

TOPIC 1 Equilibrium Constant (Ke and K_p) and its Application



1. For the reaction

$$\operatorname{Fe_2N}(s) + \frac{3}{2} \operatorname{H_2}(g) \rightleftharpoons 2 \operatorname{Fe}(s) + \operatorname{NH_3}(g)$$

(a)
$$K_c = K_p(RT)$$

(b)
$$K_{c} = K_{p}(RT)^{\frac{-1}{2}}$$

(c)
$$K_c = K_p (RT)^{\frac{1}{2}}$$

(d)
$$K_{c} = K_{p} (RT)^{2}$$

2. The value of Kc is 64 at 800 K for the reaction

 $\mathrm{N}_2(\mathrm{g}) + 3\mathrm{H}_2(\mathrm{g}) \rightleftharpoons 2\mathrm{NH}_3(\mathrm{g})$. The value of K_e for the [Sep. 06, 2020 (II)] following reaction is:

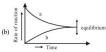
$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

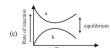
$$\begin{split} NH_3(g) &\rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \\ \text{(a)} \quad 1/64 \qquad \text{(b)} \quad 8 \qquad \text{(c)} \quad 1/4 \qquad \text{(d)} \quad 1/8 \\ \text{For a reaction } X + Y &\rightleftharpoons 2Z, \ 1.0 \ \text{mol of } X, 1.5 \ \text{mol of } Y \ \text{and } 0.5 \ \text{mol of } Z \ \text{were taken in a } 1 \ L \ \text{wessel and allowed to react.} \\ \text{At equilibrium, the concentration of } Z \ \text{was } 1.0 \ \text{mol } L^{-1}. \end{split}$$

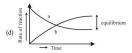
The equilibrium constant of the reaction is $\frac{x}{15}$. The value of x is _____. [NV, Sep. 05, 2020 (II)]

4. For the equilibrium A B, the variation of the rate of the forward (a) and reverse (b) reaction with time is given by: [Sep. 04, 2020 (I)]









If the equilibrium constant for $\,A \, {\ensuremath{\,\Longleftrightarrow\,}} \, B + C \,$ is $\, K_{eq}^{(l)}$ and that of $\,B + C \, {\ensuremath{\,\,\overline{\bigoplus}}} \, P \, \mbox{ is } \, K_{eq}^{(2)}, \, \mbox{ the equilibrium constant}$

(a)
$$K_{eq}^{(1)}/K_{eq}^{(2)}$$

(b)
$$K_{eq}^{(2)} - K_{eq}^{(1)}$$

(c)
$$K_{eq}^{(1)} + K_{eq}^{(2)}$$

(d)
$$K_{eq}^{(1)} K_{eq}^{(2)}$$

In the figure shown below reactant A (represented by square) is in equilibrium with product B (represented by circle). The equilibrium constant is: [Jan. 09, 2020 (II)]



(b) 8 (c) 1 (d) 2 In which one of the following equilibria, $K_p \neq K_c$?

[April 12, 2019 (II)]

- $\begin{array}{ll} \text{(a)} & 2C(s) + O_2(g) \rightleftharpoons 2CO(g) \\ \text{(b)} & 2HI(g) \rightleftharpoons H_2(g) + I_2(g) \\ \text{(c)} & NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g) \\ \end{array}$
- (d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

c-**76**

 $S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 = 10^{52}$ $2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 = 10^{129}$ The equilibrium constant for the reaction,

[April 8, 2019 (II)] $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is: (c) 10²⁵ (b) 10¹⁸¹ (d) 10⁷⁷

Two solids dissociate as follows

 $A(s) \rightarrow B(g) + C(g); K_{P_i} = x \text{ atm}^2$

 $D(s) \rightarrow C(g) + E(g); K_{P_n} = y \text{ atm}^2$

The total pressure when both the solids dissociate simultaneously is: [Jan. 12, 2019 (I)]

(b)
$$2(\sqrt{x+y})$$
 atm

(c) (x+y)atm

(d)
$$x^2 + y^2$$
 atm

10. In a chemical reaction, A+2B = 2C+D, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is: [Jan. 12, 2019 (I)]

(c) $\frac{1}{4}$ (a) 4 (b) 16 (d) 1

11. Consider the reaction

 $N_2(g)+3H_2(g) \Longrightarrow 2NH_3(g)$ The equilibrium constant of the above reaction is K_p . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that

 $P_{NH_3} {<\!\!<} P_{total} \ at \ equilibrium)$ [Jan. 11, 2019 (I)]

(a)
$$\frac{3^{3/2}K_{P}^{1/2}P^{2}}{16}$$

(b)
$$\frac{K_P^{1/2}P^2}{16}$$

c)
$$\frac{K_{P}^{1/2}P^{2}}{4}$$

(d)
$$\frac{3^{3/2}K_{P}^{1/2}P^{2}}{4}$$

12. The values of $K_{\rm p}/K_{\rm c}$ for the following reactions at 300 K are, respectively: (At 300 K, RT = $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ [Jan. 10, 2019 (I)]

 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- (a) 1, 24.62 dm3 atm mol-1, $606.0\,dm^6\,atm^2\,mol^{-2}$
- (b) 1, 24.62 dm3 atm mol-1, $1.65\times 10^{-3}\,dm^{-6}\,atm^{-2}\,mol^2$
- (c) $1, 4.1 \times 10^{-2} \, \text{dm}^{-3} \, \text{atm}^{-1} \, \text{mol},$ $606\,dm^6\,atm^2\,mol^{-2}$
- (d) 24.62 dm3 atm mol-1, 606.0 dm6 atm2 mol-2. $1.65 \times 10^{-3} \, dm^{-6} \, atm^{-2} \, mol^2$

8. For the following reactions, equilibrium constants are given: 13. 5.1 g NH₄SH is introduced in 3.0 L evacuated flask at 327°C, 5.1 g Nr1,5r1s introduced in 3.0 L evacuated mask at 3.2/7c. 30% of the solid Nr1,5r1 decomposed to Nr1, and H₂S as gases. The K_p of the reaction at 327^p C is $(R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$, molar mass of $S = 32 \text{ g mol}^{-1}$, molar mass of $S = 14 \text{ g mol}^{-1}$ (a) $0.242 \times 10^{-4} \text{ atm}^2$ (b) $1 \times 10^{-4} \text{ atm}^2$

(c) $4.9 \times 10^{-3} \text{ atm}^2$ (d) 0.242 atm²

14. Consider the following reversible chemical reactions:

$$A_2(g) + B_2(g) \xrightarrow{K_1} 2AB(g).....(1)$$

 $6 \text{ AB(g)} \xrightarrow{K_2} 3 A_2(g) + 3 B_2(g)....(2)$ The relation between K_1 and K_2 is:

[Jan. 9, 2019 (II)]

(a)
$$K_1 K_2 = \frac{1}{3}$$
 (b) $K_2 = K_1^3$

(c) $K_2 = K_1^{-3}$ (d) $K_1K_2 = 3$ At a certain temperature in a 5 L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction, $CO + Cl_2 \rightleftharpoons COCl_2$. At equilibrium, if one mole of CO is present then equilibrium constant (K_s) for the reaction is:

(a) 2.5 (b) 4 (c) 2 (d) 3

16. The equilibrium constant at 298 K for a reaction $A+B \rightleftharpoons C+D \text{ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of <math>D(\text{in mol L}^{-1})$ will be : [2016]

(a) 1.818 (b) 1.182 (c) 0.182 (d) 0.818

17. A solid XY kept in an evacuated sealed container undergoes A solid XY kept m an evacuated sealed container undergoes decomposition to form a mixture of gases X and Y at temperature T. The equilibrium pressure is 10 bar in the vessel. K, for this reaction is: [Online April 10, 2016] (a) 25 (b) 100 (c) 10 (d) 5 [Gaseous N₂O₄ dissociates into gaseous NO₂ according

to the reaction

 $[N_2O_4(g) \rightleftharpoons 2NO_2(g)]$

At 300 K and 1 atm pressure, the degree of dissociation of N_2O_4 is 0.2. If one mole of N_2O_4 gas is contained in a vessel, then the density of the equilibrium mixture is:

19. For the reaction $SO_2(g) + \frac{1}{2}O_2(g) \Longrightarrow SO_3(g)$, if

 $K_{\rm p} = K_{\rm c} (RT)^{\rm x}$ 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

20. At a certain temperature, only 50% HI is dissociated into H₂ and I₂ at equilibrium. The equilibrium constant is:

- 21. For the decomposition of the compound, represented as $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
 - the $K_p = 2.9 \times 10^{-5}$ atm³.

 If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be:
 - (d) 38.8 × 10⁻² atm
 - (a) 1.94 × 10⁻² atm
 - (c) 7.66×10^{-2} atm
- (a) \$8.8 \times 10^2 atm (d) \$8.8 \times 10^2 atm (d) \$8.8 \times 10^2 atm (e) \$2.1 \times 1.5 \times 0f[A], but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is:

 [Online April 9, 2013]

 [a) 8 [b) 4 [c] 12 [d] 6
- 23. (1) $N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g), K_1$

$$(2) N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$$

$$(3)\,\mathrm{H}_2(\mathrm{g}) + \frac{1}{2}\,\mathrm{O}_2(\mathrm{g}) \ensuremath{\ \Longleftrightarrow \ } \mathrm{H}_2\mathrm{O}(\mathrm{g}), K_3$$

The equation for the equilibrium constant of the reaction

$$\begin{split} 2NH_3(g) + \frac{5}{2}O_2(g) & \longrightarrow 2NO(g) + 3H_2O(g), (K_4) \text{ in terms} \\ of \, K_1, \, K_2 \, \text{and} \, K_3 \, \text{is} : & \textbf{[Online April 23, 2013]} \end{split}$$

- (a) $\frac{K_1.K_2}{K_3}$
- (b) $\frac{K_1.K_3^2}{K_2}$
- (c) K₁ K₂ K₃
- **24.** The ratio $\frac{K_p}{K_c}$ for the reaction

$$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$
 is:

[Online April 25, 2013]

- (a) $\frac{1}{\sqrt{RT}}$ (c) RT
- (b) $(RT)^{1/2}$
- (c) RT (d) 1

 25. The equilibrium constant (K) for the reaction N_x(g) +O_x(g) → 2NO(g) at temperature T is 4×10⁻⁴. The value of K_x for the reaction.
- $NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is: (a) 0.02 (b) 2.5×10^2 (c) 4×10^4 (d) 50.0 **26.** K_p, K_s and K_s are the equilibrium constants of the following reactions (1), (II) and (III) respectively:

- (I) $N_2 + 2O_2 \rightleftharpoons 2NO_2$
- (II) $2NO_2 \rightleftharpoons N_2 + 2O_2$
- (III) $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$
- The correct relation from the following is

- (b) $K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$
- (c) $K_1 = \sqrt{K_2} = K_3$ (d) $K_1 = \frac{1}{K_2} = K_3$ 27. 8 mol of $AB_3(g)$ are introduced into a 1.0 dm³ vessel. If it
 - dissociates as $\Delta B_3(\mathbf{g}) = \Delta A_2(\mathbf{g}) + 3B_2(\mathbf{g})$. At equilibrium, 2 mol of A_2 are found to be present. The equilibrium constant of this reaction is [Online May 12, 2012] are touth to be presented in its angle of N₂O₄(g) \approx 2 (b) 3 (c) 27 (d) The value of K_p for the equilibrium reaction N₂O₄(g) \approx 2NO₂(g) is 2.

- The percentage dissociation of N₂O₄(g) at a pressure of 0.5 atm is [Online May 19, 2012]
 (a) 25 (b) 88 (c) 50 (d) 71
- One mole of O₂(g) and two moles of SO₂(g) were heated in a closed vessel of one-litre capacity at 1098 K. At equilibrium 1.6 moles of SO₃(g) were found. The equilibrium constant K_c of the reaction would be
- [Online May 26, 2012]
 (a) 30 (b) 40 (c) 80 (d) 60 In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}.$
- Select the correct statement for a saturated 0.034 M solution of the carbonic acid.
- (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 HCO3 are approximately equal.
- (d) The concentration of H^+ is double that of CO_3^{2-} .
- 31. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, 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 For the following three reactions (i), (ii) and (iii), equilibrium constants are given:
 - (i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$
- (ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$
- (iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$
- Which of the following is correct?
- (a) $K_1\sqrt{K_2}=K_3$ (b) $K_2K_3 = K_1$
- (c) $K_3 = K_1 K_2$ (d) $K_3.K_2^3 = K_1^2$

33.	Phosphorus pentachloride dissociates as follows, in a closed reaction vessel [2006]	38.	For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ the
	$PCl_s(g) \Longrightarrow PCl_s(g) + Cl_s(g)$		$\frac{K_{\rm p}}{K_{\rm c}}$ is equal to [2004]
	If total pressure at equilibrium of the reaction mixture is P		(a) \sqrt{RT} (b) RT (c) $\frac{1}{p_T}$ (d) 1.0
	and degree of dissociation of PCl_5 is x , the partial pressure of PCl_3 will be	39.	For the reaction equilibrium [2003]
	B 91 B 92		$N_2O_4(g)$ \Longrightarrow 2 $NO_2(g)$
	(a) $\left(\frac{x}{x-1}\right)P$ (b) $\left(\frac{x}{1-x}\right)P$		the concentrations of $\rm N_2O_4$ and $\rm NO_2$ at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol $\rm L^{-1}$ respectively. The value of
	(c) $\left(\frac{x}{x+1}\right)P$ (d) $\left(\frac{2x}{1-x}\right)P$		K_c for the reaction is (a) $3 \times 10^{-1} \text{ mol L}^{-1}$ (b) $3 \times 10^{-3} \text{ mol L}^{-1}$
34.	The equilibrium constant for the reaction		(c) $3 \times 10^3 \text{mol}L^{-1}$ (d) $3.3 \times 10^2 \text{mol}L^{-1}$
	$SO_3(g) \Longrightarrow SO_2(g) + \frac{1}{2}O_2(g)$	40.	For the reaction CO (g) + (1/2) O_2 (g) \rightleftharpoons CO ₂ (g), K_p/K_c is [2002]
	is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction		(a) RT (b) $(RT)^{-1}$ (c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$
	$2SO_2(g) + O_2(g) \Longrightarrow 2SO_3(g)$	1	Relation between K, Q and G
	will be [2006]	TO	OPIC 2 and Factors Effecting
	(a) 9.8×10^{-2} (b) 4.9×10^{-2}	1	Equilibrium
25	(c) 416 (c) 2.40×10 ⁻³	41.	The variation of equilibrium constant with temperature is
35.	For the reaction: [2005]		given below: [Sep. 06, 2020 (I)]
	$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g),$		Temperature Equilibrium Constant
	$(K_c = 1.8 \times 10^{-6} \text{ at } 184 ^{\circ}\text{C}) \text{ (R} = 0.0831 \text{ kJ/ (mol. K))}$		$T_1 = 25 ^{\circ}\text{C}$ $K_1 = 10$ $T_2 = 100 ^{\circ}\text{C}$ $K_2 = 100$
	When K_p and K_c are compared at 184 °C, it is found		The values of ΔH° , ΔG° at T_1 and ΔG° at T_2 (in kj mol ⁻¹)
	that		respectively, are close to
	(a) Whether $K_{\rm p}$ is greater than, less than or equal to $K_{\rm c}$		[use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
	depends upon the total gas pressure		(a) 28.4, -7.14 and -5.71
	(b) $K_p = K_c$		(b) 0.64, -7.14 and -5.71
	(c) $K_{\rm p}$ is less than $K_{\rm c}$		(c) 28.4, -5.71 and -14.29
	(d) K_p is greater than K_c	42.	(d) 0.64, -5.71 and -14.29 Consider the following reaction: [Sep. 05, 2020 (I)]
36.	An amount of solid NH ₄ HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50	42.	N ₂ O ₄ (g) \Longrightarrow 2NO ₂ (g); Δ H ⁰ = + 58 kJ
	atm pressure. Ammonium hydrogen sulphide decomposes		For each of the following cases ((i), (ii)), the direction in
	to yield NH3 and N2S gases in the flask. When the		which the equilibrium shifts is :
	decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm? The equilibrium		(i) Temperature is decreases
	constant for NH ₄ HS decomposition at this temperature is		(ii) Pressure is increased by adding N ₂ at constant T.
	[2005]		(a) (i) towards product, (ii) towards product (b) (i) towards reactant, (ii) towards product
200000000000000000000000000000000000000	(a) 0.11 (b) 0.17 (c) 0.18 (d) 0.30		(c) (i) towards reactant, (ii) no change
37.	What is the equilibrium expression for the reaction		(d) (i) towards product, (ii) no change
	$P_4(s) + 5O_2(g) \Longrightarrow P_4O_{10}(s)$? [2004]	43.	The INCORRECT match in the following is:
	(a) $K_c = [O_2]^5$		[April 12, 2019 (II)]
	(b) $K_c = [P_4O_{10}]/5[P_4][O_2]$		(a) $\Delta G^0 < 0, K > 1$ (b) $\Delta G^0 = 0, K = 1$
		44	(c) $\Delta G^0 > 0, K < 1$ (d) $\Delta G^0 < 0, K < 1$ For the reaction,
	(c) $K_c = [P_4O_{10}]/[P_4][O_2]^5$	44.	For the reaction, $2SO_2(g) + O_2(g) \Longrightarrow 2SO_3(g)$,
	(d) $K_c = 1/[O_2]^5$		$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and } K_c = 1.7 \times 10^{16}$
			v

Which of the following statement is INCORRECT?

[April 10, 2019 (II)]

(a) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

(b) The equilibrium will shift in forward direction as the pressure increases.
 (c) The equilibrium constant decreases as the

temperature increases.

 (d) The addition of inert gas at constant volume will not affect the equilibrium constant.

45. For the equilibrium

 $2H_2O \Longrightarrow H_3O^+ + OH^-$; the value of ΔG^o at 298 K is approximately: [Jan. 11, 2019 (II)]

(a) 100 kJ mol⁻¹

(b) -80 kJ mol⁻¹

(c) 80 kJ mol-1 (d) -100 kJ mol⁻¹ 46. In which of the following reactions, an increase in the volume of the container will favour the formation of products? [Online April 15, 2018 (I)]

(a)
$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$$

(b)
$$2NO_2(g) = 2NO(g) + O_2(g)$$

(c) $3O_2 \rightleftharpoons 2O_3(g)$

(d) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

47. The gas phase reaction 2NO₂(g) → N₂O₄(g) is an exothermic reaction. The decomposition of N₂O₄, in equilibrium mixutre of NO₂(g) and N₂O₄(g), can be increased by: [Online April 16, 2018]

(a) addition of an inert gas at constant pressure

- (b) lowering the temperature
- (c) increasing the pressure

(d) addition of an inert gas at constant volume

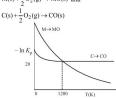
The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal: [Online April 9, 2017]

 $\text{Fe}_2\text{O}_3(s) + 3 \text{ CO}(g) \rightleftharpoons 2 \text{ Fe}(l) + 3 \text{ CO}_2(g)$ Using the Le Chatelier's principle, predict which one of

the following will not disturb the equilibrium?

(a) Removal of CO (b) Removal of CO₂ (c) Addition of Fe₂O₃ (d) Addition of Fe₂O₃ (49. The plot shows the variation of $-\ln K_p$ versus temperature for the two reactions. [Online April 9, 2016]

 $M(s) + \frac{1}{2}O_2(g) \rightarrow MO(s)$ and



Identify the correct statement:

Identify the correct statement: (a) AT < 1200 K, oxidation of carbon is unfavourable. (b) Oxidation of carbon is favourable at all temperatures. (c) At T < 1200 K, the reaction MO(s) + C(s) > M(s) + CO(g) is spontaneous. (d) At T > 1200 K, carbon will reduce MO(s) to M(s).

For the reaction, [Online April 9, 2016]

For the reaction, |Online April 9, 2016| $A(g) + B(g) \rightarrow C(g) + D(g)$, AF^2 and ΔS^2 are, respectively, -29.8 kJ mol⁻¹ and -0.100 kJ K⁻¹ mol⁻¹ at 298 K. The equilibrium constant for the reaction at 298 K is: (a) 1.0×10^{-10} (b) 10 (c) 1 (d) 1.0×10^{10}

The standard Gibbs energy change at 300 K for the reaction 2A \implies B+C is 2494.2 J. At a given time, the composition

of the reaction mixture is [A] = $\frac{1}{2}$, [B] = 2 and [C] = $\frac{1}{2}$. The reaction proceeds in the : [R = 8.314 J/K/mol, e = 2.718]

(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 O > K

(d) reverse direction because $Q > K_c$ [2015] The following reaction is performed at 298 K. [2015] $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ The standard free energy of formation of NO(g) is 86.6 KJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? $(K_p = 1.6 \times 10^{12})$

(a)
$$86600 - \frac{\ln{(1.6 \times 10^{12})}}{R(298)}$$

R (298)

(b) $0.5[2 \times 86,600 - R(298) \ln(1.6 \times 10^{12})]$ (c) $R(298) \ln(1.6 \times 10^{12}) - 86600$ (d) $86600 + R(298) \ln(1.6 \times 10^{12})$

The increase of pressure on ice

⇒ water system at constant temperature will lead to[Online April 11, 2015]

(a) a decrease in the entropy of the system
(b) an increase in the Gibb's energy of the system

(c) an increase in the Glob's chergy of the system (d) a shift of the equilibrium in the forward direction What happens when an inert gas is added to an equilibrium keeping volume unchanged? [Online April 12, 2014] keeping volume unchanged?

(a) More product will form (b) Less product will form

(c) More reactant will form

(d) Equilibrium will remain unchanged
The exothermic formation of CIF₃ 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 CIF3 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

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Chemistry

56. Consider the reaction equilibrium

[2003]

 $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g); \Delta H^2 = -198 kJ$

- 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
- 57. Change in volume of the system does not alter which of the following equilibria? [2002]
 - (a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
 - (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 - (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 - (d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$.

Theories of Acids and Bases, Ionic Product of Water and pH Scale

58. Arrange the following solutions in the decreasing order [Sep. 06, 2020 (I)] (B) 0.01 M NaOH of pOH:

(A) 0.01 M HCl

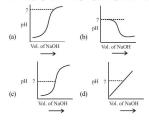
TOPIC 3

- (D) 0.01 M NaCl
- (C) 0.01 M CH₃COONa (a) (A) > (C) > (D) > (B) (b) (A) > (D) > (C) > (B)
- (c) (B) > (C) > (D) > (A) (d) (B) > (D) > (C) > (A)
- 59. A soft drink was bottled with a partial prssure of CO₂ of 3 bar over the liquid at room temperature. The partial pressure of CO2 over the solution approaches a value of 30 bar when 44g of CO2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is $\times 10^{-1}$.

(First dissociation constant of $H_2CO_3 = 4.0 \times 10^{-7}$; log 2 = 0.3; density of the soft drink = 1g mL^{-1})

[NV, Sep. 05, 2020 (I)]

60. 100 mL of 0.1 M HCl is taken in a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH is continuously measured. Which of the following graphs correctly depicts the change in pH? [Sep. 03, 2020 (II)]



61. For the following Assertion and Reason, the correct option [Jan. 08, 2020 (II)]

Assertion: The pH of water increases with increase in temperature.

Reason: The dissociation of water into H⁺ and OH⁻ is an

- exothermic reaction.

 (a) Both assertion and reason are true, and the reason is the correct explanation for the assertion.
- (b) Both assertion and reason are false.
- (c) Both assertion and reason are true, but the reason is not the correct explanation for the assertion.
- (d) Assertion is not true, but reason is true.
- 62. Two solutions, A and B, each of 100 L was made by dissolving 4g of NaOH and 9.8 g of $\rm H_2SO_4$ in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution $\it A$ and 10 L of solution. $\it B$ is [NV, Jan. 07, 2020 (I)]
- 63. 3 g of acetic acid is added to 250 mL of 0.1 M HCl and the

solution made up to 500 mL. To 20 mL of this solution $\frac{1}{2}$ mL of 5 M NaOH is added. The pH of the solution is [NV, Jan. 07, 2020 (II)]
[Given: pKa of acetic acid = 4.75, molar mass of acetic

 $acid = 60 \text{ g/mol}, \log 3 = 0.4771$ Neglect any changes in volume.

- Consider the following statements [April 10, 2019 (I)]
 - (a) The pH of a mixture containing 400 mL of 0.1 M H₂SO₄ and 400 mL of 0.1 M NaOH will be approximately 1.3.
 - (b) Ionic product of water is temperature dependent.
 - (c) A monobasic acid with $K_a 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
 - (d) The Le Chatelier's principle is not applicable to common-ion effect.

[April 10, 2019 (I)] The correct statements are:

- (a) (a), (b), and (d) (b) (a), (b) and (c)
- (c) (b) and (c) (d) (a) and (b)

(b) (A)

In an acid base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? [April 9, 2019 (II)]



(a) (B)



(c) (C)

of which one of them will be equal to 1?

[Online April 15, 2018 (II)] Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be: [2005] (a) $55 \text{ mL} \frac{\text{M}}{10} \text{HCl} + 45 \text{ mL} \frac{\text{M}}{10} \text{NaOH}$ (a) 3.98×10^{-6} (b) 3.68×10^{-6} (c) 3.88×10^6 (d) 3.98 × 10⁸ (b) $75 \text{ mL} \frac{\text{M}}{5} \text{HCl} + 25 \text{ mL} \frac{\text{M}}{5} \text{NaOH}$

78. What is the conjugate base of OH-? 120051 (c) $100 \text{ mL} \frac{M}{10} \text{HC1} + 100 \text{ mL} \frac{M}{10} \text{NaOH}$ (a) O^{2-} (b) O^{-} (c) H_2O (d)

The conjugate base of $H_2PO_4^-$ is [2004] $(d) \quad 60 \text{ mL} \frac{M}{10} \text{HCl} + 40 \text{ mL} \frac{M}{10} \text{NaOH}$ $\textbf{68.} \quad \text{Which of the following is a Lewis acid?}$ (a) H₃PO₄ (b) P,O, (c) PO₄³⁻ (d) HPO₄²⁻

Which one of the following statements is not true? [Online April 15, 2018 (I)]

- (a) pH + pOH = 14 for all aqueous solutions (b) The pH of 1×10^{-8} M HCl is 8 (c) NaH (d) B(CH₃)₃ 69. 50 mL of 0.2 M ammonia solution is treated with 25 mL of
 - (c) 96,500 coulombs of electricity when passed through a CuSO₄ solution deposits 1 gram equivalent of copper at the cathode 30 nL 01.2 W HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be: [Online April 9, 2017]
 (a) 3.75 (b) 4.75 (c) 8.25 (d) 9.25 (d) The conjugate base of H₂PO₄⁻ is HPO₄²⁻
- 70. The conjugate base of hydrazoic acid is: [Online April 12, 2014]
- When rain is accompanied by a thunderstorm, the collected rain water will have a pH value [2003] (a) N^{-3} (b) N_3^- (c) N_2^- (d) HN₃ (a) slightly higher than that when the thunderstorm is not there
- (a) N° (b) N₃ (c) N₂ (d) HN₃

 1. 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?

 (a) 0.1L (b) 0.9L (c) 2.0L (d) 9.0L

 72. NaOH is a strong base. What will be pH of 5.0×10⁻²M NaOH solution? (log 2 = 0.3)

 [Online April 22, 2013] (b) uninfluenced by occurrence of thunderstorm (c) that depends on the amount of dust in air (d) slightly lower than that of rain water without
 - thunderstorm. Species acting as both Bronsted acid and base is [2002]
- (b) Na₂CO₃ (d) OH⁻ (a) HSO₄ (a) 14.00 (b) 13.70 (c) 13.00 (d) 12.70 (c) NH₃ 73. Equimolar solutions of the following compounds are prepared separately in water. Which will have the lowest pH value? [Online April 23, 2013]

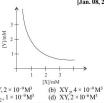
(b) SrCl,

(a) BeCl,

- TOPIC 4 Ionisation of Weak Acids and Bases and Relation between
- (a) BeCl₂ (b) SeC₂ (c) CaCl₂ (d) MgCl₂ What is the pH of a 10⁻⁴ M OH solution at 330 K, if K_w at 330 K is 10⁻¹³⁶? [Online April 23, 2013] 83. 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) 330K is 10^{-13.6}? [Online (a) 4 (b) 9.0 (c) 10 solution is [2017]
 (a) 7.2 (b) 6.9 (c) 7.0 (d) 1.0 Which one of the following arrangements represents the correct order of the proton affinity of the given species: (a) I-<F-<HS-< NH₂
 - Assuming that the degree of hydrolysis is small, the pH of 0.1 M solution of sodium acetate $(K_a = 1.0 \times 10^{-5})$ will be: [Online April 11, 2014] [Online April 25, 2013]
- (b) $HS^- < NH_2^- < F^- < I^-$ (c) F-<I-< NH₂-<HS-(d) $NH_2^- < HS^- < I^- < F^-$

85.	$ \begin{aligned} & \text{Values of dissociation constant, } K_{\text{g}} \text{ are given as follows :} \\ & \text{Acid} & K_{\text{g}} \\ & \text{HCN} & 6.2 \times 10^{-10} \\ & \text{HF} & 7.2 \times 10^{-4} \\ & \text{HNO}_2 & 4.0 \times 10^{-4} \\ & \text{Correct order of increasing base strength of the base CN}^{-} \\ & \text{F} & \text{and NO}_2^{-} \text{ will be :} & \textbf{[Online April 22, 2013]} \\ & \text{(a)} & \text{F} & < \text{CN} & < \text{NO}_5 & \text{(b)} & \text{NO}_5 & < \text{CN} & < \text{F}^{-} \end{aligned} $	92. 93.	The first and second dissociation constants of an aci $H_A A$ are 1.0×10^5 and 5.0×10^{10} respectively. The overall dissociation constant of the acid will be $(2007) \times 10^5 \times 10^{10} \times 1$
86.	(c) F ⁻ < NO ₂ ⁻ < CN ⁻ (d) NO ₂ ⁻ < F ⁻ < CN ⁻ What would be the pH of a solution obtained by mixing 5g	TO	OPIC 5 Hydrolysis, Buffer Solutions and Solubility Product
00.	of acetic acid and 7.5g of sodium acetate and making the volume equal to 500 mL ? ($K_a = 1.75 \times 10^{-5}, pK_a = 4.76$) [Online April 25, 2013] (a) pH=4.70 (b) pH<4.70 (c) pH of solution will be equal to pH of acetic acid	94.	If the solubility product of AB_2 is $3.20 \times 10^{-11} M^3$, then the solubility of AB_3 in pure water is $\times 10^{-4} \mathrm{mol} L^{-1}$ [Assuming that neither kind of ion reacts with water] [NV, Sep. 06, 2020 (II) An acidic buffer is obtained on mixing:
	(d) 4.76 < pH < 5.0		[Sep. 03, 2020 (I)
87.	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}		(a) 100 mL of 0.1 M CH ₃ COOH and 100 mL of 0.1 M NaOH (b) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl (c) 100 mL of 0.1 M CH ₃ COOH and 200 mL of 0.1 M NaOH (d) 100 mL of 0.1 M HCl and 200 mL of 0.1 M CH ₃ COON
88.	Given [Online May 12, 2012]	96.	For the following Assertion and Reason, the correct option is [Sep. 02, 2020 (I)]
89.	$ \begin{array}{lll} \text{(i)} & \text{HCN}(aq) + \text{H}_2\text{O}(1) & \Longrightarrow \text{H}_3\text{O}^{+}(aq) + \text{CN}^{-}(aq) \\ & K_a = 6.2 \times 10^{-10} & \Longrightarrow \text{HCN}(aq) + \text{OH}^{-}(aq) \\ & K_b = 1.6 \times 10^{-5} & \Longrightarrow \text{CN}^{-}(aq) + \text{H}_2\text{O}(1) & \Longrightarrow \text{HCN}(aq) + \text{OH}^{-}(aq) \\ & (a) & \text{OH}^{-} + \text{H}_2\text{O} \times \text{CN}^{-} & \text{(b)} & \text{OH}^{-} \times \text{H}_2\text{O} \\ & \text{(a)} & \text{OH}^{-} + \text{H}_2\text{O} \times \text{CN}^{-} & \text{(d)} & \text{CN}^{-} \times \text{H}_2\text{O} \\ & \text{OH} & \text{An acid HA ionises as} & \text{HA} = \Longrightarrow \text{H}^{+} + \text{A}^{-} & \text{HA} \end{array} $		Assertion (A): When Cu (II) and sulphide ions are mixed they react together extremely quickly to give a solid. Reason (R): The equilibrium constant of Cu ²⁺ (aq) + S ² (aq) = CuS (s) is high because the solubility product i low. (a) (A) is false and (R) is true (b) Both (A) and (R) are false (c) Both (A) and (R) are true but (R) is not the explanation for (A) (d) Both (A) and (R) are true and (R) is the explanation for (G)
	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}	97.	The $K_{\rm sp}$ for the following dissociation is 1.6×10^{-5} PbCl ₂ (s) \Longrightarrow Pb ²⁺ (aq) + 2Cl ⁻ (aq) Which of the following choices is correct for a mixture of 300 mL 0.134 M Pb(NO ₂), and 100 mL 0.4 M NaCl?
90.	$\begin{array}{ll} Three \ reactions \ involving \ H_2PO_4^- \ are \ given \ below: \\ (i) H_2PO_4^- + H_2O^- + H_3O^+ + H_2PO_4^- \\ (ii) H_2PO_4^- + H_2O^- + H_2O^+ + H_3O^+ \\ (iii) H_2PO_4^- + OH^- \rightarrow H_3PO_4^- + O^2^- \\ In \ which \ of \ the \ above \ does \ H_2PO_4^- \ act \ as \ an \ acid\ ? \end{array}$		(a) Not enough data provided (b) $Q < K_{sp}$ (c) $Q > K_{sp}$ (d) $Q = K_{sp}$
91.	(a) (ii) only (b) (i) and (ii) (c) (iii) only (d) (i) only The pK, of a weak acid, HA, is 4.80. The pK, 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	98.	The solubility product of $Cr(OH)_3$ at 298 K is 6.0×10^{-31} . The concentration of hydroxide ions in a saturate solution of $Cr(OH)_3$ will be: [Jan. 09, 2020 (II)] (a) $(2.22 \times 10^{-31})^{1/4}$ (b) $(18 \times 10^{-31})^{1/4}$ (c) $(18 \times 10^{-31})^{1/2}$ (d) $(4.86 \times 10^{-29})^{1/4}$

99. The stoichiometry and solubility product of a salt with



- (a) $X,Y,2 \times 10^{-9}M^3$ (b) $XY_{2},4 \times 10^{-9}M^3$ (c) $XY_{2},1 \times 10^{-9}M^3$ (d) $XY_{2},2 \times 10^{-6}M^3$ 100. What is the molar solubility of $AI(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of Al(OH)3 [April 12, 2019 (I)] (b) 12×10⁻²¹ (a) 3×10⁻¹⁹
- (d) 12×10⁻²³ (c) 3×10-22 101. The molar solubility of Cd(OH)₂ is 1.84×10⁻⁵ M in water. The expected solubility of Cd (OH)2 in a buffer solution of pH = 12 is: [April 12, 2019 (II)]
- $\frac{2.49}{1.84} \times 10^{-9} \,\mathrm{M}$ (a) 1.84×10⁻⁹ M (b) (c) 6.23×10⁻¹¹ M (d) 2.49×10⁻¹⁰ M
- 102. The pH of a 0.02 M NH₄Cl solution will be [given $K_b(NH_4OH)=10^{-5}$ and log 2=0.301]

[April 10, 2019 (II)]

- (a) 2.65 (b) 4.35 (c) 4.65 (d) 5.35
- 103. If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct? [April 8, 2019 (1)]

$$\begin{split} \text{(a)} \quad & S = \left(\frac{K_{\psi}}{144}\right)^{1/6} \\ \text{(b)} \quad & S = \left(\frac{K_{\psi}}{6912}\right)^{1/7} \\ \text{(c)} \quad & S = \left(\frac{K_{\psi}}{929}\right)^{1/9} \\ \text{(d)} \quad & S = \left(\frac{K_{\psi}}{216}\right)^{1/7} \end{split}$$

- 105. $20 \,\mathrm{mL}$ of $0.1 \,\mathrm{M}\,\mathrm{H}_2\mathrm{SO}_4$ solution is added to $30 \,\mathrm{mL}$ of 0.2M NH_4OH solution. The pH of the resultant mixture is: $[pK_b \text{ of } NH_4OH = 4.7]$. [Jan. 9, 2019 (I)] [Jan. 9, 2019 (I)] (c) 5.0 (d) 0.4 (a) 5.2 (b) 9.0
- 106. A mixture of 100 m mol of Ca(OH), and 2 g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and

- the concentration of OH^- in resulting solution, respectively, are: (Molar mass of $Ca(OH)_2$, Na_2SO_4 and Taspectively, at c whose mass of $ca(\sigma Ir)_2$, $va_3 \omega v_4$ and $va_4 \omega v_5$ and $va_5 \omega v_6$ and v
- 107. Which of the following salts is the most basic in aqueous
- solution? (a) Al(CN)₃ (b) CH₃COOK (d) Pb(CH₃COO)₂ (c) FeCl₂
- 108. An aqueous solution contains 0.10 MH₂S and 0.20 M HCI. If the equilibrium constants for the formation of HS-from H₃S is 1.0×10^{-7} and that of S²- from HS- ions is 1.2×10^{-15} then the concentration of S²- ions in aqueous solution is: (a) 5×10⁻⁸ (c) 6×10⁻²¹
 - (b) 3 × 10⁻²⁰ (d) 5 × 10⁻¹⁹
- 109. An aqueous solution contains an unknown concentration of Ba²⁺. When 50 mL of a 1 M solution of Na₂SO₂ is added, BaSO₄ just begins to precipitate. The final volume is 500 mL. The solubility product of BaSO₄ is 1 × 10⁻¹⁰. What is the original concentration of Ba^{2+} ? (a) $5 \times 10^{-9} \,\mathrm{M}$ (b) $2 \times 10^{-9} \,\mathrm{M}$ (c) $1.1 \times 10^{-9} \,\mathrm{M}$ (d) $1.0 \times 10^{-10} \,\mathrm{M}$
- 110. The minimum volume of water required to dissolve 0.1g lead (II) chloride to get a saturated solution (K_{sp} of PbCl₂ = 3.2×10^{-8} ; atomic mass of Pb = 207 u) is:
 - [Online April 15, 2018 (I)]
 - (b) 0.36L (d) 0.18L (a) 1.798 L
- 111. Addition of sodium hydroxide solution to a weak acid 111. Addition of socium nyaroxice solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is 10⁻⁵, the ratio of salt to acid concentration in the buffer solution will be: | Online April 8, 2017|
 (a) 4:5 (b) 1:10 (c) 10:1 (d) 5:4

 112. In some solutions, the concentration of H₂O' remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as:
- (a) Ideal solutions (b) Colloidal solutions (c) True solutions (d) Buffer solutions (113. Consider the following equilibrium
- $AgCl \downarrow +2NH_3 \rightleftharpoons \left[Ag(NH_3)_2\right]^+ + Cl^$ white precipitate of AgCl appears on adding which of the following? [Online April 11, 2014]

 (a) NH₃ (b) aqueous NaCl

- (a) Nr1₃ (b) aqueous NaC1
 (c) aqueous HNO₃ (d) aqueous NrL_CI

 114. Zirconium phosphate [Zr₃(PO₂)₄] dissociates into three zirconium cations of charge + 4 and four phosphate anions of charge 3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_m then which of the following relationship between S and K_m is correct?

 [Online April 19, 2014]
 - (a) $S = \{K_{sp}/(6912)^{1/7}\}$ (b) $S = \{K_{sp}/(6912)^{1/7}\}$ (c) $S = \{K_{sp}/(6912)^{1/7}\}$ (d) $S = \{K_{sp}/(6912)^{1/7}\}$ (e) $S = \{K_{sp}/(6912)^{1/7}\}$ (f) $S = \{K_{sp}/(6912)^{1/7}\}$

Chemistry $\begin{array}{ll} \textbf{115. Solid } & \text{Ba}(\text{NO}_3)_2 \text{ is gradually dissolved in a} \\ & 1.0 \times 10^{-4} \, \text{M} \, \text{Na}_2 \, \text{Co}_3 \, \text{solution. At which concentration of} \\ & \text{Ba}^{2+}, \text{precipitate of} \, \text{BaCO}_3 \, \text{begins to form } ?(K_{\text{ps}} \, \text{for BaCO}_3) \\ & = 5.1 \times 10^{-9}) & \textbf{[Online April 9, 2013]} \\ \end{array}$ (b) 10 (a) 9 (c) 11 (d) 8 123. Solid Ba(NO₃)₂ is gradually dissolved in a 1.0×10^{-4} M Na₂CO₃ solution. At what concentration of Ba²⁺ will a precipitate begin to form? ($K_{\rm sp}$ for FaCO₃ = 5.1×10^{-9}) (b) 7.1×10⁻⁸ M (a) $5.1 \times 10^{-5} \,\mathrm{M}$ (c) 4.1 × 10⁻⁵ M (d) 8.1 × 10⁻⁷ M [2009] 116. Which one of the following arrangements represents the (b) $8.1 \times 10^{-8} \,\mathrm{M}$ correct order of solubilities of sparingly soluble salts (c) $8.1 \times 10^{-7} \,\mathrm{M}$ (d) $4.1 \times 10^{-5} \,\mathrm{M}$ ${\rm Hg_2Cl_2, Cr_2(SO_4)_3, BaSO_4}$ and ${\rm CrCl_3}$ respectively? [Online April 22, 2013] 124. In a saturated solution of the sparingly soluble strong electrolyte ${\rm AgIO_3}(molecular\,mass\,{=}\,283)$ the equilibrium (a) $BaSO_4 > Hg_2Cl_2 > Cr_2(SO_4)_3 > CrCl_3$ which sets in is $AglO_3(s) \Longrightarrow Ag^*(aq) + IO_3(aq)$. If the solubility product constant K_{ap} of $AglO_3$ at a given temperature is 1.0×10^{-8} , what is the mass of $AglO_3$ contained in 100 mL of its saturated solution? [2007] $(b) \quad BaSO_4 > Hg_2Cl_2 > CrCl_3 > Cr_2(SO_4)_3 \\$ (c) $BaSO_4 > CrCl_3 > Hg_2Cl_2 > Cr_2(SO_4)_3$ $(d) \quad Hg_2Cl_2 > BaSO_4 > CrCl_3 > Cr_2(SO_4)_3$ (a) 1.0×10^{-4} g (b) 28.3×10^{-2} g (c) 2.83×10^{-3} g (d) 1.0×10^{-7} g. 125. The solubility product of a salt having general formula MX_2 , in water, is : 4×10^{-12} . The concentration of M^{2+} (c) 1.0 × 10⁻⁵ (b) 1.0 × 10⁻¹¹ ions in the aqueous solution of the salt is [2005] 118. If $K_{\rm sp}$ of CaF₂ at 25 °C is 1.7×10^{-10} , the combination amongst the following which gives a precipitate of CaF₂ is (a) 4.0 × 10⁻¹⁰ M (b) 1.6 × 10⁻⁴ M [Online May 19, 2012] (a) 1×10^{-2} M Ca²⁺ and 1×10^{-3} M F⁻ (b) 1×10^{-4} M Ca²⁺ and 1×10^{-4} M F⁻ (c) $1.0 \times 10^{-4} \text{ M}$ (d) $2.0 \times 10^{-6} \text{ M}$ 126. The molar solubility (in mol L-1) of a sparingly soluble salt (b) 1×10^{-2} M Ca²⁺ and 1×10^{-5} MF (d) 1×10^{-3} M Ca²⁺ and 1×10^{-5} MF (d) 1×10^{-3} M Ca²⁺ and 1×10^{-5} MF 119. The solubility of Pbl₂ at 25 °C is 0.7 g L⁻¹. The solubility ${\rm MX_4}$ is 's'. The corresponding solubility product is K 's' is given in term of $K_{\rm sp}$ by the relation : [200-(a) $s = (256 K_{sp})^{1/5}$ (b) $s = (128 K_{sp})^{1/4}$ product of PbI₂ at this temperature is (molar mass of PbI₂ = 461.2 g mol^{-1}) [Online May 26, 2012] (c) $s = (K_{sp} / 128)^{1/4}$ (d) $s = (K_{sp} / 256)^{1/5}$ (b) 0.14×10^{-9} (a) 1.40×10^{-9} (c) 140 × 10⁻⁹ (d) 14.0 × 10⁻⁹ 127. The solubility in water of a sparingly soluble salt AB2 is **120.** The $K_{\rm sp}$ for ${\rm Cr(OH)}_3$ is 1.6×10^{-30} . The solubility of this compound in water is : [2011RS] 1.0×10^{-5} mol L⁻¹. Its solubility product will be (a) 4×10^{-10} (b) 1×10^{-15} (c) 1 × 10⁻¹⁰ (b) $4\sqrt{1.6\times10^{-30}/27}$ (a) $4\sqrt{1.6 \times 10^{-30}}$ 128. 1 M NaCl and 1 M HCl are present in an aqueous solution. (c) $1.6 \times 10^{-30/27}$ (d) $2\sqrt{1.6 \times 10^{-30}}$ The solution is (a) not a buffer solution with pH < 7 121. Solubility product of silver bromide is 5.0×10^{-13} . The (b) not a buffer solution with pH > 7 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] (c) a buffer solution with pH < 7 (d) a buffer solution with pH > 7. (a) $1.2 \times 10^{-10} \, g$ (b) 1.2 × 10⁻⁹ g 129. Let the solubility of an aqueous solution of Mg(OH)2 be (d) 5.0×10^{-8} g x, then its $K_{\rm sp}$ is 122. At 25 °C, the solubility product of Mg(OH) $_2$ is 1.0×10^{-11} . At which pH, will Mg $^{2+}$ ions start precipitating in the form of Mg(OH) $_2$ from a solution of 0.001 M Mg $^{2+}$ ions?[2010] (a) $4x^3$ (b) 108x⁵ (c) 27x⁴ (d) 9x.

c-85



Hints & Solutions



1. (c)
$$K_{\rm p} = K_{\rm c} ({\rm RT})^{\Delta n_{\rm g}} = K_{\rm c} ({\rm RT})^{1-3/2} = K_{\rm c} ({\rm RT})^{-1/2}$$

$$\Rightarrow K_{\rm c} = K_{\rm p} ({\rm RT})^{1/2}$$

2. **(d)**
$$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$$
; K_c

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g);$$
 $\frac{1}{K_c}$

$$NH_3(g) \Longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g); \frac{1}{K_0^{1/2}}$$

$$\frac{1}{K_c^{1/2}} = \frac{1}{(64)^{1/2}} = \frac{1}{8}$$

$$K_{eq} = \frac{[Z]^2}{[X][Y]} = \frac{1}{0.75 \times [1.25]} = \frac{x}{15}$$

$$\Rightarrow x = \frac{15}{15} = 16$$

$$\Rightarrow x = \frac{15}{(0.75 \times 1.25)} = 16$$

(b) At equilibrium, rate of forward reaction = Rate of backward reaction.

5. **(d)**
$$A \rightleftharpoons B + C$$
; $K_{eq}^{(1)}$...(i)

$$B+C \Longrightarrow P ; K_{eq}^{(2)}$$
 ...(ii)

On adding equations (i) and (ii), we get

$$A \rightleftharpoons P$$

$$K_{\text{eq}}$$
 (overall) = $K_{\text{eq}}^{(1)} \cdot K_{\text{eq}}^{(2)}$

(d) Equilibrium constant

$$K_c = \frac{[B]}{[A]} = \frac{11}{6} \approx 2$$

7. (a) We know that, $K_p = K_c.(RT)^{\Delta n_g}$

$$\therefore \text{If } \Delta n_g \neq 0 \text{ then } K_p \neq K_c$$

Now,
$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

 $\Delta n_g = +1$
 $\Rightarrow K_p = K_c (RT)^1$
Hence, $K_p \neq K_c$

8. (c) Given,
$$S + O_2 \implies SO_2 ... (i)$$
; $K_1 = 10^{52}$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \dots (iii); K = ?$$

To get equation (iii) follow (ii) - 2 (i),

$$2S + 3O_2 \rightarrow 2SO_3$$
 $K = 10^{129}$

$$-(2S + 2O_2 \rightarrow 2SO_2 \quad K = 10^{104})$$

$$O_2 \rightarrow 2SO_3 - 2SO_2$$
 $K = 10^{25}$

or
$$2SO_2 + O_2 \rightarrow 2SO_3 K = 10^{25}$$

9. **(b)**
$$A(s) \longrightarrow B(g) + C(g)$$

$$K_{P_1} = P_B \times P_C$$

$$P_1(P_1 + P_2) = x \qquad \dots (i)$$

$$D(s) \longrightarrow C(g) + E(g)$$

$$K_{P_2} = P_C \times P_E$$

$$(P_1 + P_2) P_2 = y$$
 ...(ii)

Adding (i) and (ii)

$$P_{1}(P_{1}+P_{2}) + P_{2}(P_{1}+P_{2}) = x + y$$

$$P_{1}^{2} + P_{1}P_{2} + P_{2}P_{1} + P_{2}^{2} = x + y$$

$$P_{1}^{2} + P_{2}^{2} + 2P_{1}P_{2} = x + y$$

$$(P_{1}+P_{2})^{2} = x + y$$

$$P_1 + P_1 + P_2 + P_3 + P_4 + P_4 + P_5$$

$$\Rightarrow \qquad (P_1 + P_2)^2 = x + y$$

$$\Rightarrow$$
 $P_1 + P_2 = \sqrt{x + y}$

$$\therefore$$
 Total pressure $(P_T) = P_C + P_B + P_E$

$$(P_1 + P_2) + P_1 + P_2 = 2 (P_1 + P_2)$$

$$t = 0 2 3 0 0$$

$$t_{\text{eq}}$$
 $2-x$ $3-2x$ $2x$ x

Given,
$$3-2x=2-x$$

$$\Rightarrow$$
 $x=1$

$$C = 2, [D] = 1, [A] = 1, [B] = 1$$

$$\therefore K_{\rm c} = \left\{ \frac{2^2 \times 1}{1^2 \times 1} \right\} = 4$$

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$$\begin{split} \textbf{11.} \quad \textbf{(a)} \quad & \underset{P_{NH_3}}{2NH_3(g)} \underset{P_{N_2}}{\Longleftrightarrow} N_2(g) + 3H_2(g), \ K = \frac{1}{K_P} \\ & \therefore \ K = \frac{1}{K_P} = \frac{P_{N_2} \left(P_{H_2}\right)^3}{\left(P_{NH_3}\right)^2} \qquad \qquad ... (i) \\ & \Rightarrow P_{Total}(P) = P_{N_2} + P_{H_2} + P_{NH_3} \\ & \approx P_{N_2} + P_{H_2} (\because P_{NH_3} << P_T) \\ & \text{Now,} \end{split}$$

Partial pressure of $N_2 = \frac{1}{4}P$; Partial pressure of $H_2 = \frac{3}{4}P$

From eq (i),
$$\frac{1}{K_P} = \frac{\left(\frac{1}{4}P\right)\left(\frac{3}{4}P\right)^3}{\left(P_{NH_3}\right)^2}$$

$$\frac{\left(P_{NH_{3}}\right)^{2}}{K_{P}} = \frac{P}{4} \cdot \frac{P^{3}}{4^{3}} \cdot 3^{3}; \frac{\left(P_{NH_{3}}\right)^{2}}{K_{P}} = \frac{P^{4}}{4^{4}} \cdot 3^{3}$$

$$(P_{NH_3})^2 = K_P \cdot \frac{P^4}{4^4} \cdot 3^3; P_{NH_3} = \left[K_P \cdot \frac{P^4}{4^4} \cdot 3^3 \right]^{1/2}$$

$$P_{NH_3} = \frac{3^{3/2}.P^2.K_P^{1/2}}{16}$$

12. (b)
$$K_p = K_c (RT)^{\Delta^n g}$$

 $\Delta n_g = No.$ of gaseous moles of products – No. of gaseous

$$\frac{K_{\rm p}}{K_{\rm c}} = (\rm RT)^{\Delta n_g}$$

$$N_2(g) + O_2(g) \implies 2NO(g), \Delta n_g = 0$$

$$\frac{K_p}{K_c} = (24.62 \text{ dm}^3 \text{ atm mol}^{-1})^0 = 1$$

$$N_2O_4(g) = 2NO_2(g), \Delta n_g = 1$$

$$\frac{K_{\rm p}}{K_{\rm c}} = 24.62 \, {\rm dm}^3 \, {\rm atm \, mol}^{-1}$$

$$N_2(g) + 3H_2(g) \implies 2NH_3(g), \Delta n_g = -2$$

$$\begin{split} \frac{K_{\rm p}}{K_{\rm c}} &= (24.62~{\rm dm^3\,atm\,mol^{-1}})^{-2} \\ &= \frac{1}{(24.62~{\rm dm^3\,atm\,mol^{-1}})^2} \\ &= 1.65\times 10^{-3}~{\rm dm^{-6}\,atm^{-2}\,mol^2} \end{split}$$

13. (d) Concerned reaction: $NH_4SH \longrightarrow NH_3(g) + H_2S(g)$

Initial moles =
$$\frac{5.1}{51}$$
 = 0.1 mol

$$NH_4SH \longrightarrow NH_3(g) + H_2S(g)$$

 $0.1(1-0.3) \quad 0.1 \times 0.3 \quad 0.1 \times 0.3$

$$.1(1-0.3)$$
 0.1×0.3 0.1×0.3

:.
$$K_c = [NH_3][H_2S] = \left(\frac{0.03}{3}\right)^2 = 10^{-4}$$

$$K_{\rm p} = K_{\rm c} ({\rm RT})^{\Delta n} g$$

= $10^{-4} \times (0.082 \times 600)^2 = 0.242 \, {\rm atm}^2$

14. (c) Given:
$$A_2 + B_2 \xrightarrow{K_1} 2AB$$

$$\Rightarrow$$
 2AB \longrightarrow $A_2 + B_2$; $K = \frac{1}{K_1}$

$$6AB \stackrel{K_1}{\rightleftharpoons} 3A_2 + 3B_2; K_2 = \left(\frac{1}{K_1}\right)^2$$

The relation between K_1 and K_2 is $K_2 = K_1^{-3}$

(a) Initially 2 moles of CO are present.

At equilibrium, 1 mole of CO is present

Hence, 2-1=1 moles of CO has reacted.

1 mole of CO will react with 1 mole of Cl_2 to form 1 mole of

3-1=2 moles of Cl₂ remains at equilibrium

The equilibrium constant

$$K_{c} = \frac{[\text{COCl}_{2}]}{[\text{CO}][\text{Cl}_{2}]} = \frac{\frac{1 \text{ mol}}{5\text{L}}}{\frac{1 \text{ mol}}{5\text{L}} \times \frac{2 \text{ mol}}{5\text{L}}} = 2.5$$

16. (a) Given,
$$A + B \rightleftharpoons C + D$$

No. of moles initially 1 1 1 1

$$K_{\rm c} = \left(\frac{1+a}{1-a}\right)^2 = 100; \ \frac{1+a}{1-a} = 10$$

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

17. (a)
$$XY(s) \xrightarrow{p} X(g) + Y(g)$$

At eqm.,

Total pressure = 2p = 10 bar

:
$$p = 5$$
; Now $K_p = (p_x)(p_y) = p^2 = 25$.

18. (c)
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$t=0 \qquad 1 \qquad 0$$

$$t=eqm \qquad 1-\alpha \qquad 2\alpha$$

Where α = degree of dissociation.

.. Mol. wt. of mixture

$$= \frac{(1-\alpha) \times M_{N_2O_4} + 2\alpha \times M_{NO_2}}{(1-\alpha + 2\alpha)}$$
$$= \frac{(1-0.2)92 + 2 \times 0.2 \times 46}{(1+0.2)} = 76.66$$

Now, as per ideal gas equation,

$$PV = nRT$$

$$PM_{\text{mix}} = dRT$$

$$d = \frac{PM_{mix}}{RT} = \frac{1 \times 76.66}{0.0821 \times 300} = 3.11g / L$$

19. (b)
$$SO_2(g) + \frac{1}{2}O_2(g) \Longrightarrow SO_3(g)$$

$$K_{\rm p} = K_{\rm c} ({\rm RT})^x$$

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

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

20. (d)
$$2HI \rightleftharpoons H_2 + I_2$$

At
$$t = 0$$
 c 0 0
At eqm. $c-c\alpha$ $\frac{c\alpha}{2}$ $\frac{c\alpha}{2}$

Now,
$$K_c = \frac{\left(\frac{c\alpha}{2}\right)\left(\frac{c\alpha}{2}\right)}{\left(c-c\alpha\right)^2}$$

$$K_{\rm c} = \frac{\alpha}{4(1-\alpha)^2}$$
; $K_{\rm c} = \frac{0.5}{4(1-0.5)^2}$

$$K_{\cdot} = 0.25$$

21. (b) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

$$K_p = \frac{\left(p_{\text{NH}_3}\right)^2 \times \left(p_{\text{CO}_2}\right)}{p_{\text{NH}_2\text{COONH}_4}(s)} = \left(p_{\text{NH}_3}\right)^2 \times \left(p_{\text{CO}_2}\right)$$

As evident by the reaction, NH3 and CO2 are formed in molar ratio of 2:1. Thus if P is the total pressure of the system at equilibrium, then

$$p_{\text{NH}_3} = \frac{2}{3} \times p$$

$$p_{\text{CO}_2} = \frac{1}{3} \times P$$

$$K_{\rm p} = \left(\frac{2P}{3}\right)^2 \times \frac{P}{3} = \frac{4P^3}{27}$$

Given, $K_p = 2.9 \times 10^{-5}$

$$\therefore 2.9 \times 10^{-5} = \frac{4P^3}{27}$$

$$P^3 = \frac{2.9 \times 10^{-5} \times 27}{4}$$

$$P = \left(\frac{2.9 \times 10^{-5} \times 27}{4}\right)^{\frac{1}{3}} = 5.82 \times 10^{-2} \text{atm}$$

22. (b)
$$A + 2B \rightleftharpoons 2C + D$$

At $t = 0$ a $1.5a$ 0 0

At eqns. $(a-x)$ $(1.5a-2x)$ $2x$ x

Hence,
$$K_c = \frac{(2x)^2 \times x}{(a-x)(1.5a-2x)^2}$$

Given, at equilibrium

$$\therefore (a-x) = (1.5a-2x)$$

$$\therefore a = 2x$$

On solving $K_c = 4$

23. (d) To calculate the value of K_4 in the given equation we should apply:

eqn.
$$(2)$$
 + eqn. $(3) \times 3$ - eqn. (1)

hence
$$K_4 = \frac{K_2 K_3^3}{K_1}$$

24. (a)
$$K_{\rm p} = K_{\rm c} (RT)^{\Delta n_g}$$

For the reaction

$$CO(g) + \frac{1}{2}O_2(g) \iff CO_2(g)$$

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

$$\therefore K_{\rm p} = \frac{K_{\rm c}}{\sqrt{RT}}; \frac{K_{\rm p}}{K_{\rm c}} = \frac{I}{\sqrt{RT}}$$

25. (d) For the reaction

$$N_2 + O_2 \longrightarrow 2NO \quad Kc = 4 \times 10^{-4}$$

Hence for the reaction

NO
$$\longrightarrow \frac{1}{2} N_2 + \frac{1}{2} O_2$$
 $K_c = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$

26. (b) (I)
$$N_2 + 2O_2 \xrightarrow{K_1} 2NO_2$$

26. (b) (I)
$$N_2 + 2O_2 \xrightarrow{K_1} 2NO_2$$

$$K_1 = \frac{[NO_2]^2}{[N_2][O_2]^2} \qquad ...(i)$$

(II)
$$2NO_2 \xrightarrow{K_2} N_2 + 2O_2$$

$$K_2 = \frac{[N_2][O_2]^2}{[NO_2]^2}$$
 ...(ii)

(III)
$$NO_2 \xrightarrow{K_3} \frac{1}{2} N_2 + O_2$$

 $K_3 = \frac{[N_2]^{1/2} [O_2]}{[NO_2]}$

$$\therefore \ (K_3)^2 = \frac{[N_2][O_2]^2}{[NO_2]^2} \qquad ...(ii)$$

$$\therefore \text{ From equation (i), (ii) and (iii)}$$

$$K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$$

27. (c)
$$2AB_3(\mathbf{g}) \stackrel{\longleftarrow}{\longleftarrow} A_2(\mathbf{g}) + 3B_2(\mathbf{g})$$
 at $t = 0$ 8 0 0 at eqm. $(8 - 2 \times 2)$ 2 3×2 = 4 2 6 molar cones. $4/\mathbf{V}$ $2/\mathbf{V}$ $6/\mathbf{V}$

now
$$K_c = \frac{[A_2][B_2]^3}{[AB_3]^2} = \frac{2/1 \times [6/1]^3}{[4/1]^2} = 27$$

$$\begin{array}{cccc} \textbf{28.} & \textbf{(d)} & & N_2O_4(g) \Longrightarrow 2NO_2(g) \\ & & \text{Initial moles} & 1 & 0 \\ & & \text{Moles at eqm.} & (1-\alpha) & 2\alpha \\ \end{array}$$

 $(\alpha = degree of dissociation)$

Total number of moles at eqm.

$$=(1-\alpha)+2\alpha$$

$$=(1+\alpha)$$

$${p_{N_2}}_{4} = \frac{(1-\alpha)}{a(1+\alpha)} \times P$$

$$p_{NO_2} = \frac{2\alpha}{a(1+\alpha)} \times P$$

$$K_{\mathrm{p}} = \frac{(p_{NO_2})^2}{P_{N_2O_4}} = \frac{\left(\frac{2\alpha}{(1+\alpha)} \times P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) \times P}$$

$$K_{\rm p} = \frac{4\alpha^2 P}{\underbrace{(1+\alpha)^2 (1-\alpha)}}; \ K_{\rm p} = \frac{4\alpha^2 P}{(1+\alpha)(1-\alpha)}; = \frac{4\alpha^2 P}{1-\alpha^2}$$

Given, $K_p = 2$, P = 0.5 atm

:.
$$K_{p} = \frac{4\alpha^{2}P}{1-\alpha^{2}}$$
; $2 = \frac{4\alpha^{2} \times 0.5}{1-\alpha^{2}}$

$$\alpha=0.707\approx0.71$$

$$2\alpha = 1.6$$

 $\alpha = 0.8$

$$K_{\rm c} = \frac{(2\alpha)^2}{(1-\alpha)(2-2\alpha)^2} = \frac{(0.8)^2}{(1-0.8)(1-0.8)^2} = \frac{0.64}{0.002}$$

30. (c)
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$
 $K_2 = 4.8 \times 10^{-11}$

Second dissociation constant (K_2) is much smaller than the first one (K_1) . Just a small fraction of total HCO₃ formed will undergo second stage of ionization. Hence in saturated solution

$$[H^+] >>> [CO_3^{2-}]; [CO_3^{2-}] \neq 0.034 M$$

$$[HCO_3^{2-}] >> [CO_3^{2-}] \text{ and } [H^+] \approx [HCO_3^-].$$

31. (a) Let the initial moles of X be 'a' and that of Z be 'b' then for the given reactions,

$$X = \longrightarrow 2Y$$

Initial a moles 0 At eqm.
$$a(1-\alpha)$$
 2a α (moles)

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

$$= a - a\alpha + 2a\alpha$$
$$= a(1 + \alpha)$$

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

Now,
$$K_{p_1} = \frac{(n_y)}{n_x} \times \left(\frac{r_{1_1}}{\sum n}\right)$$

or,
$$K_{p_1} = \frac{(2a\alpha)^2 \cdot P_{T_1}}{[a(1-\alpha)][a(1+\alpha)]}$$

$$Z \begin{tabular}{lll} \hline Z & \longrightarrow & P & + & Q \\ b & moles & 0 & 0 \\ b(1-\alpha) & b\alpha & b\alpha \\ \hline \end{array}$$

At eqm. $b(1-\alpha)$ $b\alpha$ (moles)

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

 $=b(1+\alpha)$

Now
$$K_{p_2} = \frac{n_Q \times n_P}{n_z} \times \left[\frac{P_{T_2}}{\sum n} \right]^{\Delta n}$$

or
$$K_{p_2} = \frac{(b\alpha)(b\alpha).P_{T_2}}{[b(1-\alpha)][b(1+\alpha)]}$$

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or
$$\frac{K_{\text{Pl}}}{K_{\text{P2}}} = \frac{4\alpha^2 \cdot P_{\text{Tl}}}{(1-\alpha^2)} \times \frac{(1-\alpha)^2}{P_{\text{T2}} \cdot \alpha^2} = \frac{4P_{\text{Tl}}}{P_{\text{T2}}}$$
or
$$\frac{4P_{\text{Tl}}}{P_{\text{T2}}} = \frac{1}{9} \qquad \left[\because \frac{K_{\text{Pl}}}{K_{\text{P2}}} = \frac{1}{9} \text{ given} \right]$$
or
$$\frac{P_{\text{Tl}}}{P_{\text{T2}}} = \frac{1}{36} \text{ or } 1:36$$

32. (c) Reaction (iii) can be obtained by adding reactions (i) and (ii) therefore $K_3 = K_1$. K_2

Hence (c) is the correct answer.

33. (c)
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

 $1-x$ x x

Total moles after dissociation

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

$$p_{PCl_3} = Mole fraction of PCl_3 \times Total pressure$$

$$= \left(\frac{x}{1+x}\right)P$$

34. (c)
$$SO_3(g) \Longrightarrow SO_2(g) + \frac{1}{2}O_2(g)$$

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

On taking the square of the above reaction

$$\frac{[SO_2]^2[O_2]}{[SO_3]^2} = 24.01 \times 10^{-4}$$

Now for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3$

$$K_{\rm c}' = \frac{{{{{\left[{{{\rm SO}_3}} \right]}^2}}}{{{{{\left[{{{\rm SO}_2}} \right]}^2}\left[{{{\rm O}_2}} \right]}}} = \frac{1}{{24.01 \times {10^{ - 4}}}} = 416$$

35. (d) For the reaction:-

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

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

R=0.0831 kJ/mol. K

$$K_{\rm p} = K_{\rm c} (\rm RT)^{\Delta n}$$

$$K_{\rm p} = 1.8 \times 10^{-6} \times 0.0831 \times 457$$

$$=6.836 \times 10^{-6}$$

Hence it is clear that $K_p > K_c$

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

x = 0.17 atm.

$$p_{NH_3} = 0.5 + 0.17 = 0.67$$
 atm;

$$p_{H_2S} = 0.17 \text{ atm}$$

 $K = p_{NH_3} \times p_{H_2S} = 0.67 \times 0.17 \text{ atm}^2$
 $= 0.1139 = 0.11$

37. (d) For
$$P_4(s) + 5O_2(g) \Longrightarrow P_4O_{10}(s)$$

$$K_{\rm c} = \frac{1}{({\rm O}_2)^5}$$
.

Solids have concentration unity.

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

$$\therefore \frac{K_{\rm p}}{K_{\rm c}} = \frac{1}{\rm RT}$$

39. (b)
$$K_{c} = \frac{[NO_{2}]^{2}}{[N_{2}O_{4}]} = \frac{[1.2 \times 10^{-2}]^{2}}{[4.8 \times 10^{-2}]}$$

$$= 3 \times 10^{-3} \text{ mol/L}$$

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

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

$$\therefore \frac{K_{\rm p}}{K_{\rm c}} = ({\rm RT})^{-1/2}$$

41. (c)
$$\Delta G^{\circ} = -RT \ln K$$
, $T_1 = 25^{\circ}C$, $K_1 = 10$

$$\Delta G^{\circ}$$
 at $T_1 = -8.314 \times 298 \times 2.303 \times log 10 = -5.71$ kJ/mol

$$\Delta G^{\circ}$$
 at $T_2 = -8.314 \times 298 \times 373 \times 2.303 \times \log(100)$

 $=-14.29 \, kJ/mol$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Rightarrow$$
 -5.71 = Δ H $^{\circ}$ - 298(Δ S $^{\circ}$)

$$\Rightarrow$$
 -14.29 = ΔH° - 373(ΔS°)

 $\Delta H^{\circ} = 28.4 \text{ kJ/mol}$

- 42. (c) (i) As reaction is endothermic (ΔHz = +ve) so on decrease in temperature equilibrium will shift towards reactant side.
 - (ii) On increase in pressure by adding inert gas (N_2) at same temperature, no shifting will take place. The equilibrium changes only if the added gas is a reactant or product involved in the reaction.

43. (d)
$$\Delta G^{\circ} = -RT \ln K$$

$$\therefore$$
 If $K > 1$ then $\Delta G^{\circ} < 0$

If
$$K < 1$$
 then $\Delta G^{\circ} > 0$

If
$$K = 1$$
 then $\Delta G^{\circ} = 0$

44. (a) Equilibrium constant has no relation with catalyst. Catalyst only affects the rate of the reaction.

Catalyst, V_2O_5 in the given reaction, is used to speed up the reaction.

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45. (c) $\Delta G = \Delta G^{\circ} + RT \ln Q$

At equilibrium; $\Delta G = 0$ and $Q = K_{eq}$ $\Rightarrow \Delta G^{\circ} = -2.303 \text{ RT log K}_{w}$

 $= -2.303 \times 8.314 \times 298 \times log10^{-14}$

= $79.9 \text{ kJ/mol} \approx 80 \text{ kJ/mol}$

46. (b) Volume $\uparrow P \downarrow$, reaction proceeds in which direction where the number of moles of gases increases.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g) \Delta n_g = (2+1) - 2 = 1$$

47. (c) Reaction at equilibirium

$$N_2O_4 \Longrightarrow 2NO_2$$

According to Le chatelier's principle-

- (a) addition of an inert gas at constant pressure will increase volume and equilibirium shifts towards more number of molecules.
- (b) Decomposition of N₂O₄ will be endothermic, so reaction will move in forward reaction when temperature is increased.So, It is incorrect. It will not effect reaction (volume is constant)
- (c) Increasing the pressure on a gas reaction shifts the position of equilibirium towards the side with fewer molecules. So, it will move in backward direction which leads to formation of N₂O₄ from NO₂.

48. (d) Perturbation

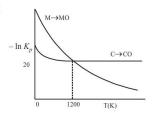
Shifts reaction towards

 $\begin{array}{ll} {\rm Removal\,of\,CO} & {\rm Left} \\ {\rm Removal\,of\,CO}_2 & {\rm Right} \\ {\rm Addition\,of\,CO}_2 & {\rm Left} \end{array}$

Addition of Fe₂O₃ No change

(This is a solid compound. Its concentration has no effect on the equilibrium.)

49. (c)



At T \leq 1200K, carbon will reduce MO(s) to M(s) hence, chemical reaction

 $MO(s) + C(s) \longrightarrow M(s) + CO(g)$ is spontaneous.

50. (c) Given
$$\Delta H^{\circ} = -29.8 \text{ kJ mol}^{-1}$$

 $\Delta S^{\circ} = -1.00 \text{ kJ K}^{-1}$

From the equation

$$\begin{split} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = -29.8 - (298 \times -0.100) \\ &= -29.8 + 29.8 = 0 \\ \text{Now, } \Delta G^\circ = -2.303 \ RT \log K_{\text{eq}} \\ 0 &= -2.303 \ RT \log K_{\text{eq}} \\ & \therefore K_{\text{eq}} = 1. \end{split}$$

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

$$[A] = \frac{1}{2}, [B] = 2, [C] = \frac{1}{2}$$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times 1/2}{\left(\frac{1}{2}\right)^2} = 4$$

 $\Delta G^{\circ} = -2.303 \text{ RT log } K_{c}.$

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

$$\begin{split} &\Rightarrow \log K_{\rm c} \! = \! -\frac{2494.2 \, {\rm J}}{2.303 \times 8.314 \, {\rm J/K/mol} \times 300 \, {\rm K}} \\ &\Rightarrow \log K_{\rm c} \! = \! -0.4341; K_{\rm c} \! = \! 0.37; Q > \! K_{\rm c}. \end{split}$$

52. (b)
$$\Delta G_{\text{rex}}^{\circ} = 2\Delta G_{f}^{\circ} (\text{NO}_{2}) - 2\Delta G_{f}^{\circ} (\text{NO}) - \Delta G_{f}^{\circ} (\text{O}_{2})$$

$$2\Delta G_f^{\circ}(NO_2) = \Delta G_{rex}^{\circ} + 2\Delta G_f^{\circ}(NO) + \Delta G_f^{\circ}(O_2)$$

 $\therefore \quad \Delta G = \Delta G^{\circ} + RT \ln K_{\rm p}$

At equilibrium,

$$\Delta G = 0$$
, $Q = K_p$; $\Delta G^{\circ} = -RT \ln K_p$

$$\Delta G_f^{\circ}(O_2) = 0$$

$$\Delta G_f^{\circ}(NO_2) = \frac{1}{2} [2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$$

53. (d) Volume of ice is greater than that of water. The direction in which the reaction will proceed can be predicted by applying Le-Chatelier's principle

Pressure
$$\propto \frac{1}{\text{Volume}}$$

So equilibrium, will shift forward.

- 54. (d) On adding inert gas at constant volume the total pressure of the system is increased, but the partial pressure of each reactant and product remains the same. Hence no effect on the state of equilibrium.
- 55. (a) The reaction given is an exothermic reaction thus accordingly to Le-Chatalier's principle lowering of temperature, addition of F₂ and or Cl₂ favour the forward direction and in hence the production of CIF₃.
- **56. (b)** Due to exothermic nature of reaction low or optimum temperature will be required. Since 3 moles are changing to 2 moles, therefore high pressure will be required.

Equilibrium - c-91

57. (a) In reaction (a) 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.

(A) 0.01 M HCl $[H^+] = 10^{-2}$, pH = $-\log 10^{-2} = 2$ pOH = 14 - 2 = 12

(B) 0.01 M NaOH $[OH^{-}] = 10^{-2}, pOH = -\log[OH] = 2$

(C) 0.01 M CH₃COONa

$$pH = 7 + \frac{1}{2} [pK_a + \log 0.01]$$

 $pH > 7 \Rightarrow pOH < 7$

(D) 0.01 M NaCl, pH=7, pOH=7 Decreasing order of pOH value is, (A) > (D) > (C) > (B).

$$\begin{array}{ccc} & \text{H}_2\text{CO}_3 & \longrightarrow & \text{H}^+ + \text{HCO}_3^- \\ & \text{1} & 0.1 & 0.1 & 0.1 \alpha \\ \text{at Equb.} & 0.1(1-\alpha) & 0.1 \alpha & 0.1 \alpha \end{array}$$

$$4.0 \times 10^{-7} = \frac{0.1\alpha^2}{1 - \alpha}$$

$$\Rightarrow (1-\alpha)=1$$

$$\alpha^2 = 4 \times 10^{-6} \Rightarrow \alpha = 2 \times 10^{-3}$$

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

$$pH = 4 \times log 2 = 3.7 \approx 37 \times 10^{-1}$$

- (c) At equivalence point pH is 7 and pH increases with addition of NaOH so correct graph is (c).
- 61. (b) Temperature plays a significant role on pH measurements. As the temperature rises, molecular vibrations increase which results in greater ability of water to ionise and form more hydrogen ions.

As a result, the pH will drop. So assertion is incorrect. The dissociation of water molecules into ions is bond breaking and is therefore an endothermic process (energy must be absorbed to break the bonds). So reason is also incorrect.

62. (10.60)
$$M_{H_2SO_4} = \frac{9.8}{98 \times 100} = 10^{-3} M$$

$$M_{NaOH} = \frac{4}{40 \times 100} = 10^{-3} M$$

After neutralisation [OH-] can be calculated as

$$[OH^{-}] = \frac{(40 \times 10^{-3}) - (2 \times 10^{-3} \times 10)}{50}$$

$$= \frac{20}{50} \times 10^{-3}$$

$$[OH^{-}] = \frac{2}{5} \times 10^{-3}$$

$$pOH = 3.397$$

$$pH = 14 - pOH$$

$$= 14 - 3.397 = 10.603$$

63. (5.22)

No. of moles = $\frac{\text{Mass}}{\text{Molar mass}}$

$$3g CH_3 COOH = \frac{3}{60} 0.5 mol = 50 m mol$$

No. of millimoles = Molarity \times Volume in mL $250 \text{ mL of } 0.1 \text{ MHCl} = 250 \times 0.1 = 25 \text{ m mol}$ 500 mL solution = 50 m mol CH₃COOH

20 mL solution =
$$\frac{50}{500} \times 20 = 2$$
 m mol CH₃COOH
500 mL solution contains = 25 m mol HCl

20 mL solution contains = $\frac{25}{500} \times 20 = 1$ m mol HCl

$$\frac{1}{2}$$
 mL of 5M NaOH = $\frac{1}{2}$ × 5 = 2.5 m mol NaOH

$$HC1 + NaOH \longrightarrow NaC1 + H_2O$$

1 Remaining NaOH = 2.5-1 = 1.5 m mol

CH₃COOH + NaOH (remaining) → CH₃COONa + Water

pH = pK_a + log
$$\frac{1.5}{0.5}$$
 = 4.74 + log3
= 4.74 + 0.48 = 5.22

64. (b)
$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$$
Initial mol 0.04 0.04 0 0
mol at eqm. 0 0 0.04 0.04
 $NaHSO_4 \rightarrow Na^+ + H^+ + SO_4^{-2-}$

$$[H^+] = \frac{0.04}{0.80} = 0.05M; pH = 1.3$$

(b) Ionic product of water increases with increase in temperature because ionisation of water is endothermic.

(c)
$$HA \rightleftharpoons H^+ + A^-$$

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Given pH = 5
$$\Rightarrow$$
 - log (H⁺) = 5

$$\therefore [H^+] = 10^{-5}$$

As we know,

$$K_a = \frac{C\alpha^2}{1-\alpha}; \ 10^{-5} = \frac{C\alpha^2}{1-\alpha} = \frac{C\alpha.\alpha}{(1-\alpha)}$$

$$10^{-5} = 10^{-5} \frac{\alpha}{1-\alpha}$$
; $\alpha = \frac{1}{2}$ i.e., 50%

- 65. (b) Graph A and B, both represents the titration curve between strong acid and strong base, i.e., HCl and NaOH but, the pH of NaOH is more than 7 and during the titration it decreases, so graph (A) is correct.
- (c) Due to the resonance stabilisation of the conjugate base, CH(CN)3 is the strongest acid amongst the given compounds.

$$CH(CN)_{3} \rightleftharpoons H^{+} + \bar{C} (CN)_{3}$$

$$C \downarrow C = N \qquad \qquad N \downarrow C \qquad \qquad C \downarrow C \rightarrow N$$

$$N \downarrow C \qquad \qquad N \downarrow C \qquad N \downarrow C \qquad N \downarrow C \qquad \qquad N \downarrow C$$

$$\longleftrightarrow \bigcup_{N \in C} C \equiv N \longleftrightarrow \bigcup_{N \in C} C = C \equiv$$

The conjugate bases of CHBr₃ and CHl₃ are stabilised by inductive effect of halogens. This is why, they are less stable. Also, the conjugate base of CHCl3 involves backbonding between 2p and 3p orbitals.

67. (b)
$$75 \text{ mL} \frac{M}{5} \text{HCl} + 25 \text{ mL} \frac{M}{5} \text{NaOH}$$

$$25 \text{ mL} \frac{M}{5} \text{ NaOH will neutralise } 25 \text{ mL} \frac{M}{5} \text{ HCl}$$

$$75-25=50 \text{ mL} \frac{M}{5} \text{ HCl will remain.}$$

Total volume will be 75 + 25 = 100 mL

$$50 \, \text{mL} \, \frac{\text{M}}{5} \, \text{HCl is diluted to } 100 \, \text{mL}$$

$$[H^+] = [HC1] = \frac{M}{5} \times \frac{50}{100} = \frac{M}{10}$$

$$pH = -\log_{10}[H^+] = -\log_{10}\frac{M}{10} = 1$$

68. (d)
$$H_{3}C$$
 E CH_{3} CH_{3}

69. (d)
$$NH_3 + HCl \longrightarrow NH_4Cl$$

moles of HCl = $0.2 \text{ M} \times 25 \times 10^{-3} \text{ L} = 0.005 \text{ moles HCl (total)}$ consumed)

moles of $NH_3 = 0.2 \text{ M} \times 50 \times 10^{-3} \text{ L} = 0.01 \text{ moles HCl}$ excess $NH_3 = 0.01 - 0.005 = 0.005$ moles 1 mole ammonia = 1 mole NH₄Cl

 $0.005 \text{ NH}_3 = 0.005 \text{ NH}_4 \text{Cl}$

Total volume = $V_{HCl} + V_{NH_3} = 25 + 50 = 75 \text{ mL}$

$$[NH_3] = [NH_4Cl] = \frac{0.005 \text{ mole}}{75 \times 10^{-3} \text{ L}} = 0.066 \text{ M}$$

$$pOH = pK_b + log \frac{[NH_4Cl]}{[NH_3]}$$

$$pOH = 4.75 + log \frac{[0.066]}{[0.066]}$$

$$pH = 14 - pOH \Rightarrow pH = 9.25$$

70. (b)
$$N_3H \rightleftharpoons N_3^- + H^+$$

i.e, conjugate base of hydrazoic acid is N₃.

71. (d) :
$$pH = 1$$
; $H^+ = 10^{-1} = 0.1 M$

$$pH = 2$$
; $H^{+} = 10^{-2} = 0.01 M$

$$M_1 = 0.1 \ V_1 = 1$$

$$M_2 = 0.01, \ V_2 = ?$$

$$\mathbf{M}_1 \mathbf{V}_1 = \mathbf{M}_2 \mathbf{V}_2$$

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

$$V_2 = 10 L$$

 \therefore Volume of water added = 10 - 1 = 9 L

72. (d) Given
$$[OH^-] = 5 \times 10^{-2}$$

$$\therefore pOH = -\log 5 \times 10^{-2}$$

$$= -\log 5 + 2\log 10 = 1.30$$

$$\therefore pH + pOH = 14$$

$$\therefore$$
 pH = 14 – pOH

$$= 14 - 1.30 = 12.70$$

73. (a) Metal halide on hydrolysis with water form corresponding hydroxides.

The basic strength of hydroxide increases as we move down in a group. This is because of the increase in size

which results in decrease of ionization energy which weakens the strength of M - O bonds in MOH and thus increases the basic strength.

Hence, Be(OH), will have lowest pH.

74. (d) Given at 330 K

$$K_{\rm w} = 10^{-13.6}$$

i.e. $pK_{\rm w} = pH + pOH$
 $\because pOH = -\log [OH^-]$
 $13.6 = pH + pOH$
 $pOH = -\log 10^{-4}$
 $pOH = 4$
 $\therefore pH = 13.6 - 4$
 $= 9.6$

75. (a) The species with the greatest proton affinity will be the strongest base, and its conjugate acid will be the weakest acid. The weakest acid will have the smallest value of Ka. Since HI is a stronger acid than HF which is a stronger acid than H2S, a partial order of proton affinity is

Since NH₃ is a very weak acid, NH₂⁻ must be a very strong base. Therefore the correct order of proton affinity is

$$I^- < F^- < HS^- < NH_2^-$$

76. (c) The correct order of acidic strength of the given

species is
$$HSO_3F > H_3O^+ > HSO_4^- > HCO_3^-$$
(iv) (ii) (iii) (iii) (i)

or (i)
$$\leq$$
 (iii) \leq (iv)

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

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

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

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

$$OH^- \longrightarrow H^+ + O^{2-}$$

Conjugate base of OH- is O2-

79. **(d)**
$$H_2PO_4^- \xrightarrow{-H^+} HPO_4^{2-}$$
 Conjugate base

Conjugate acid-base differs by H+.

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

From acid,
$$[H^+] = 10^{-8}M$$
.
From H₂O, $[H^+] = 10^{-7}M$

∴ Total [H⁺] =
$$10^{-8} + 10^{-7}$$

= $10^{-8} (1 + 10) = 11 \times 10^{-8}$
∴ pH = $-\log [H^+] = -\log 11 \times 10^{-8}$
= $-[\log 11 + 8 \log 10]$
= $-[1.0414 - 8] = 6.9586$

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

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82. (a) $(HSO_4)^-$ can accept and donate a proton $(HSO_4)^- + H^+ \rightarrow H_2SO_4$ (acting as base) $(HSO_4)^- - H^+ \rightarrow SO_4^{2-}$. (acting as acid)

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

$$\therefore pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$= 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4) = 6.9$$
84. (d) Sodium acetate is a salt of strong base and weak acid.

$$\therefore pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log c \text{ where } pK_a = -\log K_a$$

$$= 7 + \frac{5}{2} - \frac{1}{2}$$

$$= 9.0$$

$$\begin{cases} \because = -\log 10^{-5} = 5 \\ \log c = \log 10^{-1} = -1 \end{cases}$$

85. (c) Higher the value of K_a lower will be the value of pK_a i.e. higher will be the acidic nature. Further since CN-, F- and NO₂- are conjugate base of the acids HCN, HF and HNO2 respectively hence the correct order of base strength will be

$$F^- < NO_2^- < CN^-$$

(: stronger the acid weaker will be its conjugate base)

(d) Concentration of CH3COOH is computed as under. conc. = 5g in 500 mL

$$= 10 \text{ g/L} \quad [\text{Mol. wt. of CH}_3\text{COOH} = 60]$$

$$[CH_3COOH] = \frac{10}{60}M; \frac{1}{6}M$$

concentration of CH₃COONa is computed as under.

conc. =
$$7.5 \text{ g in } 500 \text{ mL}$$

= 15 g / L

$$[CH_3COOH] = \frac{15}{18}M$$

$$pK_a = -\log K_a$$

= $\log(1.8 \times 10 - 5) = 4.7447$

pH = p
$$K_a$$
 + log $\frac{\text{[salt]}}{\text{[acid]}}$
= 4.744 log $\frac{15/82}{1/6}$

$$= 4.7447 + \log 1.097$$

= $4.7447 + 0.0402$

$$=4.7447+0.0402$$

 $=4.78$

Chemistry c-94 -

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

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

$$K_{\rm a} = {\rm C}\alpha^2 = 0.1 \times 10^{-2} \times 10^{-2} = 10^{-5}$$

88. (b) The more is the value of equilibrium constant, the more is the completion of reaction or more is the concentration of products i.e. the order of relative strength would be

$$OH^- > CN^- > H_2O$$

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

$$HA \iff H^{+} + A^{-}$$

$$t = 0 \qquad c \qquad 0 \qquad 0$$

$$t_{eq} \qquad c (1 - \alpha) \qquad c \alpha \qquad c \alpha$$

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

" [HA]
$$c (1-\alpha) c$$
-
But, [H⁺] $<< c$

$$\therefore K_a = [H^+]^2 = (10^{-5})^2 = 10^{-10}$$

$$\begin{array}{llll} \textbf{90.} & \textbf{(a)} & \textbf{(i)} & H_3PO_4 + H_2O & \longrightarrow & H_3O^+ + H_2PO_4^- \\ & & \text{acid}_1 & \text{base}_2 & \text{acid}_2 & \text{base}_1 \\ & \textbf{(ii)} & H_2PO_4^- + H_2O & \longrightarrow & HPO_4^{2^-} + H_3O^+ \\ & & \text{acid}_1 & \text{base}_2 & \text{base}_1 & \text{acid}_2 \\ & \textbf{(iii)} & H_2PO_4^- + OH^- & \longrightarrow & H_3PO_4 + O^{2^-} \\ & & \text{base}_1 & \text{acid}_2 & \text{acid}_1 & \text{base}_2 \end{array}$$

Hence only in (ii) reaction, H₂PO₄ is acting as an acid. 91. (c) In aqueous solution, BA(salt) hydrolyses to give $BA + H_2O \Longrightarrow BOH + HA$

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

Substituting given values, we get

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

92. (d) $H_2A \Longrightarrow H^+ + HA^-$

$$K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]}$$
 $K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]}$

$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}^-]}$$
For the reaction,

 $H_2A \Longrightarrow 2H^+ + A^{2-}$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$
$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$

93. (d) For acidic buffer, pH = p
$$K_a$$
 + log $\left[\frac{\text{salt}}{\text{acid}}\right]$

$$pH = 4.5 + log \frac{[salt]}{[acid]}$$

As HA is 50% ionized so [salt] = [acid]

$$\therefore pH = 4.5$$

 \therefore pH+pOH=14

$$pOH = 14 - pH = 14 - 4.5 = 9.5$$

94. (2.0)

$$AB_2 \xrightarrow{} A_s^{2+} (aq) + 2B_s^{-} (aq)$$
 $K_{sp} = 4s^3 = 3.2 \times 10^{-11}$

$$K_{cn} = 4s^3 = 3.2 \times 10^{-11}$$

$$\Rightarrow s^3 = 8 \times 10^{-12}$$

$$\Rightarrow s = 2 \times 10^{-4}$$

Buffer solution contains CH₂COONa (10 millimole) and CH₃COOH (10 millimole) which is a acidic buffer.

(c) Cu²⁺ ions get precipitated every quickely due to low $K_{\rm sp}$ value even at very low concentration of S^{2-} ion.

$$CuS(s) \rightleftharpoons Cu^{2+} + S^{2-}$$

$$K_{\rm sp} = [{\rm Cu}^{2+}] [{\rm S}^{2-}]$$

$$Cu^{2+} + S^{2-} \rightleftharpoons CuS(s)$$

$$K_{\text{eq}} = \frac{1}{[\text{Cu}^{2+}][\text{S}^{2-}]} = \frac{1}{K_{\text{sp}}}$$

Due to high value of $K_{\rm eq}$, CuS precipitated easily.

97. (c) $PbCl_2 \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$ Given; $K_{sp} = 1.6 \times 10^{-5}$

Given;
$$K_{\rm sp} = 1.6 \times 10^{-5}$$

$$[Pb^{2+}] = \frac{300 \times 0.134}{400} = 0.1005$$

$$[Cl^-] = \frac{100 \times 0.4}{400} = 0.1$$

$$Q = [Pb^{2+}][Cl^{-}]^{2}$$

$$=0.1005\times(0.1)^2$$

$$= 1.005 \times 10^{-3}$$

$$Q > K_{\rm sp}$$

Equilibrium _____ c-95

98. (b)
$$Cr(OH)_3 \rightarrow Cr_s^{3+} + 3OH_{3s}^{-}$$

$$K_{sp} = s.(3s)^3$$

$$\Rightarrow$$
 6 × 10⁻³¹ = 27.s⁴; s = $\left(\frac{6}{27} \times 10^{-31}\right)^{1/4}$

$$[OH^{-}] = 3s = 3 \times \left(\frac{6}{27} \times 10^{-31}\right)^{1/4}$$

$$=(18\times10^{-31})^{1/4} \mathrm{M}$$

99. (b) From the given curve,

if [X] = 1 mM then [Y] = 2 mM

:. Salt is XY,

$$K_{sp} = [X][Y]^2 = (10^{-3})(2 \times 10^{-3})^2 = 4 \times 10^{-9} M^3$$

100. (c) Let the solubility of Al(OH)₃ in 0.2M NaOH solution

Then,

$$Al(OH)_3 \Longrightarrow Al^{3+} + 3OH^{-}_{3s}$$

and
$$NaOH \rightleftharpoons Na^+ + OH^-$$

0.2M 0.2M 0.2M

$$[Al^{3+}] = s$$
 and $[OH^-] = 3s + 0.2 \approx 0.2$

$$K_{sp} = 2.4 \times 10^{-24} = [A1^{3+}][OH]^3$$

$$2.4 \times 10^{-24} = s(0.2)^3$$

$$s = \frac{2.4 \times 10^{-24}}{8 \times 10^3} = 3 \times 10^{-22} \, mol \, / \, L$$

101.(d)
$$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH_{2s}^{-}$$

At equilibrium, $K_{\rm sp} = s (2s)^2 = 4s^3$

$$\Rightarrow K_{\rm sp} = 4 \times (1.84 \times 10^{-5})^{-3}$$

Solubility in buffer solution having pH = 12

 $[OH^{-}] = 10^{-2}$

$$Cd(OH)_2 \mathop{\Longrightarrow}\limits_{s} Cd^{2+} + \underset{2s'+10^{-2} \approx 10^{-2}}{2OH^-}$$

$$K_{\rm sp} = 4 \times (1.84 \times 10^{-5})^3 = \text{s'} (10^{-2})^2$$

$$\Rightarrow s' = \frac{24.9 \times 10^{-15}}{10^{-4}} = 2.49 \times 10^{-10} M$$

102.(d) pH =
$$7 - \frac{1}{2}$$
pK_b $-\frac{1}{2}$ log C
= $7 - \frac{5}{2} - \frac{1}{2}$ (log 2×10^{-2}) = 5.35
pH = 5.35

103. (b)
$$Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{4+} + 4P_3O_4^{3-}$$

 $K_{sp} = [Zr^{4+}]^3 [PO_4^{3-}]^4 = (3S)^3(4S)^4$
 $K_{sp}^{} = 6912 S^7$

$$S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

104. (c) As AgNO $_3$ dissociates completely, therefore in 0.1 M AgNO $_3$ solution, [Ag $^+$] = 0.1 M

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

0.1 0.1

$$Ag_2CO_3 \longrightarrow 2Ag^+ + CO_3^{2-}$$

 $0.1+2s$

$$K_{\rm sp} = [{\rm Ag}^+]^2 [{\rm CO}_3^{2-}]$$

$$8 \times 10^{-12} = (0.1 + 2s)^2 \times s$$

$$0.01 s = 8 \times 10^{-12}; (0.1 + 2s \times 0.1)$$

$$s = 8 \times 10^{-10} \,\mathrm{M}$$

105. (b) m. mol of $H_2SO_4 = 20 \times 0.1 = 2$

m. mol of $NH_4OH = 30 \times 0.2 = 6$

$$H_2SO_4 + 2NH_4OH \rightarrow (NH_4)_2 SO_4 + 2H_2O$$

Initial 2 m mol 6 m mol 0
Final (2-2)
$$(6-2\times2)$$
 2 m mol

$$[NH_4OH]_{left} = 2 \text{ m mol}$$

$$[(NH_4)_2 SO_4] = 2 \text{ m mol}$$

$$[NH_4] = 2 \times 2 = 4 \text{ m mol}$$

Total Volume = 30 + 20 = 50 mL

$$pOH = pK_b + log \left[\frac{Salt}{Base} \right]$$

$$=4.7 + \log \frac{4/50}{2/50}$$

$$=4.7 + \log 2 = 5$$

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$$pH = 14 - pOH$$

 $pH = 14 - 5 = 9$

106. (a) $Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NaOH$

m mol of Na₂SO₄ =
$$\frac{2 \times 1000}{143}$$
 = 13.98 m mol

m mol of CaSO₄ formed = 13.98 m mol

Mass of CaSO₄ formed = $13.98 \times 10^{-3} \times 136 = 1.90$ g m mol of NaOH = $28 \text{ m mol} \approx 0.028 \text{ mol}$

$$Ca(OH)_2 \Longrightarrow Ca^{2+} + 2OH^-$$

 $S^{2s+0.028}$

Value of 'S' will be negligible so

$$[OH^-] = \frac{0.028 \ mol}{0.1 \ L} = 0.28 \ mol \ L^{-1}$$

107. (b) CH₃COOK is a salt of weak acid (CH₃COOH) and strong base (KOH).

FeCl₃ is a salt of weak base [Fe(OH)₃] and strong acid

Pb(CH₃COO)₂ is a salt of weak base Pb(OH)₂ and weak

Al(CN)3 is a salt of weak base [Al (OH)3] and weak acid

108. (b)
$$H_2S = 2H^+ + S^{2-}, K_{a_1}, K_{a_2} = K_{eq}$$

$$\therefore \quad \frac{\left[H^{+}\right]^{2}\left[S^{2-}\right]}{\left[H_{2}S\right]} = 1 \times 10^{-7} \times 1.2 \times 10^{-13}$$

$$\frac{\left[0.2\right]^2 \left[S^{2-}\right]}{\left[0.1\right]} = 1.2 \times 10^{-20}$$

$$[S^{2-1} = 3 \times 10^{-20}]$$

109. (c) Concentration of SO₄²⁻ in BaSO₄ solution $M_1V_1 = M_2V_2$

$$1\times50 = M_2\times500$$

$$M_2 = \frac{1}{10}$$

For just precipitation

Ionic product = K_{sp}

$$[Ba^{2+}][SO_4^{2-}] = K_{sn}(BaSO_4)$$

$$[Ba^{2+}] \times \frac{1}{10} = 10^{-10}$$

 $[Ba^{2+}] = 10^{-9} M \text{ in } 500 \text{ mL solution}$

Thus [Ba²⁺] in original solution

$$(500-50=450 \,\mathrm{mL})$$

$$\Rightarrow$$
 M₁ × 450 = 10⁻⁹ × 500

[where $M_1 = Molarity of original solution]$

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$$M_1 = \frac{500}{450} \times 10^{-9} = 1.11 \times 10^{-9} M$$

110. (d)
$$(K_{\rm sp})_{\rm PbCl_2} = 3.2 \times 10^{-8} = 32 \times 10^{-9}$$

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^{-}$$

$$C = [Pb^{2+}][Cl^{-}l^{2}]$$

$$K_{\rm sp} = [{\rm Pb^{2+}}][{\rm Cl^-}]^2$$

 $K_{\rm sp} = 4{\rm s^3} = 32 \times 10^{-9}$

$$s^3 = 8 \times 10^{-9}$$

$$s = 2 \times 10^{-3} \, M$$

$$\frac{w}{M.W.} \times \frac{1}{V_L} = 2 \times 10^{-3}$$

$$\frac{0.1}{278} \times \frac{1}{V_L} = 2 \times 10^{-3}$$

$$V_{L} = \frac{0.1 \times 1000}{278 \times 2} = 0.18 \text{ L}$$

111. (c)
$$HA \Longrightarrow H^+ + A^-$$

(Unionized, weak acid and common ion effect)

$$HA + NaOH \longrightarrow NaA + H_2O$$

$$NaA \longrightarrow Na^+ + A^-$$
 (ionized)

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm A}^-]}{[{\rm HA}]}$$

Given, pH = 6, $[H^+] = 1 \times 10^{-6}$

$$[H^+] = \frac{K_a [Acid]}{[Salt]}$$

$$\frac{\text{[Salt]}}{\text{[Acid]}} = \frac{K_{\text{a}}}{\text{[H}^+]} = \frac{10^{-5}}{10^{-6}} = 10:1$$

112. (d) Solutions which resist the change in the value of pH when small amount of acid or base is added to them are known as buffers.

113. (c)
$$2HNO_3(aq) + [Ag(NH_3)_2]^+ + Cl^-$$

$$\longrightarrow$$
 AgCl(s) \downarrow +2NH₄ + 2NO₃

When nitric acid is added to amine solution, solution is made acidic and the complex ion dissociates and liberate silver ion to recombine with chloride ion. This is the conformatory test for silver in group 1.

114. (c)
$$\left[Zr_3 \left(PO_4 \right)_4 \right] \Longrightarrow 3Zr^{4+} + 4PO_4^{3-}$$

$$K_{sp} = (3s)^3 (4s)^4$$

$$= 27s^3 \times 256 \text{ s}^4$$

$$= 6912 \text{ s}^7.$$

$$\therefore \text{ s} = \left(\frac{K_{sp}}{6912} \right)^{1/7}$$

115. (a) Conc. of Na₂CO₃ =
$$1.0 \times 10^{-4}$$
 M

$$\therefore [CO_3^{2-}] = 1.0 \times 10^{-4}$$
 M
i.e. $s = 1.0 \times 10^{-4}$ M
At equilibrium

$$[Ba^{2+}] [CO_3^{2-}] = K_{sn} \text{ of BaCO}_3$$

$$[Ba^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}}$$

116. **(b)**
$$\operatorname{Cr}_2(\operatorname{SO}_4)_3 \stackrel{\longrightarrow}{=} 2\operatorname{Cr}^{3+} + 3\operatorname{SO}_4^2$$

 $K_{\operatorname{sp}} = (2\operatorname{s})^2 (3\operatorname{s})^3 = 4\operatorname{s}^2 \times 27\operatorname{s}^3 = 108\operatorname{s}^5$
 $\operatorname{s} = \left(\frac{K_{\operatorname{sp}}}{108}\right)^{1/5}$

Hg₂Cl₂
$$\Longrightarrow$$
 2Hg²⁺ + 2Cl⁻
2s
 $K_{sp} = (2s)^2 \times (2s)^2 = 16s^4$
$$s = \left(\frac{K_{sp}}{16}\right)^{1/4}$$

BaSO₄
$$\longrightarrow$$
 Ba²⁺ + SO₄²
 $K_{sp} = s^2$ s
$$s = \sqrt{K_{sp}}$$

$$\operatorname{CrCl}_{3} \Longrightarrow \operatorname{Cr}^{3+} + 3\operatorname{Cl}^{-}_{3s}$$

$$K_{sp} = s \times (3s)^{3} = 27 \text{ s}^{4}$$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

Hence the correct order of solubilities of salts is

$$\sqrt{K_{\rm sp}} > \left(\frac{K_{\rm sp}}{16}\right)^{1/4} > \left(\frac{K_{\rm sp}}{27}\right)^{1/4} > \left(\frac{K_{\rm sp}}{108}\right)^{1/5}$$

117. (a) Let solubility of AgCl = s mol/L

AgCl
$$\Longrightarrow$$
 Ag⁺ + Cl⁻
i.e., $K_{sp(AgCl)} = s \times s$
KCl \Longrightarrow KCl = 0.1 M
Total [Cl⁻] in solution = s + 0.1
 $K_{sp}(AgCl) = [Ag^{\pm}] [Cl^{-}] = s (s + 0.1)$
1.0 × 10⁻¹⁰ = s(s + 0.1)
1.0 × 10⁻¹⁰ = s² + 0.1s
1.0 × 10⁻¹⁰ = 0.1s (as s² << 1)
s = 1.0 × 10⁻⁹ mol/L

118. (a) When ionic product i.e. the product of the concentration of ions in the solution exceeds the value of solubility product, formation of precitpiate occurs.

119. (d)
$$PbI_2 \Longrightarrow Pb^{2+} + 2I^-$$

 $K_{sp} = s \times (2s)^2 = 4s^3$
 $= 4 \times \left(\frac{0.7}{461.2}\right)^3 = 14.0 \times 10^{-9}$

120. (b)
$$Cr(OH)_3(s) = Cr^{3+}(aq.) + 3OH^-(aq.)$$

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

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

121. (b) $AgBr = Ag^{+} + Br^{-}$

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

For precipitation to occur

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

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i.e., precipitation just starts when 10-11 moles of KBr is added to 1L AgNO3 solution

.. Number of moles of Br needed from KBr = 10^{-11} .. Mass of KBr = $10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

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

122. (b)
$$Mg(OH)_2 \longrightarrow Mg^{2+} + 2OH^{-}$$

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

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

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

$$\therefore pH + pOH = 14$$

123. (a)
$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$$

 $1 \times 10^{-4} M$ $1 \times 10^{-4} M$ $1 \times 10^{-4} M$

$$K_{\rm sp(BaCO_3)} = [{\rm Ba}^{2+}][{\rm CO}_3^{2-}]$$

$$[Ba^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5} M$$
124. (c) Let s = solubility

$$\begin{split} \text{AgIO}_3 & \longrightarrow \text{Ag}^+ + \text{IO}_3^- \\ \text{s} & \text{s} & \text{s} \\ K_{\text{sp}} &= [\text{Ag}^+] [\text{IO}_3^-] = \text{s} \times \text{s} = \text{s}^2 \\ \text{Given } K_{\text{sp}} &= 1 \times 10^{-8} \end{split}$$

$$\begin{array}{ll} \therefore & {\rm s} = \sqrt{K_{\rm sp}} & = \sqrt{1 \times 10^{-8}} \\ & = 1.0 \times 10^{-4} \, {\rm mol/L} = 1.0 \times 10^{-4} \times 283 \, {\rm g/L} \end{array}$$

(: Molecular mass of AgIO₃ = 283)

$$=\frac{1.0\!\times\!10^{-4}\!\times\!283\!\times\!100}{1000}\,g/100\,mL$$

$$= 2.83 \times 10^{-3} \ g / \ 100 \ mL$$

125. (c)
$$MX_2 = M^{2+} + 2X^{-}$$

Where s is the solubility of MX,

then
$$K_{\rm sp} = 4 \, {\rm s}^3$$

$$4 \times 10^{-12} = 4s^3$$

or
$$s = 1 \times 10^{-4}$$

126. (d)
$$MX_4 \Longrightarrow M_S^{4+} + 4X_-^{-}$$

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

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

127. (d)
$$AB_2 = A^{2+} + 2B^{-}$$

$$[A] = 1.0 \times 10^{-5}, [B] = [2.0 \times 10^{-5}]$$

$$K_{so} = [B]^2 [A] = [2 \times 10^{-5}]^2 [1.0 \times 10^{-5}] = 4 \times 10^{-15}$$

128. (a) 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.

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

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