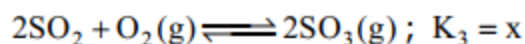
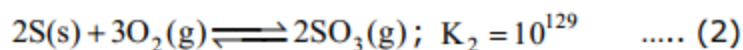
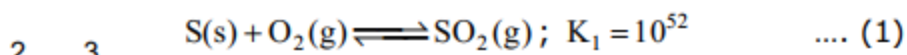


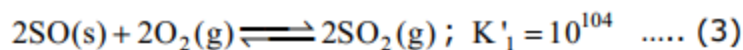
CHAPTER - 06

CHEMICAL AND IONIC EQUILIBRIUM

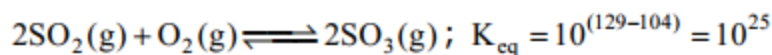
1. 2 At equilibrium, rate of forward reaction = Rate of backward reaction



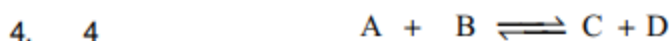
Multiplying equ. (1) by (2);



Subtracting (3) from (2); we get



3. 3 Equilibrium will shift in endothermic direction on increasing temperature. Equilibrium constant of an endothermic reaction will increase with increase in temperature



Initial conc: 1M 1M 0 0

At eqbm: $1 - \frac{1}{3}$ $1 - \frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{3}$

Thus, $K_c = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{2}{3} \times \frac{2}{3}} = 0.25$

5. 2
$$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$$

 Initial moles: 0.3 0.3 0
 Eqbm moles: $(0.3 - x)$ $(0.3 - x)$ $2x$

$$\frac{(2x)^2}{(0.3 - x)^2} = 64$$

$$\frac{2x}{0.3 - x} = 8 \Rightarrow 2x = 2.4 - 8x \Rightarrow x = 0.24$$

 Thus, amount of unreacted $\text{I}_2 = 0.3 - 0.24 = 0.06 \text{ mol}$
6. 4 $[\text{H}^+]$ in water increases with increase in temperature, thus pH decreases. Dissociation of water is endothermic
7. 4 $[\text{OH}^-] = 2 \times 0.05 = 0.1 \text{ M}$
 $\therefore \text{pOH} = -\log(0.1) = 1$
 Thus, $\text{pH} = 14 - 1 = 13$
8. 2 $[\text{H}^+] = C\alpha = 0.01 \times \frac{12.5}{100} = 1.25 \times 10^{-3} \Rightarrow \text{pH} = 2.9$
9. 1 $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log(2 \times 10^{-5}) + \log \frac{0.2}{0.1} = 5$
10. 1 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
 Hydrolysis of NH_4^+ produces H^+ ions
11. 2 (a)
$$\text{H}_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

 Initial: 40 mmol 40 mmol 0 0
 Final: 20 mmol 0 20 mmol 20 mmol

$$\text{pH} = -\log \left[\frac{40 \times 10^{-3}}{800 \times 10^{-3}} \right] = -\log \frac{1}{20} = 1.3$$

 (b) Common ion effect
 (c) For weak acid, $\text{pH} = \text{pK}_a$ when $\alpha = 0.5$
 (d) Due to common ion effect, solubility of Ag_2CO_3 is lower in Na_2CO_3 solution
12. 4 $K_{sp} = 4\text{S}^3 = 4 \times (5 \times 10^{-3})^3 = 5 \times 10^{-7}$

$$13. \quad 3 \quad [Ag^+][Cl^-] = 1.7 \times 10^{-10} \Rightarrow [Ag^+] = \frac{1.7 \times 10^{-10}}{0.1} = 1.7 \times 10^{-9}$$

$$[Ag^+][CrO_4^{2-}] = 1.9 \times 10^{-12} \Rightarrow [Ag^+] = \sqrt{\frac{1.9 \times 10^{-12}}{0.001}} = 4.4 \times 10^{-5}$$

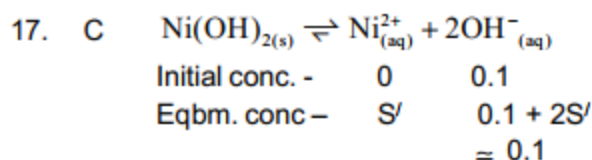
Clearly, concentration of Ag^+ required for precipitation of $AgCl$ is lower. Thus $AgCl$ will precipitate out first.

$$14. \quad 0 \quad x = \Delta n_g = 4 - 4 = 0$$

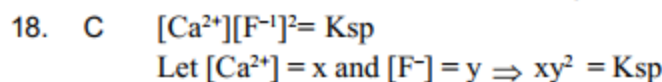
15. 2 Reactions 1 and 2 will shift in forward direction as Δn_g is positive

16. 7 pH of a salt of weak acid and weak base is given by,

$$pH = 7 + \frac{1}{2}(pK_a - pK_b) = 7 + \frac{1}{2}(4.76 - 4.75) = 7.005$$

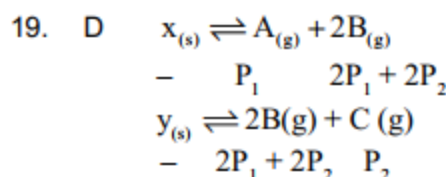


$$\text{Now, } S' \times 0.1^2 = K_{sp} \Rightarrow S' = 2 \times 10^{-13} \text{ molL}^{-1}$$



$$\text{Now, If } [Ca^{2+}] = 4x, \text{ then } 4x \times [F^-]^2 = K_{sp} \text{ or } [F^-]^2 = \frac{K_{sp}}{4x}$$

$$\text{i.e., } [F^-]^2 = \frac{y^2}{4} \text{ or } [F^-] = \frac{y}{2}$$



$$\text{Now, } P_1 \times (2P_1 + 2P_2)^2 = 9 \times 10^{-3}$$

$$\text{and } P_2 \times (2P_1 + 2P_2)^2 = 4.5 \times 10^{-3}$$

$$\text{So, } \frac{P_1}{P_2} = 2 \Rightarrow P_1 = 2P_2$$

$$\text{Thus, } P_1(2P_1 + P_1)^2 = 9 \times 10^{-3} \Rightarrow P_1 = 0.1 \text{ atm}$$

$$\text{and } P_2 = 0.05 \text{ atm}$$

Total pressure over a mixture of x and y is

$$P_{\text{total}} = P_1 + 2P_1 + 2P_2 + P_2 = 3P_1 + 3P_2 = 0.3 + 0.15 = 0.45 \text{ atm}$$

20. B Consider the equilibrium, $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$; $K_c = K_w$
 Now, $K_{w,298} = 10^{-14}$ and $K_{w,308} = 10^{-12}$
 we know, $\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$; take $T_1 = 298\text{K}$ and $T_2 = 308\text{K}$
 Now, $\Delta H^\circ = \log 10^2 \times 2.303R \times \frac{T_1 T_2}{(T_2 - T_1)} = \frac{2 \times 2.303 \times 2 \times 298 \times 308}{10}$
 $= 84.551\text{kcal}$
 So, enthalpy for formation of H_2O from H^+ and OH^- is, $-84.551\text{kcalmol}^{-1}$
21. A $[\text{Ag}^+]$ required to start precipitation of $\text{AgCl} = 1.7 \times 10^{-9}\text{M}$ and $\text{Ag}_2\text{CrO}_4 = \sqrt{19} \times 10^{-6}\text{M}$. So AgCl precipitates out first
 $[\text{Cl}^-]$ when Ag_2CrO_4 starts precipitating is given by
 $(\sqrt{19} \times 10^{-6}) \times [\text{Cl}^-] = 1.7 \times 10^{-10}$
 $[\text{Cl}^-] = \frac{1.9}{\sqrt{19}} \times 10^{-4} = 3.9 \times 10^{-5}\text{M}$
22. D 0.2mol aniline mixed with 0.1mol HCl gives a buffer containing 0.1mol anilinium chloride and 0.1mol aniline
23. D $\text{pOH} = \text{pK}_b + \log \frac{[\text{conj.acid}]}{[\text{base}]}$
 $= 4.74 + \log \frac{0.02}{0.02}$ ($\because \text{pK}_b(\text{NH}_4\text{OH}) = 4.74$; $[\text{NH}_4^+] = 0.02\text{M}$) $= 4.74$
 Thus, $\text{pH} = 14 - 4.74 = 9.26$
24. B After $t = 3\text{min}$, reaction has shifted in the forward direction. This would be due to an increase in temperature (as the reaction is endothermic in the forward direction)
25. A For a salt of weak acid and strong base,
 $\text{pH} = 7 + \frac{1}{2}(\text{pK}_a + \log c)$, where c is the concentration of conjugates base of the weak acid
 Now, $\text{pK}_a = 2 (\text{pH} - 7) - \log c = 2 (14 - 56 - 7) - \log \left(0.6 \times \frac{90}{100} \right)$ ($\because [\text{Ca}(\text{Lac})_2] = \frac{0.6\text{mol}}{2\text{L}}$)
 $= 2.8 - \log 0.54$
26. D Solubility of $\text{Al}(\text{OH})_3$ is given by
 $S = [\text{Al}^{3+}] + [\text{Al}(\text{OH})_4^-] = \frac{K_{sp}}{[\text{OH}^-]^3} + K_c [\text{OH}^-]$
 $\frac{dS}{d[\text{OH}^-]} = 0 \Rightarrow \frac{-3K_{sp}}{[\text{OH}^-]^4} + K_c = 0 \Rightarrow [\text{OH}^-] = \left(\frac{3K_{sp}}{K_c} \right)^{\frac{1}{4}}$

27. A,C $[S^{2-}]$ for precipitation of $ZnS = \frac{1.25 \times 10^{-22}}{0.05} = 25 \times 10^{-22} M$

Now, minimum value of H^+ is given by

$$\frac{[H^+]_{\min}^2 [S^{2-}]}{[H_2S]} = 10^{-21} \quad (\because H_2S \rightleftharpoons 2H^+ + S^{2-})$$

$$[H^+]_{\min}^2 = \frac{10^{-21} \times 10^{-1}}{25 \times 10^{-22}} \Rightarrow [H^+]_{\min} = \frac{1}{5} = 0.2M$$

$$\begin{aligned} \text{Solubility of AB} &= \sqrt{K_{sp} \left[\frac{[H^+] + K_a}{K_a} \right]} = \sqrt{2 \times 10^{-10} \times \left(\frac{10^{-3} + 10^{-8}}{10^{-8}} \right)} \\ &= \sqrt{20 \times 10^{-6}} = 4.47 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

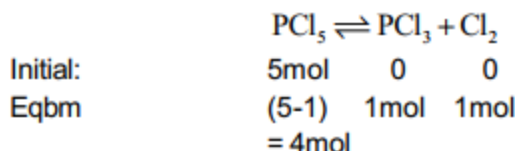
28. A,C,D

For polyprotic acids, $K_{a1} > K_{a2} > K_{a3}$

$$\text{pH of } H_2PO_4^- \text{ solution} = \frac{pK_{a1} + pK_{a2}}{2}$$

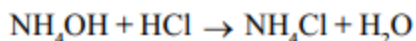
$$\begin{array}{ccccc} H_2PO_4^- & \xrightleftharpoons{K_{a2}} & H^+ & + & HPO_4^{2-} \\ 0.2M & & x & & 0.1M \end{array} \Rightarrow \frac{0.1x}{0.2} = K_{a2} \Rightarrow \text{pH} = -\log x = pK_{a2} - \log 2$$

29. 28



$$\text{Now, } K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\frac{1}{7} \times 1\text{atm}\right) \left(\frac{1}{7} \times 1\text{atm}\right)}{\left(\frac{4}{7} \times 1\text{atm}\right)} = \frac{1}{28}$$

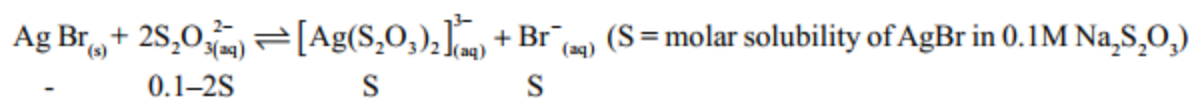
30. 5.24



Initial	2mmol	2mmol	0	-
final	0	0	2mmol	-

$$\text{pH} = 7 - \frac{1}{2} [\log c + pK_b] = 7 - \frac{1}{2} \left[\log \frac{2}{60} + 5 \right] = 5.24$$

31. 4.54



$$\text{Now, } \frac{S \cdot S}{(0.1 - 2S)} = 5 \Rightarrow S = 0.04545 \text{ or } 4.54 \times 10^{-2} \text{ molL}^{-1}$$

32. B At the beginning $[\text{H}^+] = \sqrt{K_a C} \Rightarrow \text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log c$

when acid is 50% neutralised, $\text{pH} = \text{pK}_a$

when acid is 100% neutralised, $\text{pH} = 7 + \frac{1}{2}(\text{pK}_a + \log c)$

when acid is 20% neutralised, $\text{pH} = \text{pK}_a + \log \frac{20}{80} = \text{pK}_a + \log \frac{1}{4}$