

CHAPTER

Equilibrium

7

1. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is **[2002]**
 - (a) not a buffer solution with $\text{pH} < 7$
 - (b) not a buffer solution with $\text{pH} > 7$
 - (c) a buffer solution with $\text{pH} < 7$
 - (d) a buffer solution with $\text{pH} > 7$.
2. Species acting as both Bronsted acid and base is **[2002]**
 - (a) $(\text{HSO}_4)^{-1}$
 - (b) Na_2CO_3
 - (c) NH_3
 - (d) OH^{-1} .
3. Let the solubility of an aqueous solution of $\text{Mg}(\text{OH})_2$ be x then its K_{sp} is **[2002]**
 - (a) $4x^3$
 - (b) $108x^5$
 - (c) $27x^4$
 - (d) $9x$.
4. Change in volume of the system does not alter which of the following equilibria? **[2002]**
 - (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 - (b) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - (c) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - (d) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$.
5. For the reaction $\text{CO}(\text{g}) + (1/2)\text{O}_2(\text{g}) = \text{CO}_2(\text{g})$, K_p/K_c is **[2002]**
 - (a) RT
 - (b) $(RT)^{-1}$
 - (c) $(RT)^{-1/2}$
 - (d) $(RT)^{1/2}$
6. Which one of the following statements is not true? **[2003]**
 - (a) $\text{pH} + \text{pOH} = 14$ for all aqueous solutions
 - (b) The pH of 1×10^{-8} M HCl is 8
 - (c) 96,500 coulombs of electricity when passed through a CuSO_4 solution deposits 1 gram equivalent of copper at the cathode
 - (d) The conjugate base of H_2PO_4^- is HPO_4^{2-}
7. The solubility in water of a sparingly soluble salt AB_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Its solubility product number will be **[2003]**
 - (a) 4×10^{-10}
 - (b) 1×10^{-15}
 - (c) 1×10^{-10}
 - (d) 4×10^{-15}
8. For the reaction equilibrium **[2003]**

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$

the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and $1.2 \times 10^{-2} \text{ mol L}^{-1}$ respectively. The value of K_c for the reaction is

 - (a) $3 \times 10^{-1} \text{ mol L}^{-1}$
 - (b) $3 \times 10^{-3} \text{ mol L}^{-1}$
 - (c) $3 \times 10^3 \text{ mol L}^{-1}$
 - (d) $3.3 \times 10^2 \text{ mol L}^{-1}$
9. Consider the reaction equilibrium **[2003]**

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}); \Delta H^\circ = -198 \text{ kJ}$$

On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is

 - (a) increasing temperature as well as pressure
 - (b) lowering the temperature and increasing the pressure
 - (c) any value of temperature and pressure
 - (d) lowering of temperature as well as pressure
10. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value **[2003]**
 - (a) slightly higher than that when the thunderstorm is not there
 - (b) uninfluenced by occurrence of thunderstorm
 - (c) which depends on the amount of dust in air
 - (d) slightly lower than that of rain water without thunderstorm.
11. The conjugate base of H_2PO_4^- is **[2004]**
 - (a) H_3PO_4
 - (b) P_2O_5
 - (c) PO_4^{3-}
 - (d) HPO_4^{2-}
12. What is the equilibrium expression for the reaction **[2004]**

$$\text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightleftharpoons \text{P}_4\text{O}_{10}(\text{s})$$
 - (a) $K_c = [\text{O}_2]^5$

Equilibrium

c-33

- (b) $K_c = [P_4O_{10}]/5[P_4][O_2]$
- (c) $K_c = [P_4O_{10}]/[P_4][O_2]^5$
- (d) $K_c = 1/[O_2]^5$
13. For the reaction,
- $$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \text{ the } K_p/K_c$$
- is equal to [2004]
- (a) \sqrt{RT} (b) RT
- (c) $1/RT$ (d) 1.0
14. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ at temperature T is 4×10^{-4} . The value of K_c for the reaction $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is [2004]
- (a) 4×10^{-4} (b) 50
- (c) 2.5×10^2 (d) 0.02
15. The molar solubility (in mol L⁻¹) of a sparingly soluble salt MX₄ is 's'. The corresponding solubility product is K_{sp} . 's' is given in term of K_{sp} by the relation : [2004]
- (a) $s = (256 K_{sp})^{1/5}$ (b) $s = (128 K_{sp})^{1/4}$
- (c) $s = (K_{sp}/128)^{1/4}$ (d) $s = (K_{sp}/256)^{1/5}$
16. If α is the degree of dissociation of Na₂SO₄, the Vant Hoff's factor (i) used for calculating the molecular mass is [2005]
- (a) $1 - 2\alpha$ (b) $1 + 2\alpha$
- (c) $1 - \alpha$ (d) $1 + \alpha$
17. The solubility product of a salt having general formula MX₂, in water is : 4×10^{-12} . The concentration of M²⁺ ions in the aqueous solution of the salt is [2005]
- (a) 4.0×10^{-10} M (b) 1.6×10^{-4} M
- (c) 1.0×10^{-4} M (d) 2.0×10^{-6} M
18. The exothermic formation of ClF₃ is represented by the equation :
- $$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g) ;$$
- $$\Delta H = -329 \text{ kJ}$$
- Which of the following will increase the quantity of ClF₃ in an equilibrium mixture of Cl₂, F₂ and ClF₃ ? [2005]
- (a) Adding F₂
- (b) Increasing the volume of the container
- (c) Removing Cl₂
- (d) Increasing the temperature
19. For the reaction : [2005]
- $$2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)},$$
- ($K_c = 1.8 \times 10^{-6}$ at 184°C) ($R = 0.0831 \text{ kJ/(mol.K)}$)
- When K_p and K_c are compared at 184°C, it is found that
- (a) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
- (b) $K_p = K_c$
- (c) K_p is less than K_c
- (d) K_p is greater than K_c
20. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be : [2005]
- (a) 3.98×10^{-6} (b) 3.68×10^{-6}
- (c) 3.88×10^{-6} (d) 3.98×10^{-8}
21. What is the conjugate base of OH⁻ ? [2005]
- (a) O²⁻ (b) O⁻
- (c) H₂O (d) O₂
22. An amount of solid NH₄HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH₃ and H₂S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH₄HS decomposition at this temperature is [2005]

c-34

Chemistry

- (a) 0.11 (b) 0.17
(c) 0.18 (d) 0.30
23. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel [2006]
- $$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$
- If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be
- (a) $\left(\frac{x}{x-1}\right)P$ (b) $\left(\frac{x}{1-x}\right)P$
(c) $\left(\frac{x}{x+1}\right)P$ (d) $\left(\frac{2x}{1-x}\right)P$
24. The equilibrium constant for the reaction
- $$\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$$
- is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
- will be [2006]
- (a) 9.8×10^{-2} (b) 4.9×10^{-2}
(c) 416 (d) 2.40×10^{-3}
25. Given the data at 25°C
- $$\text{Ag} + \text{I}^- \longrightarrow \text{AgI} + \text{e}^- \quad E^\circ = 0.152 \text{ V}$$
- $$\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^- \quad E^\circ = -0.800 \text{ V}$$
- What is the value of $\log K_{\text{sp}}$ for AgI? ($2.303 RT/F = 0.059 \text{ V}$) [2006]
- (a) -37.83 (b) -16.13
(c) -8.12 (d) +8.612
26. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be [2007]
- (a) 0.2×10^5 (b) 5.0×10^{-5}
(c) 5.0×10^{15} (d) 5.0×10^{-15}
27. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is [2007]
- (a) 7.0 (b) 4.5
(c) 2.5 (d) 9.5
28. In a saturated solution of the sparingly soluble strong electrolyte AgIO_3 (molecular mass = 283) the equilibrium which sets in is $\text{AgIO}_3(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{IO}_3^-(\text{aq})$. If the solubility product constant K_{sp} of AgIO_3 at a given temperature is 1.0×10^{-8} , what is the mass of AgIO_3 contained in 100 ml of its saturated solution? [2007]
- (a) $1.0 \times 10^{-4} \text{ g}$ (b) $28.3 \times 10^{-2} \text{ g}$
(c) $2.83 \times 10^{-3} \text{ g}$ (d) $1.0 \times 10^{-7} \text{ g}$
29. The equilibrium constants K_{p1} and K_{p2} for the reactions $\text{X} \rightleftharpoons 2\text{Y}$ and $\text{Z} \rightleftharpoons \text{P} + \text{Q}$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is [2008]
- (a) 1:36 (b) 1:1
(c) 1:3 (d) 1:9
30. For the following three reactions a, b and c, equilibrium constants are given: [2008]
- (i) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}); K_1$
(ii) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}); K_2$
(iii) $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}); K_3$
- (a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$
(c) $K_3 = K_1K_2$ (d) $K_3.K_2^3 = K_1^2$
31. Four species are listed below: [2008]
- i. HCO_3^- ii. H_3O^+
iii. HSO_4^- iv. HSO_3F
- Which one of the following is the correct sequence of their acid strength?
- (a) $\text{iv} < \text{ii} < \text{iii} < \text{i}$ (b) $\text{ii} < \text{iii} < \text{i} < \text{iv}$
(c) $\text{i} < \text{iii} < \text{ii} < \text{iv}$ (d) $\text{iii} < \text{i} < \text{iv} < \text{ii}$
32. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be [2008]
- (a) 9.58 (b) 4.79
(c) 7.01 (d) 9.22
33. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M}$ Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$) [2009]
- (a) $5.1 \times 10^{-5} \text{ M}$ (b) $8.1 \times 10^{-8} \text{ M}$
(c) $8.1 \times 10^{-7} \text{ M}$ (d) $4.1 \times 10^{-5} \text{ M}$
34. Three reactions involving H_2PO_4^- are given below: [2010]
- (i) $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$

Equilibrium

c-35

- (ii) $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$
 (iii) $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}^{2-}$
 In which of the above does H_2PO_4^- act as an acid ?
 (a) (ii) only (b) (i) and (ii)
 (c) (iii) only (d) (i) only
35. In aqueous solution the ionization constants for carbonic acid are
 $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.
 Select the correct statement for a saturated 0.034 M solution of the carbonic acid. [2010]
 (a) The concentration of CO_3^{2-} is 0.034 M.
 (b) The concentration of CO_3^{2-} is greater than that of HCO_3^- .
 (c) The concentrations of H^+ and HCO_3^- are approximately equal.
 (d) The concentration of H^+ is double that of CO_3^{2-} .
36. Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol⁻¹) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is [2010]
 (a) 1.2×10^{-10} g (b) 1.2×10^{-9} g
 (c) 6.2×10^{-5} g (d) 5.0×10^{-8} g
37. At 25°C, the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions? [2010]
 (a) 9 (b) 10
 (c) 11 (d) 8
38. An acid HA ionises as
 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
 The pH of 1.0 M solution is 5. Its dissociation constant would be : [2011RS]
 (a) 5 (b) 5×10^{-8}
 (c) 1×10^{-5} (d) 1×10^{-10}
39. The K_{sp} for $\text{Cr}(\text{OH})_3$ is 1.6×10^{-30} . The solubility of this compound in water is : [2011RS]
 (a) $4\sqrt{1.6 \times 10^{-30}}$
 (b) $4\sqrt{1.6 \times 10^{-30}} / 27$
 (c) $1.6 \times 10^{-30/27}$
 (d) $2\sqrt{1.6 \times 10^{-30}}$
40. The equilibrium constant (K_c) for the reaction
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ at temperature T is 4×10^{-4} . The value of K_c for the reaction [2012]
 $\text{NO}(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ at the same temperature is:
 (a) 0.02 (b) 2.5×10^2
 (c) 4×10^{-4} (d) 50.0
41. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is : [2012]
 (a) 3×10^{-1} (b) 1×10^{-3}
 (c) 1×10^{-5} (d) 1×10^{-7}
42. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? [2013]
 (a) 0.1 L (b) 0.9 L
 (c) 2.0 L (d) 9.0 L
43. For the reaction $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$, if
 $K_P = K_C (RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality): [2014]
 (a) -1 (b) $-\frac{1}{2}$
 (c) $\frac{1}{2}$ (d) 1
44. The standard Gibbs energy change at 300 K for the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[\text{A}] =$, $[\text{B}] = 2$ and $[\text{C}] =$. The reaction proceeds in the : $[\text{R} = 8.314 \text{ J/K/mol}, e = 2.718]$ [JEE M 2015]
 (a) forward direction because $Q < K_c$
 (b) reverse direction because $Q < K_c$
 (c) forward direction because $Q > K_c$
 (d) reverse direction because $Q > K_c$
45. The equilibrium constant at 298 K for a reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L⁻¹) will be : [JEE M 2016]
 (a) 1.818 (b) 1.182
 (c) 0.182 (d) 0.818
46. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is [JEE M 2017]
 (a) 7.2 (b) 6.9
 (c) 7.0 (d) 1.0

Answer Key														
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(a)	(a)	(a)	(a)	(c)	(b)	(d)	(b)	(b)	(d)	(d)	(d)	(c)	(b)	(d)
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
(b)	(c)	(a)	(d)	(a)	(a)	(a)	(c)	(c)	(b)	(d)	(d)	(c)	(a)	(c)
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
(c)	(c)	(a)	(a)	(i)	(c)	(b)	(b)	(d)	(b)	(d)	(c)	(d)	(b)	(a)
46														
(b)														

SOLUTIONS

1. (a) **NOTE** A buffer is a solution of weak acid and its salt with strong base and vice versa.

HCl is strong acid and NaCl is its salt with strong base. pH is less than 7 due to HCl.

2. (a) $(\text{HSO}_4)^- \text{ can accept and donate a proton}$
 $(\text{HSO}_4)^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4 \text{ (acting as base)}$
 $(\text{HSO}_4)^- - \text{H}^+ \rightarrow \text{SO}_4^{2-} \text{ (acting as acid)}$

3. (a) $\text{Mg}(\text{OH})_2 \rightarrow [\text{Mg}^{2+}] + 2[\text{OH}^-]$

$$K_{\text{sp}} = [\text{Mg}][\text{OH}]^2 = [x][2x]^2 = x \cdot 4x^2 = 4x^3.$$

4. (a) In this reaction the ratio of number of moles of reactants to products is same i.e. 2 : 2, hence change in volume will not alter the number of moles.

5. (c) $K_p = K_c(\text{RT})^{\Delta n};$

$$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = -\frac{1}{2}.$$

$$\therefore \frac{K_p}{K_c} = (\text{RT})^{-1/2}$$

6. (b) pH of an acidic solution should be less than 7. The reason is that from H_2O , $[\text{H}^+] = 10^{-7}\text{M}$ which cannot be neglected in comparison to 10^{-8}M . The pH can be calculated as.

from acid, $[\text{H}^+] = 10^{-8}\text{M}$.

from H_2O , $[\text{H}^+] = 10^{-7}\text{M}$

$$\therefore \text{Total } [\text{H}^+] = 10^{-8} + 10^{-7} \\ = 10^{-8}(1 + 10) = 11 \times 10^{-8}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 11 \times 10^{-8} \\ = -[\log 11 + 8 \log 10] \\ = -[1.0414 - 8] = 6.9586$$

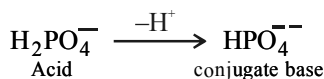
7. (d) $\text{AB}_2 \rightleftharpoons \text{A}^{+2} + 2\text{B}^-$
 $[\text{A}] = 1.0 \times 10^{-5}, [\text{B}] = [2.0 \times 10^{-5}],$
 $K_{\text{sp}} = [\text{B}]^2[\text{A}] = [2 \times 10^{-5}]^2 [1.0 \times 10^{-5}] = 4 \times 10^{-15}$

8. (b) $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[1.2 \times 10^{-2}]^2}{[4.8 \times 10^{-2}]}$
 $= 3 \times 10^{-3} \text{ mol/L}$

9. (b) Due to exothermicity of reaction low or optimum temperature will be required. Since 3 moles are changing to 2 moles.
 \therefore High pressure will be required.

10. (d) The rain water after thunderstorm contains dissolved acid and therefore the pH is less than rain water without thunderstorm.

11. (d) **NOTE** Conjugate acid-base differ by H^+



12. (d) For $\text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightleftharpoons \text{P}_4\text{O}_{10}(\text{s})$

$$K_c = \frac{1}{(\text{O}_2)^5}. \text{ The solids have}$$

concentration unity

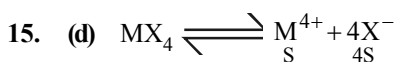
13. (c) $K_p = K_c(\text{RT})^{\Delta n};$
 Here $\Delta n = 1 - 2 = -1$

$$\therefore \frac{K_p}{K_c} = \frac{1}{\text{RT}}$$

14. (b) $K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4 \times 10^{-4}$

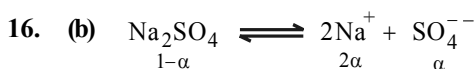
$$K'_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}}$$

$$= \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

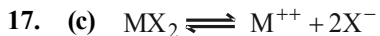


$$K_{sp} = [s][4s]^4 = 256s^5$$

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



$$\text{Vant. Hoff's factor } i = \frac{1-\alpha+2\alpha+\alpha}{1} = 1+2\alpha$$

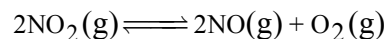


Where s is the solubility of MX_2
then $K_{sp} = 4s^3$; $s \times (2s)^2 = 4 \times 10^{-12}$
 $= 4s^3$; $s = 1 \times 10^{-4}$

$$\therefore [\text{M}^{++}] = s = 1[\text{M}^{++}] = 1.0 \times 10^{-4}$$

18. (a) The reaction given is an exothermic reaction thus accordingly to Lechatalier's principle lowering of temperature, addition of F_2 and or Cl_2 favour the forward direction and hence the production of ClF_3 .

19. (d) For the reaction:-



Given $K_c = 1.8 \times 10^{-6}$ at 184°C

$R = 0.0831 \text{ kJ/mol.k}$

$$K_p = 1.8 \times 10^{-6} \times 0.0831 \times 457 = 6.836 \times 10^{-6}$$

$$[\because 184^\circ\text{C} = (273 + 184) = 457\text{K}, \\ \Delta n = (2 + 1, -1) = 1]$$

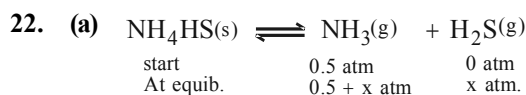
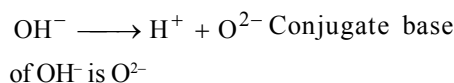
Hence it is clear that $K_p > K_c$

20. (a) $\text{pH} = -\log [\text{H}^+] = \log \frac{1}{[\text{H}^+]}$

$$5.4 = \log \frac{1}{[\text{H}^+]}$$

On solving, $[\text{H}^+] = 3.98 \times 10^{-6}$

21. (a) Conjugate acid-base pair differ by only one proton.



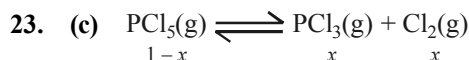
Then $0.5 + x + x = 2x + 0.5 = 0.84$ (given)

$$\Rightarrow x = 0.17 \text{ atm.}$$

$$p_{\text{NH}_3} = 0.5 + 0.17 = 0.67 \text{ atm}$$

$$; p_{\text{H}_2\text{S}} = 0.17 \text{ atm}$$

$$K = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = 0.67 \times 0.17 \text{ atm}^2 \\ = 0.1139 = 0.11$$

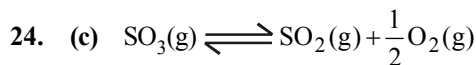


Total moles after dissociation

$$1 - x + x + x = 1 + x$$

p_{PCl_3} = mole fraction of

$$\text{PCl}_3 \times \text{Total pressure} = \left(\frac{x}{1+x} \right) P$$



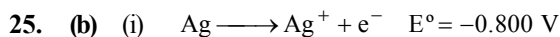
$$K_c = \frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} = 4.9 \times 10^{-2};$$

On taking the square of the above reaction

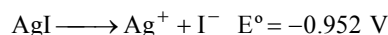
$$\frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = 24.01 \times 10^{-4}$$

now K'_c for $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3$

$$= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{1}{24.01 \times 10^{-4}} = 416$$



From (i) and (ii) we have,



$$E_{\text{cell}}^\circ = \frac{0.059}{n} \log K$$

$$\therefore -0.952 = \frac{0.059}{1} \log [\text{Ag}^+][\text{I}^-]$$

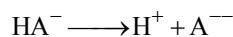
$$[\therefore k = [\text{Ag}^+][\text{I}^-]]$$

$$\text{or } -\frac{0.952}{0.059} = \log K_{\text{sp}} \quad \text{or } -16.13 = \log$$

$$K_{\text{sp}}$$



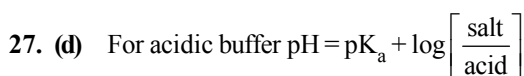
$$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad (\text{Given})$$



$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]} \quad (\text{Given})$$

$$K = \frac{[\text{H}^+]^2[\text{A}^{2-}]}{[\text{H}_2\text{A}]} = K_1 \times K_2$$

$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$



$$\text{or } \text{pH} = \text{pK}_a + \log \left[\frac{[\text{A}^-]}{[\text{HA}]} \right]$$

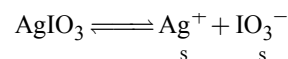
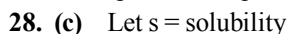
Given $\text{pK}_a = 4.5$ and acid is 50% ionised.

$[\text{HA}] = [\text{A}^-]$ (when acid is 50% ionised)

$$\therefore \text{pH} = \text{pK}_a + \log 1$$

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

$$\text{pOH} = 14 - \text{pH} = 14 - 4.5 = 9.5$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-] = s \times s = s^2$$

$$\text{Given } K_{\text{sp}} = 1 \times 10^{-8}$$

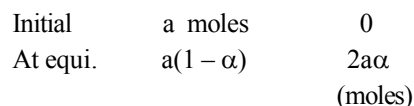
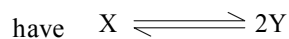
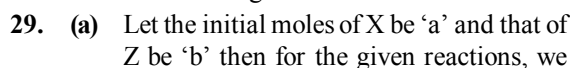
$$\therefore s = \sqrt{K_{\text{sp}}} = \sqrt{1 \times 10^{-8}}$$

$$= 1.0 \times 10^{-4} \text{ mol/lit} = 1.0 \times 10^{-4} \times 283 \text{ g/lit}$$

$$(\because \text{Molecular mass of Ag IO}_3 = 283)$$

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ gm/100ml}$$

$$= 2.83 \times 10^{-3} \text{ gm/100 ml}$$



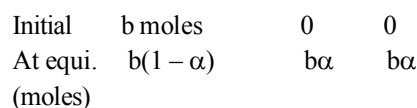
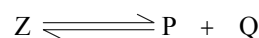
$$\text{Total no. of moles} = a(1 - \alpha) + 2\alpha$$

$$= a - a\alpha + 2\alpha$$

$$= a(1 + \alpha)$$

$$\text{Now, } K_{\text{P}_1} = \frac{(n_{\text{Y}})^2}{n_{\text{X}}} \times \left(\frac{P_{\text{T}_1}}{\sum n} \right)^{\Delta n}$$

$$\text{or, } K_{\text{P}_1} = \frac{(2\alpha)^2 \cdot P_{\text{T}_1}}{[a(1 - \alpha)][a(1 + \alpha)]}$$



$$\text{Total no. of moles} = b(1 - \alpha) + b\alpha + b\alpha$$

$$= b - b\alpha + b\alpha + b\alpha$$

$$= b(1 + \alpha)$$

$$\text{Now } K_{\text{P}_2} = \frac{n_{\text{Q}} \times n_{\text{P}}}{n_{\text{Z}}} \times \left[\frac{P_{\text{T}_2}}{\sum n} \right]^{\Delta n}$$

$$\text{or } K_{\text{P}_2} = \frac{(b\alpha)(b\alpha) \cdot P_{\text{T}_2}}{[b(1 - \alpha)][b(1 + \alpha)]}$$

$$\text{or } \frac{K_{\text{P}_1}}{K_{\text{P}_2}} = \frac{4\alpha^2 \cdot P_{\text{T}_1}}{(1 - \alpha^2)} \times \frac{(1 - \alpha)^2}{P_{\text{T}_2} \cdot \alpha^2} = \frac{4P_{\text{T}_1}}{P_{\text{T}_2}}$$

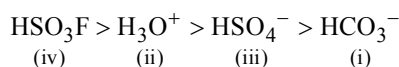
$$\text{or } \frac{P_{T_1}}{P_{T_2}} = \frac{1}{9} \left[\because \frac{K_{P_1}}{K_{P_2}} = \frac{1}{9} \text{ given} \right]$$

$$\text{or } \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36} \text{ or } 1 : 36$$

i.e., (a) is the correct answer.

30. (c) Reaction (c) can be obtained by adding reactions (a) and (b) therefore $K_3 = K_1 \cdot K_2$. Hence (c) is the correct answer.

31. (c) The correct order of acidic strength of the given species in



or (i) < (iii) < (ii) < (iv)

It corresponds to choice (c) which is correct answer.

32. (c) In aqueous solution BA(salt) hydrolyses to give



Now pH is given by

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

substituting given values, we get

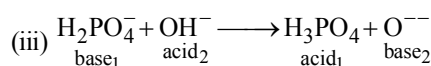
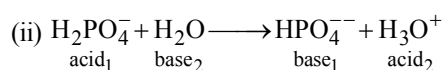
$$\text{pH} = \frac{1}{2} (14 + 4.80 - 4.78) = 7.01$$

33. (a) $\text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}^+ + \text{CO}_3^{2-}$
 $1 \times 10^{-4} \text{M} \quad 1 \times 10^{-4} \text{M} \quad 1 \times 10^{-4} \text{M}$

$$K_{\text{SP}}(\text{BaCO}_3) = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

$$[\text{Ba}^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5} \text{M}$$

34. (a)(i) $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$
acid₁ base₂ acid₂ base₁



Hence only in (ii) reaction H_2PO_4^- is acting as an acid.

35. (c) $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq)$
 $0.034 - x \quad \quad \quad x \quad \quad \quad x$

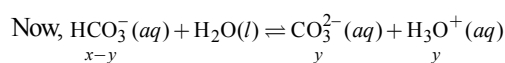
$$K_1 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{x \times x}{0.034 - x}$$

$$\Rightarrow 4.2 \times 10^{-7} \simeq \frac{x^2}{0.034} \Rightarrow x = 1.195 \times 10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of

H_2CO_3 will remain 0.034 as $0.034 \gg x$.

$$x = [\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4}$$



As HCO_3^- is again a weak acid (weaker than H_2CO_3) with $x \gg y$.

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = \frac{y \times (x + y)}{(x - y)}$$

Note : $[\text{H}_3\text{O}^+] = \text{H}^+$ from first step (x) and from second step (y) = (x + y)

[As $x \gg y$ so $x + y \simeq x$ and $x - y \simeq x$]

$$\text{So, } K_2 \simeq \frac{y \times x}{x} = y$$

$$\Rightarrow K_2 = 4.8 \times 10^{-11} = y = [\text{CO}_3^{2-}]$$

So the concentration of $[\text{H}^+] \simeq [\text{HCO}_3^-] =$ concentrations obtained from the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.

Thus the final concentrations are

$$[\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4} \text{ \&}$$

$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-11}$$

36. (b) $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$$

For precipitation to occur

Ionic product > Solubility product

$$[\text{Br}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1ℓ AgNO_3 solution

∴ Number of moles of Br^- needed from

c-40

Chemistry

$$\text{KBr} = 10^{-11}$$

$$\therefore \text{Mass of KBr} = 10^{-11} \times 120 = 1.2 \times 10^{-9} \text{ g}$$

37. (b) $\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{++} + 2\text{OH}^-$

$$K_{sp} = [\text{Mg}^{++}][\text{OH}^-]^2$$

$$1.0 \times 10^{-11} = 10^{-3} \times [\text{OH}^-]^2$$

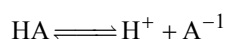
$$[\text{OH}^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

$$\therefore \text{pOH} = 4$$

$$\therefore \text{pH} + \text{pOH} = 14$$

$$\therefore \text{pH} = 10$$

38. (d) $\text{pH} = 5$ means
 $[\text{H}^+] = 10^{-5}$



$$\begin{array}{cccc} t=0 & c & 0 & 0 \\ \text{teq} & c(1-\alpha) & c\alpha & c\alpha \end{array}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]}$$

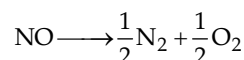
But, $[\text{H}^+] \ll c$
 $\therefore K_a = (10^{-5})^2 = 10^{-10}$

39. (b) $\text{Cr(OH)}_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq.}) + 3\text{OH}^-(\text{aq.})$

$$27S^4 = K_{sp}$$

$$S = \left(\frac{K_{sp}}{27} \right)^{1/4} = \left(\frac{1.6 \times 10^{-30}}{27} \right)^{1/4}$$

40. (d) For the reaction
 $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO} \quad K = 4 \times 10^{-4}$
Hence for the reaction



$$K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

41. (c) $\text{H}^+ = C\alpha; \alpha = \frac{[\text{H}^+]}{C}$

$$\text{or } \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

$$K_a = C\alpha^2 = 0.1 \times 10^{-2} \times 10^{-2} = 10^{-5}$$

42. (d) $\therefore \text{pH} = 1; \text{H}^+ = 10^{-1} = 0.1 \text{ M}$
 $\text{pH} = 2; \text{H}^+ = 10^{-2} = 0.01 \text{ M}$
 $\therefore M_1 = 0.1 \quad V_1 = 1$

$$M_2 = 0.01 \quad V_2 = ?$$

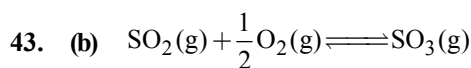
From

$$M_1 V_1 = M_2 V_2$$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ litres}$$

$$\therefore \text{Volume of water added} = 10 - 1 = 9 \text{ litres}$$

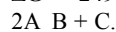


$$K_P = K_C(RT)^x$$

where $x = \Delta n_g =$ number of gaseous
moles in product
– number of gaseous moles in reactant

$$= 1 - \left(1 + \frac{1}{2} \right) = 1 - \frac{3}{2} = -\frac{1}{2}$$

44. (d) $\Delta G^\circ = 2494.2 \text{ J}$



$$R = 8.314 \text{ J/K/mol}$$

$$e = 2.718$$

$$[\text{A}] = , [\text{B}] = 2, [\text{C}] =$$

$$Q = 4$$

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

$$2494.2 \text{ J} = -2.303 \times (8.314 \text{ J/K/mol}) \times (300 \text{ K})$$

$$\log K_C$$

$$\Rightarrow \log K_C = -$$

$$\Rightarrow \log K_C = -0.4341$$

$$K_C = 0.37$$

$$Q > K_C$$

45. (a) Given,

	A	+	B	C	+	D
No. of moles initially	1		1		1	1
At equilibrium	1-a		1-a		1+a	

$$\therefore K_c = 100$$

$$\therefore = 10$$

On solving

$$a = 0.81$$

$$[\text{D}]_{\text{At eq}} = 1 + a = 1 + 0.81 = 1.81$$

46. (b) Given

$$\text{p}K_a(\text{HA}) = 3.2$$

$$\text{p}K_b(\text{BOH}) = 3.4$$

The salt (AB) given is a salt of weak acid
and weak base. Hence the pH can be
calculated by the formula

$$\begin{aligned} \therefore \text{pH} &= 7 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \\ &= 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4) \\ &= 6.9 \end{aligned}$$