 225 = +815 \text{ KJ/mol.}$$

Q.4 (A, D)



(A)  $T_1 = T_2$  (due to isothermal)

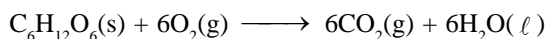
(B)  $T_3 > T_1$  (incorrect) cooling will take place in adiabatic expansion)

(C)  $W_{\text{isothermal}} > W_{\text{adiabatic}}$  { with sign, this is incorrect }

(D)  $\Delta U_{\text{isothermal}} = 0 > \Delta U_{\text{adiabatic}} = -ve$

So, answer is (A, D).

Q.5 (C)



$$\Delta_c H = 6 \times \Delta_f H(CO_2) + 6 \Delta_f H(H_2O) - \Delta_f H(C_6H_{12}O_6) - 6 \Delta_f H(O_2, g)$$

$$= 6 \times (-400 - 300) - (-1300) - 0$$

$$= -4200 + 1300$$

$$= -2900 \text{ KJ/mol}$$

For one gram of glucose, enthalpy of combustion =

$$- \frac{2900}{180} = -16.11 \text{ KJ/g.}$$

Q.6 (B)

For  $H_2O(l) \rightarrow H_2O(g)$  at  $T = 100^\circ\text{C}$ , 1atm equilibrium exists.  $\therefore \Delta G = 0, \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S > 0$  for system, since evaporation is endothermic

$$\therefore (\Delta S)_{\text{system}} > 0, \text{ also } (\Delta S)_{\text{surrounding}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}$$

Heat gained by system = heat lost by surroundings

$$\therefore q_{\text{surr.}} < 0 \therefore (\Delta S)_{\text{surr.}} < 0$$

Q.7 (A, B, C)

Since the vessel is thermally insulated so

$$q = 0$$

$$p_{\text{ext}} = 0, \text{ so } w = 0$$

so  $\Delta U = 0$  (ideal gas)

Hence  $\Delta T = 0$

$$\Rightarrow \Delta T = 0$$

$$\Rightarrow T_2 = T_1$$

$$\Rightarrow P_2 V_2 = P_1 V_1$$

The process is however adiabatic irreversible.

So we cannot apply  $P_2 V_2^\gamma = P_1 V_1^\gamma$

Hence ans is (A), (B), (C)

Q.8 (A-R, T) (B-P, Q, S) (C-P, Q, S) (D-P, Q, S, T)

(A)  $H_2O(l) \longrightarrow H_2O(s)$  at 273 K. & 1 atm

$$\Delta H = -ve = q$$

$$\Delta S_{\text{sys}} < 0, \quad \Delta G = 0.$$

$w \neq 0$  (as water expands on freezing),  $\Delta U \neq 0$

(B) Free expansion of ideal gas.

$$q = 0 \quad w = 0 \quad \Delta U = 0 \quad \Delta S_{\text{sys}} > 0 \quad \Delta G < 0$$

(C) Mixing of equal volume of ideal gases at constant pressure & temp in an isolated container

$$q = 0, \quad w = 0, \quad \Delta U = 0, \quad \Delta S_{\text{sys}} > 0 \quad \Delta G < 0$$

(D)  $H_2(g)$  300 K  $\xrightarrow[\text{Heating, 1atm}]{\text{Reversible}}$  600 K

$$\xrightarrow[\text{Cooling, 1atm}]{\text{Reversible}} 300 \text{ K.}$$

$$q = 0, w = 0, \Delta U = 0, \Delta G = 0, \Delta S_{\text{sys}} = 0$$

**Comprehension # 1 (Q. No. 9 to 10)**
**Q.9 (A)**

Let the heat capacity of insulated beaker be C.

 Mass of aqueous content in expt. 1 =  $(100 + 100) \times 1 = 200$  g

 $\Rightarrow$  Total heat capacity =  $(C + 200 \times 4.2)$  J/K

 Moles of acid, base neutralised in expt. 1 =  $0.1 \times 1 = 0.1$ 
 $\Rightarrow$  Heat released in expt. 1 =  $0.1 \times 57 = 5.7$  KJ

 $\Rightarrow 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T$ .

$$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$$

 $\Rightarrow (C + 200 \times 4.2) = 1000$ 

In second experiment,

$$n_{\text{CH}_3\text{COOH}} = 0.2, \quad n_{\text{NaOH}} = 0.1$$

Total mass of aqueous content = 200 g

 $\Rightarrow$  Total heat capacity =  $(C + 200 \times 4.2) = 1000$ 
 $\Rightarrow$  Heat released =  $1000 \times 5.6 = 5600$  J.

 Overall, only 0.1 mol of  $\text{CH}_3\text{COOH}$  undergo neutralization.

$$\Rightarrow \Delta H_{\text{neutralization}} \text{ of } \text{CH}_3\text{COOH} = \frac{-5600}{0.1} = -56000$$

J/mol

$$= -56 \text{ KJ/mol.}$$

$$\Rightarrow \Delta H_{\text{ionization}} \text{ of } \text{CH}_3\text{COOH} = 57 - 56 = 1 \text{ KJ/mol}$$

**Q.10 (B)**

 Final solution contain 0.1 mole of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  each.

Hence it is a buffer solution.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$= 5 - \log 2 + \log \frac{0.1}{0.1} = 4.7$$

**Q.11 (C)**
 $\therefore$  Process is done against const. External P, process will be irreversible.

$$\therefore "S_{\text{surr}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T} =$$

$$\frac{-3 \times (2-1) \times 101.3}{300} = -1.013 \text{ J / K}$$

**Q.12 (C)**

$$dG = VdP - SdT$$

 At 298 K,  $SdT = 0$ 

$$\therefore dG = VdP$$

$$\int_1^P dG = \int_1^P VdP \therefore G - G^\circ = V(P-1)$$

 $[\therefore \text{Solids involved } \therefore V \text{ almost constant}]$ 

$$\therefore \Delta_r G = [G^\circ_{\text{diamond}} + V_d(P-1)] - [G^\circ_{\text{graphite}} + V_g(P-1)]$$

$$0 = 2.9 \times 10^3 + (P-1) 10^5 (-2 \times 10^{-6})$$

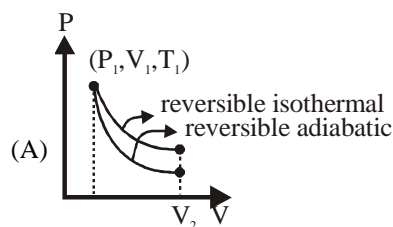
$$\therefore P = 14501 \text{ bat}$$

**Q.13 (A,B)**

$$\Delta S_{\text{Surr}} = \frac{-\Delta H}{T_{\text{Surr}}}$$

 For endothermic, if  $T_{\text{surr}}$  increases,  $\Delta S_{\text{surr}}$  will increase.

 For exothermic, if  $T_{\text{surr}}$  increases,  $\Delta S_{\text{surr}}$  will decrease.

**Q.14 (ACD)**


Area under curve in reversible isothermal is more. So, more work will be done by gas.

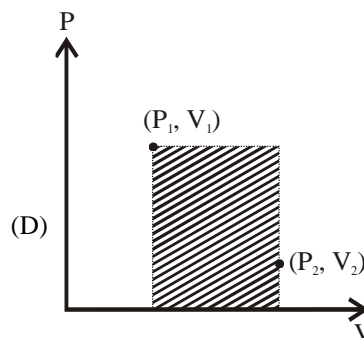
$$(B) T_1 = T_2 \Rightarrow \Delta U = nC_v \Delta T = 0$$

 In reversible adiabatic expansion,  $T_2 < T_1$ 

$$\therefore \Delta T = -ve \therefore \Delta U = -ve$$

 (C) In Free expansion,  $P_{\text{ext}} = 0 \therefore W = 0$ 

 If carried out isothermally ( $\Delta U = 0$ )  $\Rightarrow q = 0$  (Adiabatic); From I law

 If carried out adiabatically ( $q = 0$ )  $\Rightarrow \Delta U = 0$  (isothermal); From I law


During irreversible compression, maximum work is done on the gas (corresponding to shaded area)

**Q.15** (B,C)

AC → Isochoric

AB → Isothermal

BC → Isobaric

$$\# \quad q_{AC} = \Delta U_{BC} = nC_V(T_2 - T_1)$$

$$W_{AB} = nRT_1 \ln \left( \frac{V_2}{V_1} \right) \quad \text{A (wrong)}$$

$$\# \quad q_{BC} = \Delta H_{AC} = nC_P(T_2 - T_1)$$

$$W_{BC} = -P_2(V_1 - V_2) \quad \text{B (correct)}$$

$$\# \quad nC_P(T_1 - T_2) < nC_V(T_1 - T_2) \quad \text{C (correct)}$$

$$\Delta H_{CA} < \Delta U_{CA}$$

# D (wrong)

**Q.16** (A,B)

Enthalpy of formation is defined as enthalpy change for formation of 1 mole of substance from its elements, present in their natural most stable form.

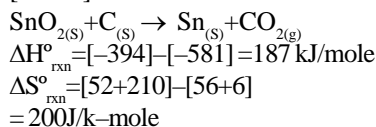
**Q.17** (A,B,C)

For 1 mole Vander Waal's gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

If  $P_{\text{ext}} = P$ , means process is reversible. For Vanderwaal gas, expression is correct for all reversible process.

**Q.18** [935.00]



$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{187 \times 1000}{200} = 935 \text{ K}$$

**Q.19** [166.28]

$$\Delta G^{\circ} = -RT \ln \left( \frac{P}{1} \right) = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\ln \left( \frac{P}{1} \right) = - \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

$$\text{Slope} = - \frac{\Delta H^{\circ}}{R} = 10^4 \times \left( - \frac{4}{2} \right)$$

$$\Rightarrow \Delta H^{\circ} = 2 \times 10^4 \times R$$

$$= 166.28 \text{ kJ/mole}$$

**Q.20** [141.33 or 141.34]

$$\text{From the plot when, } \frac{10^4}{T} = 10 \Rightarrow T = 1000 \text{ K}$$

$$\ln \left( \frac{P_2}{1} \right) = -3$$

Substituting in equation

$$\ln \left( \frac{P_2}{1} \right) = - \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

We get,

$$-3 = - \frac{2 \times 10^4 \times R}{R \times 1000} + \frac{S^{\circ}}{R}$$

$$\Rightarrow \Delta S^{\circ} = 17R$$

$$\Rightarrow \Delta S^{\circ} = 17 \times 8.314 \text{ J/K-mol}$$

$$\Rightarrow \Delta S^{\circ} = 141.34 \text{ J/K-mol}$$

**Q.21** (A, B, D)

From state I to II (Reversible isothermal expansion)

⇒ P decreases, V increases, T constant

H constant & S increases.

From state II to III (Reversible adiabatic expansion)

⇒ P decreases, V increases, T decreases

H decreases, S constant

∴ Plots (A), (B), (D) are correct while (C) is wrong as from II to III, H is decreasing.

**Q.22** [10]