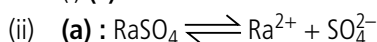


EXAM
DRILL

Equilibrium

ANSWERS

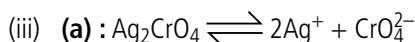
1. (i) (c)



$$K_{sp} = [\text{Ra}^{2+}][\text{SO}_4^{2-}]$$

Concentration of SO_4^{2-} from $\text{Na}_2\text{SO}_4 = 0.10 \text{ M}$

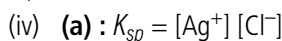
$$[\text{Ra}^{2+}] = \frac{4 \times 10^{-11}}{0.10} = 4 \times 10^{-10} \text{ M}$$



$$[\text{Ag}^+] = 1.5 \times 10^{-4} \text{ M}$$

$$[\text{CrO}_4^{2-}] = 0.75 \times 10^{-4} \text{ M} \left(\frac{1}{2} \text{ of } [\text{Ag}^+] \right)$$

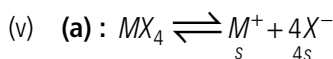
$$K_{sp} = (1.5 \times 10^{-4})^2 \times (0.75 \times 10^{-4}) = 1.687 \times 10^{-12}$$



$$[\text{Cl}^-] = \text{NaCl} = 0.05 \text{ M}$$

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-10}}{0.05} = 3 \times 10^{-9} \text{ M}$$

$$[\text{Ag}^+] = \text{solubility} = 3 \times 10^{-9} \text{ M}$$



$$K_{sp} = s \times (4s)^4 = 256s^5$$

2. Equilibrium constant

3. Homogeneous

4. Forward

5. HA

6. Acidic



Initial moles 1 0 0

Equilibrium moles 1 - α α α

Total moles = 1 - α + α + α = 1 + α

Total pressure = P

$$\therefore p_{\text{PCl}_5} = \frac{(1-\alpha)P}{(1+\alpha)}; p_{\text{PCl}_3} = \frac{\alpha \cdot P}{1+\alpha}; p_{\text{Cl}_2} = \frac{\alpha \cdot P}{1+\alpha}$$

$$\text{Now, } K_p = \frac{p_{\text{PCl}_3} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\alpha^2 \cdot P^2}{(1+\alpha)(1-\alpha)P} = \frac{\alpha^2 P}{1-\alpha^2}$$

8. (a) : $K_p = K_c (RT)^{\Delta n_g}$, Here $\Delta n_g = 1$

$$K_p = K_c (RT) \therefore K_p > K_c$$

OR

$$(b) : Q = \frac{[\text{P}_{2(g)}]^2}{[\text{P}_{4(g)}]} = \frac{\left(\frac{2}{2}\right)^2}{(3/2)} = \frac{2}{3}$$

9. (a) : pK_a of acid A = 4 ; pK_a of acid B = 5We know that $pK_a = -\log K_a$ \therefore For acid A, $K_a = 10^{-4}$; For acid B, $K_a = 10^{-5}$

Hence, A is ten times stronger than that of B.



$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

At a given temperature, K_a is a measure of the strength of the acid. Greater the value of K_a , more is the dissociation of HX possible.

11. (c) : Value of equilibrium constant will remain constant.

12. (a)

13. (d) : pH of water decreases with increase in temperature.

14. (c) : K_{sp} of AgCl > K_{sp} of AgBr.

For the precipitation to occur, its ionic product should exceed solubility product.

15. (i) By convention, concentration of solids is taken unity.

$$\therefore K_p = p_{\text{CO}_2(g)} ; K_c = [\text{CO}_2]$$

(ii) $K_p = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$

$$K_c = [\text{NH}_3][\text{H}_2\text{S}]$$

16. $\Delta n_g = 2 - 4 = -2$

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

$$= 6.02 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \times (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 773 \text{ K})^{-2}$$

$$= 1.5 \times 10^{-5} \text{ atm}^{-2}$$

17. For equation, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

$$K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \dots(i)$$

and for $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$

$$K_2 = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} \quad \dots(ii)$$

$$\text{or, } (K_2)^2 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \dots(iii)$$

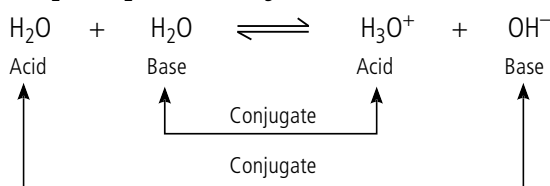
From (i) and (iii),

$$K_1 = (K_2)^2 \text{ or } \sqrt{K_1} = K_2$$

18. (i) NH_3 donates a lone pair, hence it acts as a Lewis base. NH_3 combines with proton ($\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$).

Thus, it acts as a Bronsted base also.

(ii) $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$



OR

$$\text{pH} = 5 \text{ i.e., } [\text{H}^+] = 10^{-5} \text{ mol L}^{-1}$$

$$\text{On dilution by 100 times } [\text{H}^+] = 10^{-7} \text{ mol L}^{-1}$$

For a very dilute solution,

$$\begin{aligned} \text{Total } [\text{H}^+] &= [\text{H}_3\text{O}^+ \text{ from acid}] + [\text{H}_3\text{O}^+ \text{ ions from water}] \\ &= 10^{-7} + 10^{-7} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] = -\log(2 \times 10^{-7}) = 7 - \log 2 \\ &= 7 - 0.3010 = 6.6990 \end{aligned}$$

19. (i) $[\text{H}^+] = \sqrt{CK_a} = \sqrt{0.01 \times 4 \times 10^{-8}}$
 $= 2 \times 10^{-5} \text{ M}$

(ii) $K_{sp}(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-]$

$$[\text{Br}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{4 \times 10^{-13}}{1 \times 10^{-6}} = 4 \times 10^{-7} \text{ mol L}^{-1}$$

20. For the reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

As per definition $p_i = x_i P$

Where x_i is the mole fraction of the component i , P is the total pressure of the system.

$$\begin{aligned} \text{Then, } K_p &= \frac{(x_C P)^c \times (x_D P)^d}{(x_A P)^a \times (x_B P)^b} \\ &= \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b} \times P^{(c+d)-(a+b)} = K_x P^{\Delta n_g} \end{aligned}$$

$$\text{Thus, } K_p = K_x P^{\Delta n_g}$$

OR

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

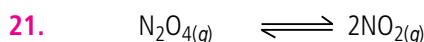
$$\text{or } \log K = \frac{-\Delta G^\circ}{2.303 RT}$$

$$\Delta G^\circ = -8.1 \text{ kJ mol}^{-1}, T = 1000 \text{ K}$$

$$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\therefore \log K = \frac{-8.1}{2.303 \times 8.314 \times 10^{-3} \times 1000} = 0.423$$

$$\Rightarrow K = 2.64$$



Initial	1 mol	0
Equilibrium	$(1 - 0.2) \text{ mol}$	$2 \times 0.2 \text{ mol} = 0.4 \text{ mol}$

$$\text{So, } n_{\text{total}} = 1 - 0.2 + 0.4 = 1.2 \text{ mol}$$

$$\text{Then, } P_{\text{total}} V = 1.2 \times R \times 600$$

$$\text{For } \text{N}_2\text{O}_4 \text{ at } 300 \text{ K, } 1 \times V = 1 \times R \times 300$$

$$\text{From the above equation, } P_{\text{total}} = \frac{1.2 \times 600}{300} = 2.4 \text{ atm}$$

22. pH of solution A = 6

$$[\text{H}^+] = 10^{-6} \text{ mol L}^{-1}$$

pH of solution B = 4

$$[\text{H}^+] = 10^{-4} \text{ mol L}^{-1}$$

On mixing one litre of each solution

$$\text{Total volume} = 1 \text{ L} + 1 \text{ L} = 2 \text{ L}$$

Total amount of H^+ in 2 L solution formed by mixing solutions A and B = $(10^{-6} + 10^{-4}) \text{ mol}$

$$\text{Total } [\text{H}^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2}$$

$$= 5 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-5})$$

$$= -\log 5 - (-5 \log 10) = -\log 5 + 5$$

$$= 5 - \log 5 = 5 - 0.6990 = 4.3010 = 4.3$$

23. (a) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.7 \times 10^{-6}} = 5.88 \times 10^{-9}$

(b) $h = \sqrt{\frac{K_h}{C}} \Rightarrow h = \sqrt{\frac{5.88 \times 10^{-9}}{0.01}}$

$$= 7.67 \times 10^{-4}$$

(c) $\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$

$$\text{p}K_w = 14$$

$$\text{p}K_b = -\log K_b = -\log(1.7 \times 10^{-6}) = 5.7695$$

$$\log C = \log 0.01 = -2$$

Thus,

$$\text{pH} = \frac{1}{2}[14 - 5.7695 - (-2)] = 5.115$$

24. (i) Sugar is a covalent compound hence does not ionise in water. NaCl being ionic, ionises in water and produces Na^+ and Cl^- ions, hence solution becomes conducting. Conductance increases with increase in concentration of salt due to increase in number of ions.

(ii) Greater is the ionization constant (K_b) of a base, greater is the ionisation of the base.

Order of extent of ionization at equilibrium is dimethylamine > ammonia > pyridine > urea. Dimethylamine is the strongest base due to maximum value of K_b .

25. (a) Ammonium formate is a salt of weak acid and weak base. Hence,

$$\text{pH} = 7 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b = 7 + \frac{1}{2} \times 3.8 - \frac{1}{2} \times 4.8$$

$$= 7 + 1.9 - 2.4 = 6.5$$

(b) Neutral solution : KCl, Na₂SO₄

Acidic solution : NH₄NO₃

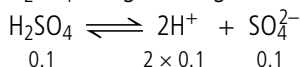
Basic solution : KCN, NaNO₃

26. (i) $[H^+] = \sqrt{K_a \cdot C}$; $pH = -\log [H^+] = -\log(K_a \cdot C)^{1/2}$

or $pH = -\log [1.8 \times 10^{-5} \times 0.1]^{1/2}$

or $pH = 2.8723$

(ii) H₂SO₄ being a strong acid dissociates completely.



$[H^+] = 0.2$ g ion/L

∴ $pH = -\log 0.2$

or $pH = 0.6990$

(iii) $pOH = -\log [OH^-] = -\log (K_b \cdot C)^{1/2}$

$= -\log [1.8 \times 10^{-5} \times 10^{-1}]^{1/2} = 2.8723$

∴ $pH = 14 - pOH = 14 - 2.8723$

or $pH = 11.1277$

OR

(a) $HCl + aq. \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

∴ $[H^+] = [HCl] = 4 \times 10^{-3}$ M,

$pH = -\log (4 \times 10^{-3}) = 2.39$

(b) $KOH + aq. \rightarrow K^+_{(aq)} + OH^-_{(aq)}$

∴ $[OH^-] = 5 \times 10^{-3}$ M,

∴ $[H^+] = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12}$ M

$pH = -\log (2 \times 10^{-12}) = 11.70$

(c) $HF + aq. \rightarrow H^+ + F^-$,

∴ $[H^+] = 2 \times 10^{-3}$ M,

$pH = -\log (2 \times 10^{-3}) = 2.70$

27. When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

(i) When H₂ is added, the rate of forward reaction will increase.

(iii) Removal of CO will increase rate of backward reaction.

28. (i) Conjugate acid of H₂O is H₃O⁺.

Conjugate base of H₂O is OH⁻.

Conjugate acid of HSO₄⁻ is H₂SO₄.

Conjugate base of HSO₄⁻ is SO₄²⁻.

(ii) Limitation of Arrhenius theory :

According to Arrhenius concept, an acid must contain H⁺ and a base must contain OH⁻ groups. However, a number of substances like CO₂, SO₂ etc. are known to be acidic but do not contain any hydrogen and similarly substances like NH₃, Na₂CO₃ etc. are known to be basic but do not contain any hydroxyl groups.

(iii) The equilibrium constant for the reaction :

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ is

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$[N_2] = 3.0 \times 10^{-4}$ M, $[O_2] = 4.2 \times 10^{-4}$ M,

$[NO] = 2.8 \times 10^{-4}$ M

$$\therefore K_c = \frac{(2.8 \times 10^{-4} \text{ M})^2}{(3.0 \times 10^{-4} \text{ M})(4.2 \times 10^{-4} \text{ M})} = 0.622$$

OR

(a) $BaO + H_2O \rightleftharpoons Ba(OH)_2$ (Base)

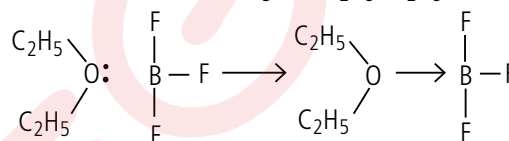
$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (Weak acid)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strong acid)

the decreasing order of basicity is

$BaO > CO_2 > SO_3$

(b) The reaction between BF₃ and C₂H₅OC₂H₅ is



As BF₃ accepts a pair of electrons hence BF₃ is the Lewis acid.

(c) $KOH = \frac{0.561}{56} \times \frac{1000}{200} = 0.05$ M

As, $KOH \longrightarrow K^+ + OH^-$

$[K^+] = [OH^-] = 0.05$ M

$[H^+] = K_w/[OH^-] = 10^{-14}/0.05$

$= 10^{-14}/(5 \times 10^{-2}) = 2.0 \times 10^{-13}$ M

$pH = -\log 2 \times 10^{-13} = 13 - \log 2 = 12.69$

29. (i) 1.5 M Na₂CO₃ gives $[CO_3^{2-}] = 1.5$ M

K_{sp} for Ag₂CO₃ = $[Ag^+]^2[CO_3^{2-}]$

$$\therefore [Ag^+] = \sqrt{\frac{K_{sp} \text{ for Ag}_2\text{CO}_3}{[CO_3^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}}$$

$= 2.34 \times 10^{-6}$ M

K_{sp} for AgCl = $[Ag^+][Cl^-]$

$$= (2.34 \times 10^{-6}) \left(\frac{0.0026}{35.5} \right) = 1.71 \times 10^{-10}$$

(ii) $Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

∴ $K_{sp} = [Pb^{2+}][OH^-]^2 = s \times (2s)^2 = 4s^3$

$= 4 \times (6.7 \times 10^{-6})^3$

$= 1.20 \times 10^{-15}$

In a solution with $pH = 8$, $[H^+] = 10^{-8}$

and $[OH^-] = 10^{-6}$

∴ $1.2 \times 10^{-15} = [Pb^{2+}] \times (10^{-6})^2$

or $[Pb^{2+}] = \frac{1.2 \times 10^{-15}}{(10^{-6})^2} = 1.2 \times 10^{-3}$ M

OR

(a) The solutions which resist the change in their pH value on addition of small amount of acid or base are called buffer solutions.

These are generally a mixture of weak acid and its conjugate base or weak base and its conjugate acid.

e.g., $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$

$$(b) K'_c = \frac{1}{K_c} = \frac{1}{4} = 0.25$$



Initial moles : 1 0

Moles at equilibrium : $1-x$ $2x$

Total moles at equilibrium = $1-x+2x=1+x$

$$\text{But } \frac{2x}{1+x} = 0.4 \quad (\text{given})$$

$$\therefore x = \frac{1}{4}$$

$$\text{So, mole fraction of I}_2 = \frac{1-\frac{1}{4}}{1+\frac{1}{4}} = \frac{3}{5} = 0.6,$$

$$\text{Mole fraction of I} = \frac{2 \times \frac{1}{4}}{1 + \frac{1}{4}} = \frac{2}{5} = 0.4$$

$$p_1 = 0.4 \times 10^5 \text{ Pa or } p_{\text{I}_2} = 0.6 \times 10^5 \text{ Pa}$$

$$K_p = \frac{p_1^2}{p_2} = \frac{(0.4)^2 (10^5)^2}{(0.6)(10^5)} = 2.67 \times 10^4$$

30. (a) (i) Low T , high P , excess of N_2 and H_2 .

(ii) High T , excess of N_2 and O_2 .

(iii) Low T , high P , excess of NO and O_2 .

(iv) High T , low P , excess of PCl_5 .

(v) High T , low P , excess of N_2O_4 .

(b) (i) Addition of an inert gas at constant pressure favours the equilibrium towards larger number of moles.

(ii) When the volume of the container is increased, the pressure exerted by the molecule will decrease. Thus the effect of increase of volume is equivalent to the effect of decrease of pressure. As the effect of decrease of pressure is to shift the equilibrium in the direction in which number of moles increases thus increase in volume or decrease in pressure will favour the forward reaction.

(iii) On adding PCl_5 , forward reaction will be favoured.

