CLASS : CC -AD

Revision Worksheet Chemical Equilibrium

Single correct :

Q.1 For the reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociated (α) of HI(g) is related to equilibrium constant K_P by the expression

(A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$ (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

Q.2 The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature?

(A) 53.3% (B) 106.6% (C) 26.7% (D) None

Q.3 For the reaction : $A.3H_2O(s) \rightleftharpoons A.H_2O(s) + 2H_2O(g)$; $K_P = 9\ atm^2$

A 24.63 litre flask contains 1 mole of $A.H_2O(s)$ at 300 K. How many moles of $H_2O(g)$ should be added to the flask at the given temperature to drive the backward reaction for completion.

(A) 3 moles (B) 5 moles (C) 8 moles (D) 2 moles

Q.4 Ammonia at a pressure of 5 atm and H_2S gas at a pressure of 10 atm are introduced into an evacuated vessel.

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ $K_p = 62.5\ atm^2$

The total pressure of gases after long time is :

(A) 15 atm (B) more than 15 atm (C) less than 15 atm (D) unpredicted

Q.5 The conditions favourable for the reaction :

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

are :

(A) low temperature, high pressure (B) any value of T and P

(C) low temperature and low pressure (D) high temperature and high pressure

Q.6 Densities of diamond and graphite are 3.5 and 2.3 gm/mL.

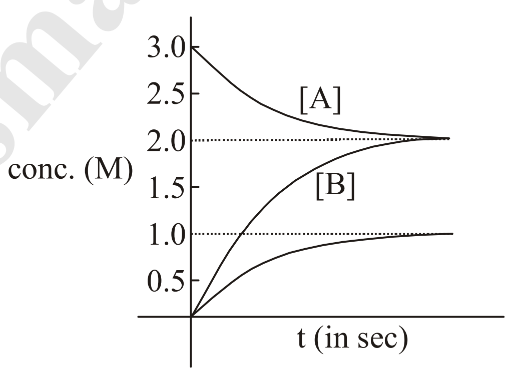
C (diamond) $\rightleftharpoons$ C (graphite) $\Delta_r H = -1.9$ kJ/mole

favourable conditions for formation of diamond are

(A) high pressure and low temperature (B) low pressure and high temperature

(C) high pressure and high temperature (D) low pressure and low temperature

Q.7 The progress of reaction : $A(g) \rightleftharpoons xB(g) + yC(g)$ with time is presented in figure. What is the value of $K_C°$ at 300 K.



(A) 1 (B) 2 (C) 3 (D) 4

Q.8 Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (II) $2HI(g) \rightleftharpoons H_2(g) + I_2 (g)$

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

Extent of the reactions taking place is:

(A) I > II > III (B) I < II < III (C) II < III < I (D) III < I < II

Q.9 A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 0.84 atm. The equilibrium constant for the reaction is :

(A) 0.30 (B) 0.18 (C) 0.17 (D) 0.11

Q.10 At certain temperature (T) for the gas phase reaction

$$2H_2O(g) + 2Cl_2 (g) \rightleftharpoons 4HCl(g) + O_2(g) \qquad K_p = 12 \times 10^8 \text{ atm}$$

If Cl_2, HCl & O_2 are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brough into contact with excess of liquid water. What would be approximate partial pressure of Cl_2 when equilibrium is attained at temperature (T)?

[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]

(A) 3.6×10^{-5} atm (B) 10^{-4} atm (C) 3.6×10^{-3} atm (D) 0.01 atm

Q.11 A vessel of 250 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as $Sb_2S_3 (s) + 3H_2 (g) \rightleftharpoons 2Sb (s) + 3H_2S (g)$.

After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.195 g of PbS (Molecular weight = 239) precipitate.

What is value of K_c of the reaction at 440°C?

(A) 1 (B) 2 (C) 4 (D) None of these

Q.12 For the following Equilibria : $H_2O (l) \rightleftharpoons H_2O(g)$ $\qquad K_P = P_{H_2O}$

where $P_{H_2O} \longrightarrow$ Vapour pressure of $H_2O(g)$

By which of the following ways P_{H_2O} can be changed

(A) By adding more $H_2O(l)$ (B) By adding more H_2O (g)

(C) By changing temperature (D) All of the above

Q.13 For the reaction : $A(s) \rightleftharpoons B(g) + C(g)$ .What will be the value of natural logarithm of ratio of total pressure at 400K to that at 300K $\left[= \ln \frac{P_{400}}{P_{300}} \right]$ if $\Delta H = 16.628$ kJ. (**Given :** R = 8.314J/K-mole)

(A) 5/3 (B) 5/6 (C) 3/5 (D) 6/5

Q.14 At a equilibrium pressure of 3.3 atm N_2O_4 undergoes 10% decomposition to NO_2. At same temperature what will be equilibrium pressure required for 20% dissociation.

(A) 3.3 atm (B) 6.6 atm (C) 4 atm (D) 0.8 atm

Comprehension :

Paragraph for question nos. 15 to 17

Following reaction is at equilibrium in basic medium at 300 K.

$$I_2 (s) \rightleftharpoons I^- (aq.) + IO_3^- (aq.)$$

Equilibrium concentration at 300 K are , $[I^-] = 0.1$ M, $[IO_3^-] = 0.1$ M

Given : $\Delta G_f^\circ (I^-, aq) = -50$ kJ/ mol

$\Delta G_f^\circ (IO_3^-, aq) = -123.5$ kJ/ mol

$\Delta G_f^\circ (H_2O, l) = -233$ kJ/ mol

$\Delta G_f^\circ (OH^-, aq) = -150$ kJ/ mol

$R = \frac{25}{3}$ J mol^{-1} K^{-1} $\log_{10} e = 2.3$

Q.15 $\Delta G°$ of the reaction in KJ mol^{-} is

(A) – 150.7 (B) – 172.5 (C) 172.5 (D) 150.7

Q.16 Value of equilibrium constant is

(A) 10^{25} (B) 10^{35} (C) 10^{30} (D) 10^{27}

Q.17 pH value at equilibrium is

(A) 8 (B) 6 (C) 9 (D) 5

Assertion and Reason:

Q.18 **Statement-1:** An increase in pressure (caused by decrease in volume) at equilibrium results in increase in molar concentration of each gaseous substance involved.

Statement-2: An increase in pressure (caused by decrease in volume) at equilibrium results in increase in number of moles of each gaseous substance involved.

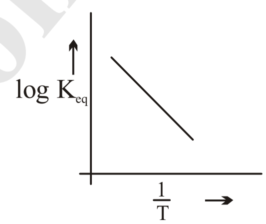
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

More than one correct :

Q.19 For the reaction

$$2ClF_3(g) \rightleftharpoons Cl_2(g) + 3F_2(g)$$

$\log K_{eq}$ v/s $\frac{1}{T}$ (where temperature is in K) curve is obtained as following



Which of the following change will increase the concentration of Cl_2 in an equilibrium mixture of Cl_2, F_2 & ClF_3 :

(A) Addition of inert gas at constant pressure (B) Increase in temperature at constant volume
(C) Addition of catalyst at equilibrium (D) Removal of $F_2(g)$ at equilibrium

Q.20 For a gaseous reaction : $A_{(g)} \rightleftharpoons 3B_{(g)} + C_{(g)}$, ΔH is positive and the reaction attains equilibrium at 1 bar total pressure and 400K. Identify the **incorrect** statements regarding the above reaction.

(A) On increase of temperature, equilibrium will be shifted in forward direction.
(B) When inert gas is introduced into a rigid container containing above equilibria equilibrium shifts towards left.
(C) $\Delta G^{\circ}_{400} = 0$ for the above reaction.
(D) If volume of vessel containing the above equilibria is increased without change in temperature then partial pressure of B decreases as compared to original equilibrium partial pressure of B.

Q.21 Consider the equilibrium $HgO(s) + 4I^{-}(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^{-}(aq)$, which changes will decrease the equilibrium concentration of HgI_4^{2-}

(A) Addition of 0.1 M HI (aq) (B) Addition of HgO (s)
(C) Addition of H_2O (l) (D) Addition of KOH (aq)

Q.22 For the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

$N_2O_5(g)$ decomposed at a constant volume and temperature. Initial pressure of N_2O_5 is 600 mm of Hg and total pressure at equilibrium is 960 mm of Hg. Assuming ideal behavior of gases, Select the correct

option(s).
(A) Involved reaction is intramolecular redox reaction
(B) The mole fraction of NO_2 in the equilibrium mixture is 0.5
(C) The equilibrium constant K_P for the above reaction is 540 mm of Hg
(D) For the above reaction $K_C = K_P (RT)^3$

Q.23 Select correct statement(s)
(A) K_P depends upon equilibrium pressure
(B) Dissociation of $NH_4HS(s)$ is suppressed at high pressure [$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$]
(C) Low pressure is favourable for melting of ice
(D) During dissociation of $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$, M_{avg} decreases with progress of reaction

Q.24 Which of the following is/are correct statement(s)?
(A) The vapour pressure of a solid is zero at absolute zero.
(B) The maximum vapour pressure of a solid is its vapour pressure at the triple point.
(C) The minimum vapour pressure of a liquid is its vapour pressure at the triple point.
(D) The maximum vapour pressure of a liquid is its vapour pressure at critical temperature.

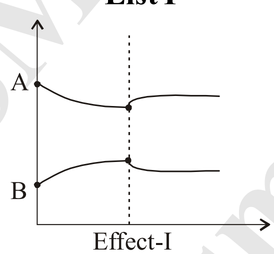
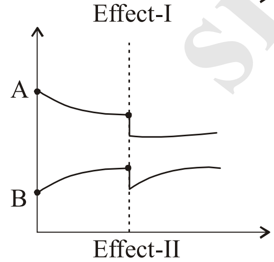
Q.25 The equilibrium between, gaseous isomers A, B and C can be represented as

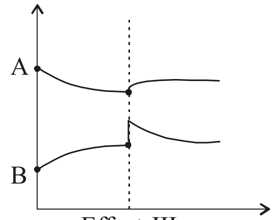
Reaction		**Equilibrium constant**
$A(g) \rightleftharpoons B(g)$	:	$K_1 = ?$
$B(g) \rightleftharpoons C(g)$	:	$K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$	:	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then
(A) [A] + [B] + [C] = 1 M at any time of the reactions
(B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions
(C) The value of K_1 is $\frac{1}{0.24}$
(D) Isomer [A] is least stable as per thermodynamics.

Match the column :

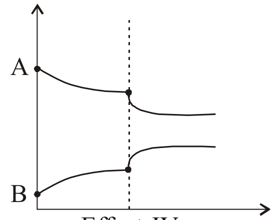
Q.26 For the endothermic reaction, $A_{(g)} \rightleftharpoons 2B_{(g)}$. Certain changes were caused & the behaviour of equilibria was analysed by plotting changes in concentration v/s time. Match **List-I** with **List-II**.

List I	**List II**
(P) 	(P) Increase in temperature
(Q) 	(Q) Addition of inert gas at constant pressure.

(R) 

Effect-III

(R) Decrease in temperature

(S) 

Effect-IV

(S) Addition of $B_{(g)}$ at equilibrium

Q.27

Column I		Column II
(A) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(P)	Introduction of hydrogen gas at constant volume shift equilibrium back.
(B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(Q)	α increases on increasing temperature.
(C) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$	(R)	On adding inert gas at constant volume, equilibrium state does not change
(D) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$	(S)	On increasing the pressure, concentration of all reactants increases
	(T)	α is independent of equilibrium pressure.

Subjective :

Q.28 5 moles each of 'A', 'B' and 'D' are added to a 1 litre container. Calculate the number of moles of 'B' at equilibrium if following reaction occurs.

$A(g) + B(g) \rightleftharpoons C(s) \quad K_C = 2 \times 10^{10}\ M^{-2}$

$A(g) + D(g) \rightleftharpoons E(s) \quad K_C = 10^{10}\ M^{-2}$

[Fill your answer by multiplying it with 150]

Q.29 PCl_5 dissociates according to the reaction $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$. At 523 K, $K_p = 1.78$ atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

Q.30 When 1 mole of A(g) is introduced in a closed rigid 1 litre vessel maintained at constant temperature the following equilibria are established.

$$A(g) \rightleftharpoons B(g) + C(g) \quad : \quad K_{C_1}$$

$$C(g) \rightleftharpoons D(g) + B(g) \quad : \quad K_{C_2}$$

The pressure at equilibrium is twice the initial pressure. Calculate the value of $\frac{K_{C_2}}{K_{C_1}}$ if $\frac{[C]_{eq}}{[B]_{eq}} = \frac{1}{5}$

REVISION FLOW CHART

Chemical Equilibrium

Application of equilibrium constant
- Law of mass action — (T)
- Type of K_{eq} (K_c & K_p)
- Relation between K_p & K_c
- Homogenous/Heterogenous equilibrium
  - (N)
- Predicting the direction of reaction (Q & K_{eq})
- Predicting the extent of reaction (values of K_{eq})
- Calculation of equilibrium concentration
  - (N)

L.C. principle
- Rule
- Effect of concentration of (R) or (P)
- Effect of P, V, at constant T
- Effect of catalyst
- Effect of adding inert gas at constant pressure & constant volume
  - (T) + (G)

Effect of T on K_{eq}
- Exp. of Arrhenius Equation
- Exp. of K_{eq} with T (Vant Hoff Equation)
- Effect of T on Endo / Exothermic reaction
  - (T) + (N) + (G)

Thermodynamics
- Relationship between ΔG & ΔG^o — (N)
- Variation of G vs State of reaction
- Phase diagram
  - (G)

(G) → represents topic of graphical importance

(T) → represents topic of theoretical importance

(N) → represents topic of numerical importance

LIST OF IMPORTANT FORMULAS

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

  $\Delta n_g \Rightarrow \sum$Stoichiometric coefficient of gaseous products – $\sum$Stoichiometric coefficient of gaseous reactants

* $$d\frac{(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

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

* $\Delta G = \Delta G^\circ + RT \ln Q$ — $Q \Rightarrow$ Reactant quotient

* $\Delta G^\circ = -RT \ln K$ — $K \Rightarrow$ Equilibrium constant

LAST MOMENT REVIEW

CHEMICAL EQUILIBRIUM

Theory : ....

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Exercise - 1 : Question ....

Exercise - 2 : Question ....

Exercise - 3 : Question ....

Exercise - 4 : Question ....

DPPs : ....

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Other Sources : ....

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CLASS : CC -AD

Revision Worksheet Ionic Equilibrium

Single correct

Q.1 Three solution of strong electrolytes 25 ml of 0.1 M HX, 25 ml of 0.1 M H_2Y and 50 ml of 0.1 $NZ(OH)_2$ are mixed. What is the pOH of the solution ? [Given log 5 = 0.7]
(A) 1.6 (B) 7 (C) 11.6 (D*) 12.6

Q.2 0.1 M NH_3 (aq) solution is titrated against 0.1 M HNO_3 (aq) solution. What would be the difference in pOH between $\frac{1}{4}$ and $\frac{3}{4}$ stages of neutralization of base?
(A) 2 log 3/4 (B) 2 log 1/4 (C) log 1/3 (D*) 2 log 3

Q.3 What is the pH of 0.1M $NaHCO_3$? $K_1 = 5.0 \times 10^{-7}$, $K_2 = 7.0 \times 10^{-11}$ for carbonic acids.
(A) pH = 7 (B) pH much less than 7
(C) pH slightly less than 7 (D*) pH greater than 7

Q.4 The degree of hydrolysis of 0.1 M solution of conjugate base of HA is 0.01. Find the $\mathbf{H^+}$ concentration in 0.4 M solution of $\mathbf{A^-}$.
(A) 5×10^{-11} M (B*) 5×10^{-12} M (C) 2×10^{-3} M (D) 2×10^{-4} M

Q.5 What is the aq. ammonia concentration of a solution prepared by dissolving 0.15 mole of $NH_4^+CH_3COO^-$ in 1L H_2O.[$K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$; $K_{b(NH_4OH)} = 1.8 \times 10^{-5}$]
(A*) 8.3×10^{-4} (B) 0.15 (C) 6.4×10^{-4} (D) 3.8×10^{-4}

Q.6 An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH.
The concentration of OH^- is nearly :
(A) 2.414×10^{-4} (B) 10^{-4} M (C) 1.414×10^{-4} (D*) 2×10^{-4}

Q.7 At 90°C, pure water has $[H^+] = 10^{-6}$M, if 100 ml of 0.2 M HNO_3 is added to 20 ml of 1 M NaOH at 90°C then pH of the resulting solution will be
(A) 5 (B*) 6 (C) 7 (D) None of these

Q.8 Calcium lactate is a salt of weak organic acid and strong base represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.6 mole in 2 litre solution. pOH of solution is 5.60. If 90% dissociation of the salt takes place then what is pK_a of lactic acid
(A*) 2.8 – log(0.54) (B) 2.8 + log(0.54) (C) 2.8 + log (0.27) (D) none

Q.9 What is the degree of dissociation of weak acid HA (C = 0.1 M) in presence of strong acid HB (C = 0.1M). Given : K_a (weak acid) = 10^{-6}
(A*) 10^{-5} (B) 10^{-6} (C) 10^{-4} (D) 10^{-3}

Q.10 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is
($K_w = 1 \times 10^{-14}$ at 25°C)
(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M (C) 3.2×10^{-2} M (D*) 2.7×10^{-2} M

Q.11 An aqueous solution of CH_3COOH has a pH = 3 and acid dissociation constant of CH_3COOH is 10^{-5}. What will be the concentration of acid taken initially?
(A) 0.1M (B) 0.11 M (C) 0.09 M (D*) 0.101 M

Q.12 pH of a saturated solution of silver salt of monobasic acid HA is found to be 9.
Find the K_{sp} of sparingly soluble salt AgA(s). **Given :** K_a (HA) = 10^{-10}
(A*) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 10^{-12} (D) None of these

Q.13 Which of the following expression regarding % ionisation of a monobasic weak acid in aqueous solution at appreciable concentration is not correct?
(A) $100\sqrt{\frac{K_a}{C}}$ (B) $\left\{\frac{K_a}{K_a+[H^+]}\right\}\times 100$ (C*) $\left\{\frac{[H^+]}{K_a+[H^+]}\right\}\times 100$ (D) $\frac{100}{1+10}(pK_a - pH)$

Q.14 The pH of a saturated solution of $X(OH)_3$ will be if its solubility product = 2.7×10^{-43}.
[**Given :** log 3 = 0.5 , log 2 = 0.3]
(A) 10.5 (B*) 7 (C) 3.5 (D) 3.8

Q.15 Let solubility of a sparingly soluble salt of strong base and weak acid in pure water is equal to $\mathbf{s_1}$, in a buffer solution with pH < 7 is equal to $\mathbf{s_2}$ and in another buffer solution with pH > 7 is equal to $\mathbf{s_3}$. If hydrolysis is considered in all the solutions then the **correct** relation between $\mathbf{s_1}$, $\mathbf{s_2}$ and $\mathbf{s_3}$ is :
(A) $s_1 = s_2 = s_3$ (B) $s_1 > s_2 > s_3$ (C) $s_1 < s_2 < s_3$ (D*) $s_2 > s_1 > s_3$

Q.16 The salt $Zn(OH)_2$ is involved in the following two equilibria,
$Zn(OH)_2\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2OH^-\,(aq)$; $K_{sp} = 10^{-17}$
$Zn(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons [Zn(OH)_4]^{2-}\,(aq.)$; $K_c = 0.1$
The pH of solution at which solubility is minimum is
(A*) 10 (B) 9 (C) 8 (D) 11

Q.17 From separate solutions of four sodium salts NaW, NaX, NaY and NaZ had pH 7.0, 9.0, 10.0 and 11.0 respectively. When each solution was 0.1 M, the strongest acid is:
(A*) HW (B) HX (C) HY (D) HZ

Q.18 How many moles NH_3 must be added to 2.0 litre of 0.80 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5×10^{-8} M. K_f of $[Ag(NH_3)_2^+] = 10^8$
(A) 0.4 (B) 2 (C) 3.52 (D*) 4

Q.19 A_3B_2 is a sparingly soluble salt of molar mass M (g mol^{-1}) and solubility x g lit^{-1}. The ratio of the molar concentration of B^{3-} to the solubility product of the salt is

(A) $108\frac{x^5}{M^5}$ (B) $\frac{1}{108}\frac{M^4}{x^4}$ (C*) $\frac{1}{54}\frac{M^4}{x^4}$ (D) None

Assertion and Reason

Q.20 **Statement-1**: pH of acidic buffer solution always increases on increasing dilution.

Statement-2: pH of any acidic solution always increases on increasing dilution.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false. (D*) Statement-1 is false, statement-2 is true.

Comprehension :

Paragraph for question nos. 21 to 23

Solubility is defined as the maximum number of moles of solute which can be dissolved in 1 litre of solvent. It is affected by presence of common ion, hydrolysis of ions. In a container equal volume of 0.02 M $AgNO_3$ and 0.02 HCN solution is mixed.

K_{sp} of AgCN = 4×10^{-16} M^2 ,

K_a (HCN) = 4×10^{-10} M

Q.21 Concentration of Ag^+ ions in the final solution would be

(A) 10^{-6} (B) 2×10^{-5} (C) 2×10^{-8} (D*) 10^{-4}

Q.22 pH of final solution would be

(A*) 2 (B) 3 (C) 4 (D) Can not find

Q.23 Concentration of CN^- in the final solution would be

(A) 4×10^{-10} (B) 2×10^{-11} (C*) 4×10^{-12} (D) 2×10^{-8}

Paragraph for question nos. 24 to 25

Selective precipitation of ions from a mixture in the form of salts can be done by adding common ion gradually. Let us consider selective precipitation of Cl^- & CrO_4^{2-} ions in the form of AgCl & Ag_2CrO_4 from a mixture having 0.01 M Cl^- and 0.02 M CrO_4^{2-}. For this, salt having Ag^+ [like $AgNO_3$(s)] is added gradually.

Given : K_{sp} AgCl = 10^{-10} and K_{sp} Ag_2CrO_4 = 4×10^{-14}.

Q.24 Minimum concentration of Ag^+ ion at which precipitation of at least one ion starts.

(A*) 10^{-8} (B) 1.41×10^{-6} (C) 10^{-10} (D) 2×10^{-8}

Q.25 The percentage of one of the ion precipitated when another ion starts precipitation is

(**Given :** $\frac{1}{\sqrt{2}}$ = 0.7)

(A) 98.7 % (B*) 99.3 % (C) 97.6 % (D) 92.7 %

More than one correct :

Q.26 At 25°C , the dissociation constant of a weak monoprotic acid, HA **(K_a)** is **numerically equal** to the dissociation constant of its conjugate base, A^- **(K_b)**. Which of the following statement(s) is/are **correct**?

(A*) The dissociation constant of the acid, HA, is 10^{-7}.

(B*) The pH of 0.1 M aqueous solution of the acid, HA, is 4.0.

(C*) The pH of 0.1 M aqueous solution of the conjugate base (A^-) is 10.0.

(D*) The pH of an aqueous solution containing 0.1 M - HA and 0.01 M - HCl is 2.0.

Match the column

Q.27 Match column I having components with column II having pH or pOH of solution.

	Column I	Column II
(A)	Saturated solution of $A(OH)_2$ having $k_{sp} = 5 \times 10^{-31}$	(P) 7
(B)	Mixing equal volumes of 0.1 M CH_3COONa & 0.1 M XNO_3	(Q) 10
(C)	Solution obtained at $\frac{10}{11}$ of the equivalence point when 0.1 M XOH is titrated with HCl 0.1 M	(R) 5
		(S) 4

Given data : $K_h\ X^+ = 10^{-5}$, $K_{a,CH_3COOH} = 10^{-5}$

[Ans. (A) P (B) R (C) QS]

Subjective :

Q.28 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x. [Ans.0.05 mol]

Q.29 50ml of a weak monoprotic acid was titrated with 0.1M solution of NaOH. If pH of the solution after adding 50 ml and 75 ml of base is 4.699 and 5 then calculate a four digit number **'abcd'** where : **ab** = pK_a of the weak acid; **cd** = pH of the solution when 7.5 millimoles of HCl are added in the solution at the equivalence point without changing volume.[**Given :** log 2 = 0.301] [Ans. 0505]

Q.30 A solution contains 0.01M Mg^{+2} and 0.1M Sr^{+2} and H_2CO_3 maintained at 0.05M. At what minimum & maximum pH will $SrCO_3$ will precipitate without any precipitation of $MgCO_3$.
[**Given:** $K_{sp}MgCO_3 = 2.5 \times 10^{-7}$, $K_{sp}SrCO_3 = 9 \times 10^{-9}$, $K_{a(overall)}\ H_2CO_3 = 5 \times 10^{-16}$, log5 = 0.7, log 3 = 0.5] ***Express your asnwer as abcd where*** **ab** = Ten times minimum pH for the above condition; **cd** = Ten times maximum pH for the above condition. [Ans. 4860]

REVISION FLOW CHART

Ionic Equilibrium

Theoretical Concept
- Different theories of Acid-base, Arrhenius, Bronsted lowry & Lewis — T
- Arrhenius Theory of dissociation K_w, K_a & K_b relation between K_a & K_b of conjugate acid-base — T + N
- Ostwald dilution law & factor affecting α — N + G
- Factor affecting α — T + N
- Dissociation of water, pH definition & variation of pH with T — T + N

pH Calculation
- Solution of only acid or bases — N
  - (i) strong
  - (ii) weak
    - mono
    - polyprotic
- Mixtures of only Acids or Only bases — N
  - SA + SA
  - SA + WA
  - WA + WA
- Salt solutions — N
  - Salt of SA/SB
  - Salt of SA/WB
  - Salt of WA/WB
  - Amphiprotic salt
  - Polyvalent hydrolysis
- Mixtures of salt & Acid or salt & base — N
  - Buffer solution
  - Mixture of only acids/ or only base

Buffer
- Type of Buffer — T
- pH calculation — N
- pH variation of dilution & on adding acid or base — N
- Buffer capacity — N + G

Indicator / Titration
- Theory of indicator — T
- Titration of SA+SB, WA+SB, SA+WB, WA+WB — useful indicator — N + G

Solubility
- Definition — N
- K_{sp} & solubility — N
- K_{SP} & K_{IP} — T + N
- Factor affecting solubility — T
- Common ion effect — N
- Complex formation — N
- Hydrolysis of cation, anion — N
- Precipitation/Condition for precipitation — T + N

(G) → represents topic of graphical importance

(T) → represents topic of theoretical importance

(N) → represents topic of numerical importance

LIST OF IMPORTANT FORMULAS

* **Basic Relationships**

(a) $K_w = [H^+][OH^-] = 10^{-4}$ (at 25°C) , K_a (for water) $= \dfrac{K_w \times 18}{1000}$

(b) $\ln \dfrac{K_{w_2}}{K_{w_1}} = \dfrac{\Delta H}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$; $\Delta H = \Delta H$ neutralise of SA and SB

(c) $pH + pOH = pK_w = 14$ at 25°C

(d) For weak conjugate acid / base pair

$pK_a + pK_b = pK_w$

(e) Ostwald dil law for an electrolyte AB, $\dfrac{C\alpha^2}{1-\alpha} = K$

pH CALCULATUION

1. pH of a solution containing strong monoprotic acid.

(i) at moderate conc. ($C \geq 10^{-6}$ M)

$pH = -\log C$

(ii) at low conc. ($C < 10^{-6}$ M)

$K_\omega = (C + x)(x)$

$[H^+] = C + x$ $x \rightarrow$ contribution of water

2. pH of a solution containing weak monoprotic acid.

Case-I : *If $C \geq 10^{-6}$ M*

$K_a = \dfrac{x^2}{C - x}$ If $C >> x$ $pH = \dfrac{1}{2}(pK_b - \log C)$

Case-II : If $C < 10^{-6}$ M

Weak acid can be treated as a strong acid but contribution due to water cannot be neglected.

$[H^+] = c + x$

$K_\omega = (c + x)\, x$

3. pH of a solution containing more than one acid.

Case I : **Mixture of SA + SA**

$[HA] = c_1$

[HB] = c_2

$[H^+] = c_1 + c_2$

Depending upon the final $[H^+]$ condition, Contribution from water may be neglected or taken.

Case II : **Mixture of SA + WA**

[HCl] = c_1 [HA] = c_2

$$HA \rightleftharpoons H^+ + A^-$$

$c_2 - x$ $\quad c_1 + x$ $\quad x$

$$K_a = \frac{(c_1 + x)x}{(c_2 - x)}$$

Case-III : **Mixture of WA + WA**

$$HA \rightleftharpoons H^+ + A^-$$

$c_1 - x$ $\quad x + y$ $\quad x$

$$K_1 = \frac{(x+y)x}{c_1 - x}$$

$$HB \rightleftharpoons H^+ + B^-$$

$c_2 - y$ $\quad x + y$ $\quad y$

$$K_2 = \frac{(x+y)y}{c_2 - y}$$

* For polyprotic acid $K_1 >> K_2 >> K_3$

All the formulaes derived above are applicable for bases also. Only $[H^+]$ will be replaced with $[OH^-]$

SALT HYDROLYSIS

Case-I : ***Salts of strong acids and strong bases*** do not undergo hydrolysis.

Neutral $\Rightarrow pH = 7$

Case-II : ***Salts of strong base and weak acid*** give a basic solution (pH>7) when dissolved in water.

e.g. : CH_3COONa, NaCN

$$K_b = \frac{K_\omega}{K_a} = K_h$$

$$K_h = K_h = \frac{K_\omega}{K_a} = \frac{(ch)^2}{c(1-h)}$$

if $\frac{K_h}{c} \le 10^{-3}$ then $h << 1$

$$pH = \frac{1}{2}\left(pK_{\omega} + pK_a + \log C\right)$$

In case of substantial hydrolysis the above expression will not be applicable

Case-III : ***Salts of a strong acids and weak bases*** give an acidic solution.

$$K_a = \frac{K_{\omega}}{K_b} = K_2$$

$$\frac{K_{\omega}}{K_b} = \frac{(ch)^2}{c(1-h)} = K_h$$

if $\frac{K_h}{c} \le 10^{-3}$ $h << 1$

$$= \frac{1}{2}\left(-\log K_{\omega} + \log K_b - \log C\right) = \frac{1}{2}\left(pK_{\omega} - pK_b - \log C\right)$$

In case of substantial hydrolysis the above expression will not be applicable

(iv) ***Salts of weak base and weak acid***

Assuming degree of hydrolysis to be same for the both the ions,

$K_h = K_w / (K_a.K_b)$, $[H^+] = [K_a K_w/K_b]^{1/2}$

$$pH = \frac{1}{2}(pk_w + pk_a - pk_b)$$

(v) ***Amphiprotic salts***

e.g. $NaHCO_3$

$$pH = \frac{1}{2}(pK_1 + pK_2)$$

pH of such salt solution is independent of concentration od salt.

* ***Buffer solution***

Acidic Buffer

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

$$\left[\text{Actually } pH = pK_a + \log\frac{[\text{conjugate base}]}{[acid]}\right]$$

* Basic buffer

$$pOH = pK_b + \log\frac{[salt]}{[base]}$$

$$\left[\text{Actually } pOH = pK_b + \log\frac{[\text{conjugate acid}]}{[base]}\right]$$

* Simple buffer (Salt of Weak acid & weak base)

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

* ***Solubility***

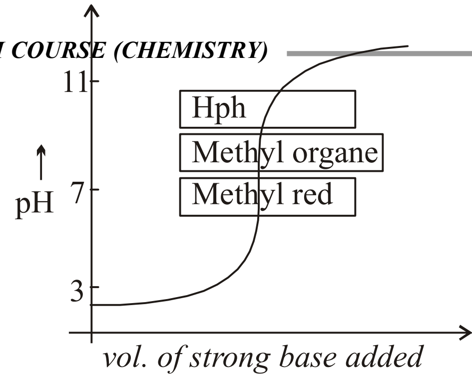
For A_xB_y $K_{sp} = (xS)^x (yS)^y$

Effect of hydrolysis on solubility $S = \sqrt{K_{sp}\left[1+\frac{[H^+]}{K_a}\right]}$

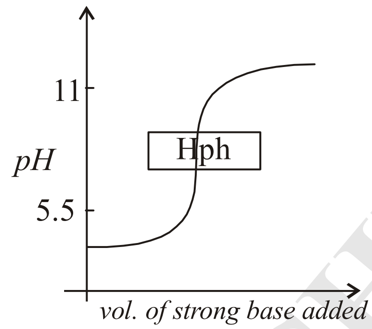
* **Indicators**

Indicators	**pH range**		**Colour**
		acid medium	basic medium
Methyl Orange	3.1-4.4	pink	yellow
Phenolphathlene	8.3-10	colourless	pink

Case I : **Titration of SA + SB**

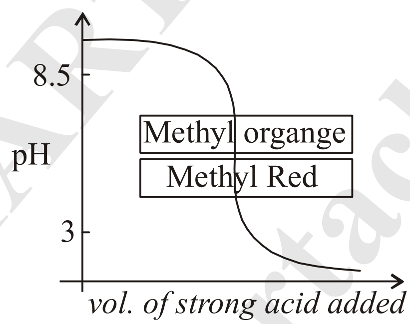


Case II : **Titration of WA + SB**



Methyl orange can't be used. Nothing definite can be said about the use of methyl red.

Case-III : **Titration of WB + SA**



Case-IV : **Titration of WB + WA :** No sharp change in pH. No suitable indicator.

* For complex formation

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_1$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_2$$

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_{form} = K_1K_2$$

$$K_d \text{ (dissociation or instability constant)} = \frac{1}{K_{form} \text{ (formation or stability constant)}}$$

LAST MOMENT REVIEW

IONIC EQUILIBRIUM

Theory : ....

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Exercise - 1 : Question ....

Exercise - 2 : Question ....

Exercise - 3 : Question ....

Exercise - 4 : Question ....

DPPs : ....

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Other Sources : ....

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