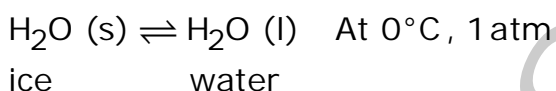


- We study chemical equilibrium to answer : “ To what extent reactants will convert to products”
- The answer is linked to “ How far does a reaction proceed towards completion before it reaches a **state of chemical equilibrium** ? ”
- At this state reaction does not stop, however, rate of forward reaction is same as backward reaction. In other words, rate at which reactants is changing to products is same as products changing to reactants

- Dynamic equilibrium is observed in phase transformations also  
for example : Solid  $\rightleftharpoons$  Liquid



At equilibrium, rate of melting = rate of freezing , but intense activity at the boundary of ice and water.

- **Phase Transformation processes**

Solid  $\rightarrow$  Liquid (Fusion / melting)

Solid  $\rightarrow$  Gas (Sublimation)

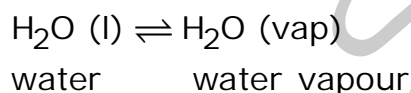
Liquid  $\rightarrow$  Solid (Freezing)

Liquid  $\rightarrow$  Gas (Evaporation)

Gas  $\rightarrow$  Liquid (Condensation)

Gas  $\rightarrow$  Solid (Deposition)

- For Liquid  $\rightleftharpoons$  Gas



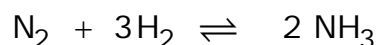
At equilibrium and constant temperature , the pressure exerted by molecules in vapour phase is - **Vapour pressure of liquid**

- If temperature increases, more molecules of liquid have speed enough to escape into vapour phase, this results in increased Vapour pressure

Temp (K)	Vapour Pressure of water (Pa)
273	610
303	4,240
333	19,918
373	101,325

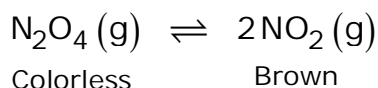
- The temperature, at which vapour pressure becomes equal to external atmospheric pressure, is called **Boiling Point of liquid**
- At a given temperature, different liquids have different vapour pressure, as intermolecular forces are different
- Lower intermolecular force leads to higher vapour pressure, i.e., more volatile liquid
- Common characteristics of physical equilibria
  - Possible only in a closed system at a given temperature.
  - The opposing processes occur at the same rate and there is a dynamic but stable condition.
  - Equilibrium is characterised by constant value of one of its parameters at a given temperature. (e.g. vapour pressure)
  - The magnitude of these quantities at any stage indicates the extent to which the reaction has proceeded before reaching equilibrium
- Equilibrium in Chemical Process**

In chemical reactions, the equilibrium is the state of reaction at which concentration of reactants and products remain constant over a period of time



Rate of forward reaction (from left to right, i.e.,  $\text{N}_2$  and  $\text{H}_2$  combining to form Ammonia) = Rate of reverse reaction (Ammonia dissociating into  $\text{N}_2$  and  $\text{H}_2$ )

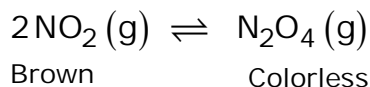
- Let us start with initial concentration of  $N_2O_4$  in a reaction vessel of 1 L.



- concentration of  $N_2O_4$  starts decreasing and concentration of  $NO_2$  starts increasing
- After some time, concentration of  $NO_2$  starts declining as  $NO_2$  starts combining to form  $N_2O_4$  (reverse reaction)
- At equilibrium, rate of decomposition of  $N_2O_4$  = rate of combination of  $NO_2$

- In chemical reactions, the equilibrium is the state of reaction at which concentration of reactants and products remain constant over a period of time

- If we start with 0.08 moles of  $NO_2$  in a reaction vessel of 1 L



same equilibrium state is achieved as :

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

Colorless                      Brown

- In case of chemical equilibrium, at equilibrium,
  - Concentration of reactants and products becomes constant
  - Rate of forward reaction = Rate of backward reaction
  - At equilibrium the free energy change of the system is equal to zero

Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of products.

- Law of Mass Action ( for Chemical Equilibrium)**

Let us consider a reaction represented by :  $aA + bB \rightleftharpoons cC + dD$

At equilibrium, concentrations are related by the following relations

equilibrium constant 
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where a,b,c and d are stoichiometric coefficients and [A], [B], [C] and [D] are concentration ( mol L<sup>-1</sup>)

- Law of Chemical Equilibrium :**

At a given temperature,

- The product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation

divided by

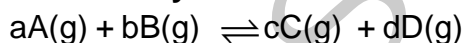
- The product of concentrations of the reactants raised to their individual stoichiometric coefficients

has a constant value.

- Equilibria in gas-phase reactions ( $K_p$ )**

Homogeneous Equilibria	Heterogeneous Equilibria
Equilibria in a system where <b>all the reactants and product are in one phase</b>	Equilibria in a system where <b>all the reactants and product are in more than one phase</b>

- Gaseous system :**



$$\therefore K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

However, for gases pressure can be easily measured , so rather than concentration we use partial pressure. As  $p_A \propto [C]$

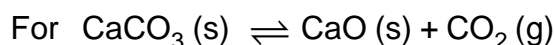
Equilibrium constant may be redefined as : 
$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

- As  $p_A = [A] RT$ ,  $p_B = [B] RT$ ,  $p_C = [C] RT$  and  $p_D = [D] RT$

$$\therefore K_p = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right) (RT)^{(c+d-a-b)} ; \therefore K_p = (K_c) (RT)^{\Delta n}$$

$\Delta n$  = No. of moles of gaseous products – No. of moles of gaseous reactants

- In case of heterogeneous equilibria, concentration of pure solids and liquid is constant and is combined with equilibrium constants to evaluate equilibrium constants for heterogeneous equilibria.



$$K = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

As molar concentration of pure solid and liquid is constant at a given temperature.

$$K_c = [\text{CO}_2]$$

- To compute equilibrium concentrations ,  
 Step 1 : Write balanced equation  
 Step 2 : Make a table for each substance , writing  
 (a) Initial concentration  
 (b) change in concentration for equilibrium  
 (c) Equilibrium concentration  
 Step 3 : Substitute equilibrium concentration in equilibrium equation and solve.
- Equilibrium Constant is temperature dependent and does not depend on initial concentration of reactants and products
- Numerical value of  $K_c$  suggests extent of conversion of reactants to products. As rule of thumb is  $K_c > 10^3$ , we say that reaction has proceeded nearly to completion.

- If reaction has not reached equilibrium , the ratio  $\frac{[C]^c [D]^d}{[A]^a [B]^b}$  is referred to as

### Reaction Quotient ( $Q_c$ )

- At equilibrium  $Q_c = K_c$
- If  $Q_c < K_c$ , reaction will move from left to right
- If  $Q_c > K_c$ , reaction will move from right to left

- Factors affecting equilibrium mixture
  - Change in concentration of reactants and products
  - Change in pressure and volume
  - Change of temperature

- **Le Chatelier's Principle**

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in a direction that relieves the stress

Change in any of the factors such as temperature, pressure concentration of reactants or products will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

- If we **add more reactants / products**, the equilibrium is disturbed then net reaction will occur **in direction where reactants/ products are consumed** as a result stress is released.

e.g.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ;  $K_c = 0.29$  at 700 K

Let at initial equilibrium,  $[\text{N}_2]_0 = 1$ ,  $[\text{H}_2]_0 = 1$  and  $[\text{NH}_3]_0 = 0.54$

Now if we add  $\text{N}_2$  so as  $[\text{N}_2] = 2$

then Now  $Q_c = \frac{(0.54)^2}{(2)(1)^3} = 0.145$ ;

Now  $Q_c < K_c$ , reaction will move from left to right, i.e., more of  $\text{NH}_3$  will get formed and  $\text{N}_2$  will get consumed.

- Effect of change in Pressure by change in volume  
If pressure is increased by decreasing volume, this will lead to increase in concentration, then reaction will move so as there is overall decrease in no. of moles.

e.g.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ;  $K_c = 0.29$  at 700 K

Let at initial equilibrium,  $[\text{N}_2]_0 = 1$ ,  $[\text{H}_2]_0 = 1$  and  $[\text{NH}_3]_0 = 0.54$

Now if we double the pressure by halving the volume so as

$[\text{N}_2] = 2$ ,  $[\text{H}_2] = 2$  and  $[\text{NH}_3] = 1.08$ , then Now  $Q_c = \frac{(1.08)^2}{(2)(2)^3} = 0.0729$

Now  $Q_c < K_c$ , reaction will move from left to right, i.e., more of  $\text{NH}_3$  will get formed and  $\text{N}_2$  and  $\text{H}_2$  will get consumed and there will be overall decrease in no. of moles

- Effect of addition of Inert gas ,  
If inert gas is added at constant volume and temperature , then there will be resultant increase in pressure, no impact as partial pressure remain same.

If inert gas is added at constant pressure , then there will be resultant increase in volume, and concentration will decrease , then net reaction will move towards increase in no. of moles.

e.g.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ;  $K_c = 0.29$  at 700 K

Let at initial equilibrium ,  $[\text{N}_2]_0 = 1$ ,  $[\text{H}_2]_0 = 1$  and  $[\text{NH}_3]_0 = 0.54$

Now if we add some inert gas is added to the constant pressure to the system resulting in increase in volume from 1L to xL , where  $x > 1$   
new concentrations are  $[\text{N}_2] = 1/x$ ,  $[\text{H}_2] = 1/x$  and  $[\text{NH}_3] = 0.54/x$  then

$$Q_c = \frac{\left(\frac{0.54}{x}\right)^2}{\left(\frac{1}{x}\right)\left(\frac{1}{x}\right)^3} = x^2(0.29); \quad Q_c > K_c$$

Hence, reaction will move towards right ( in direction of increasing no. of moles)

- Free Energy change and equilibrium constant

$$\Delta G = \Delta G^0 + RT \log_e(Q_c)$$

At equilibrium ,  $\Delta G = 0$  ;  $\Delta G^0 = -RT \log_e(K_c)$

- Effect of Temperature on  $K_c$

$$\log \frac{K_{c2}}{K_{c1}} = \frac{\Delta H}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), T_2 > T_1$$

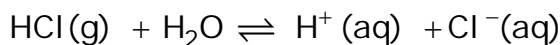
For an endothermic reaction, ( $\Delta H$  is +ve) , increase in temp  $K_{c2} > K_{c1}$ ,  
favoured by high temperature

While for an exothermic reaction ( $\Delta H$  is -ve),  $K_{c2} < K_{c1}$   
favoured by low temperature

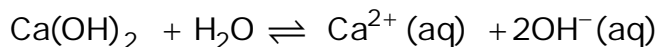
## Ionic Equilibrium

- Arrenius ( 1887)**

Acid : The substances furnishing  $H^+$  ions in aqueous solution



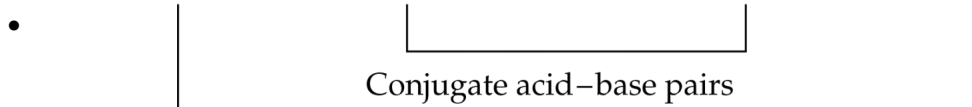
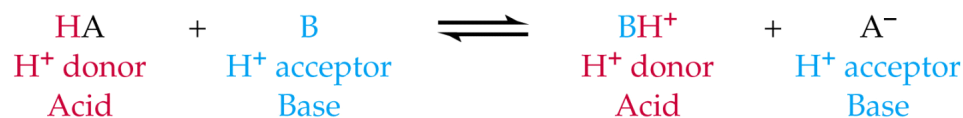
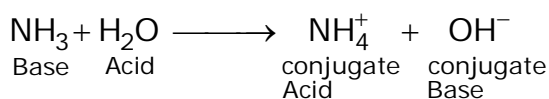
Base : The substances furnishing  $OH^-$  ions in aqueous solution



- Bronsted - Lowry ( 1923)**

Acid : The substances that has tendency to donate proton ( $H^+$ ) to other substance

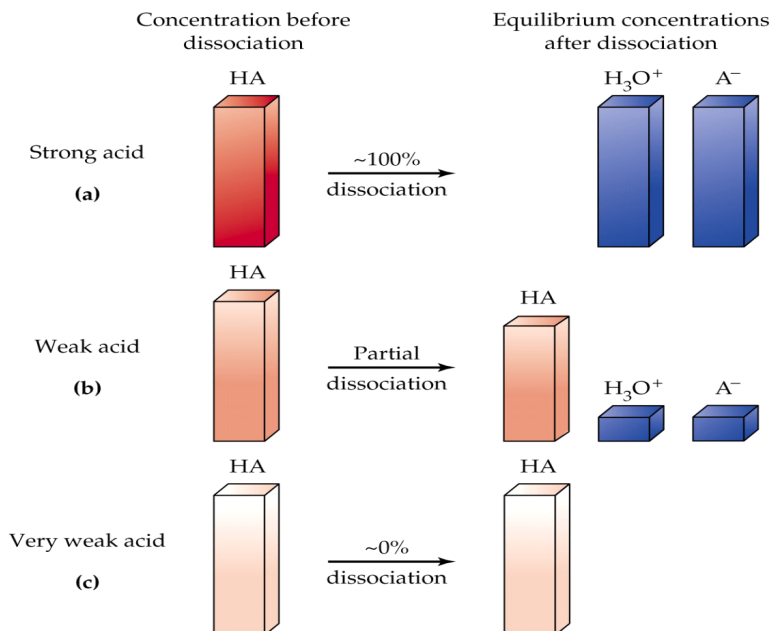
Base : The substances that has tendency to accept proton ( $H^+$ ) to other substance



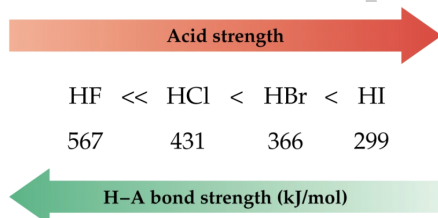
- HA is acid ( donating proton ) ;  $A^-$  is conjugate base
- B is base ( accepting proton ) ;  $BH^+$  is conjugate acid
- The stronger an acid is weaker is its conjugate base.
- Water can act both as acid or base



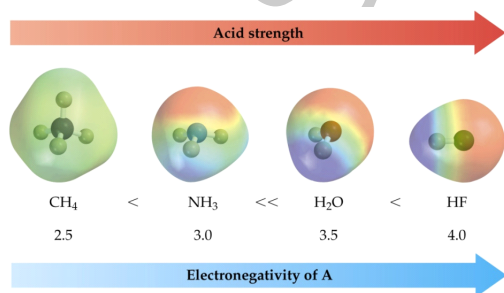
- Relative strength of Acid



- Across group in periodic table, Acid strength increases as bond strength decreases



- Across period, electronegativity increases, thus strength of acid increases



- In case of oxacids, acidic strength increases if attached atom is of higher electronegativity  
HOI < HOBr < HOCl

- In case of oxacids, acidic strength is higher if a large number of terminal O atoms are present in the molecule.  
HOCl (hypochlorous) < HOClO (Chlorous) < HClO<sub>3</sub> (chloric) < HClO<sub>4</sub> (Perchloric)

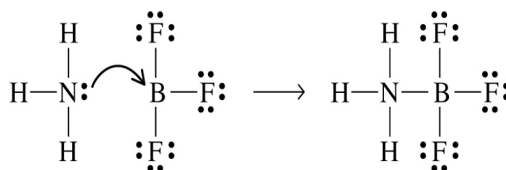
- Acidity and basicity also depends on nature of solvent

- Levelling Effect :

The solvent water has a levelling effect on the acidities of HClO<sub>4</sub>, HCl and HI : aqueous solutions of these acids at the same (moderately low) concentrations have the same acidities. Please note that relative acid strength HClO<sub>4</sub>, HCl and HI are different but as water as a solvent will not get us any result about which is stronger acid.

- Lewis Concept of Acid and Base :**

Acid : Species capable of accepting a pair of electrons to form a covalent bond  
Base : Species capable of donating a pair of electrons to form a covalent bond.



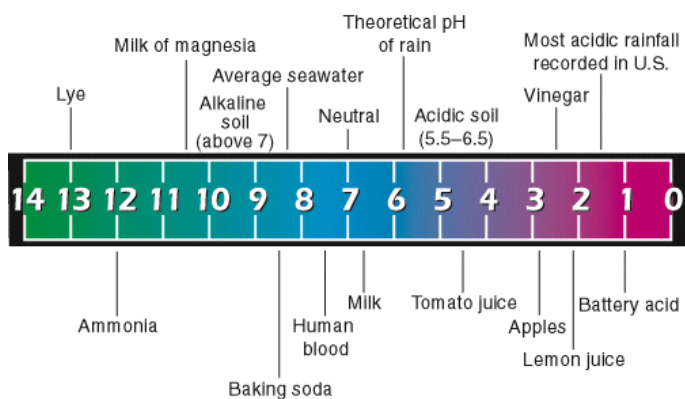
<b>Bronsted – Lowry</b>	<b>Lewis</b>
Acid – Proton Donor, Base – Proton Acceptor	Acid – Electron Pair Acceptor Base – Electron Pair Donor
All Lewis Bases are BL Bases	Base – Unshared Electron Pair in outer orbital
Not All Lewis acid are BL Acid	Acid : Substance with Vacant Orbitals

- Self ionisation of Water :**



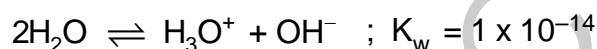
$$K_w = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] \quad ; \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M at } 25^\circ\text{C}$$

- $K_w$  (Ionic product of water) =  $1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$  at  $25^\circ \text{C}$
- Dissociation of water is endothermic process, value of  $K_w$  increases with temperature.
- **The pH Scale (Puissance d'hydrogene - power of hydrogen)**  
 $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$  and  $\text{pOH} = -\log_{10}[\text{OH}^-]$



- Can  $\text{pH} < 0$  or  $> 14$  ?

**Dissociation of weak acid (for example, Acetic acid,  $K_a = 1.8 \times 10^{-5}$ )**



Initial Conc.            C                                    0                                    0  
 At Eq.                    C(1-  $\alpha$ )                            C $\alpha$                                     C $\alpha$  ; where  $\alpha$  is degree of dissociation

$$\therefore K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

(Assumed that  $C\alpha \gg 10^{-7}$ , hence only principal reaction is taken into account for concentration and  $K_a$  evaluation)

$$\therefore \alpha \ll 1 \quad \therefore 1 - \alpha \approx 1 ; \quad K_a = C\alpha^2$$

$$\text{and } \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} ;$$

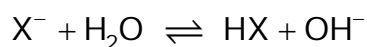
This means that more dilute weak acid will exhibit more dissociation

$$\text{and } [\text{H}_3\text{O}^+] = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a C} , \text{ and correspondingly we can find pH.}$$

- If  $C\alpha \gg 10^{-7}$  but  $\alpha > 0.1$  then we use  $K_a = \frac{C\alpha^2}{(1-\alpha)}$ , and solve  $\alpha$  in a quadratic equation to get its value and then only compute  $[H_3O^+]$  and the pH
- If  $C\alpha < 10^{-7}$  but  $\alpha > 0.1$  (e.g.  $10^{-7}$  M HCl) ..... ?
- For acid HX,  $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]}; \quad pK_a = -\log_{10} K_a$$

For conjugate base of acid HX



$$K_b = \frac{[HX][OH^-]}{[X^-]}; \quad pK_b = -\log_{10} K_b$$

- $K_a K_b = [H_3O^+][OH^-] = K_w$
- $pK_a + pK_b = 14$

### Hydrolysis of Salts ( Solution of Salts in Water)

- Salts +  $H_2O$ , dissolve almost completely



Reaction of  $B^+$ ,  $A^-$  with  $OH^-$  or  $H_3O^+$  is known as Hydrolysis

- **Hydrolysis of Salts ( BA) of Strong Acid and Strong Base ( NaCl)**

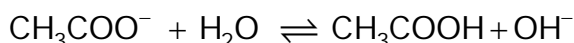
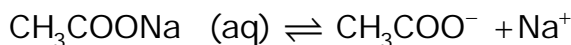
$B^+$  ( $Na^+$ ,  $K^+$ , ...) and  $A^-$  ( $Cl^-$ ,  $NO_3^-$ ...) gets hydrated Hence no reaction with  $OH^-$ ,  $H_3O^+$ .

As a result, no pH remains that of neutral solution ( Water)

- **Hydrolysis of Salts ( BA) of Weak Acid and Strong Base ( CH<sub>3</sub>COONa)**

B<sup>+</sup> ( Na<sup>+</sup>, K<sup>+</sup>, ...) and A<sup>-</sup> ( Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>...) gets hydrated Hence no reaction with OH<sup>-</sup>

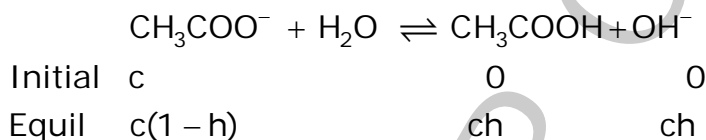
A<sup>-</sup> ( CH<sub>3</sub>COO<sup>-</sup>, CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, ...) are stronger bases than H<sub>2</sub>O but weaker than OH<sup>-</sup>, therefore, A<sup>-</sup> will react with water and produce HA and OH<sup>-</sup>



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}$$

$$K_h = \frac{K_w}{\frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}} \Rightarrow K_h = \frac{K_w}{K_a}$$

Let initial concentration of CH<sub>3</sub>COONa is "c" and degree of hydrolysis as "h" then



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{ch^2}{(1-h)}$$

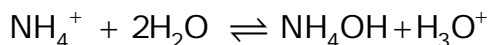
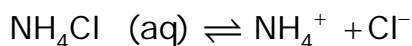
$$\text{If } h \ll 1, \text{ then } K_h = ch^2; \Rightarrow h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{cK_a}}$$

$$\text{As } [\text{OH}^-] = ch; \therefore [\text{H}_3\text{O}^+] = \frac{K_w}{ch} = \sqrt{\frac{K_w K_a}{c}}$$

- Hence,  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log_{10} C)$

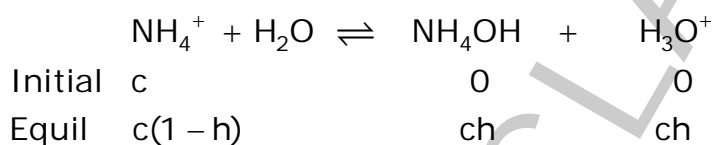
- Hydrolysis of Salts ( BA) of Strong Acid and Weak Base (NH<sub>4</sub>Cl)**

A<sup>-</sup> (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ...) gets hydrated Hence no reaction with H<sub>3</sub>O<sup>+</sup>. and B<sup>+</sup> (NH<sub>4</sub><sup>+</sup>, C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>...) are acid than H<sub>2</sub>O but weaker than H<sub>3</sub>O<sup>+</sup>, therefore, B<sup>+</sup> will react with water and produce BOH and H<sub>3</sub>O<sup>+</sup>.



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{[\text{NH}_4\text{OH}][\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{K_w}{[\text{NH}_4^+][\text{OH}^-]}$$

$$\Rightarrow K_h = \frac{K_w}{K_b}$$



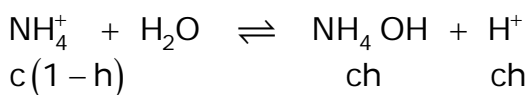
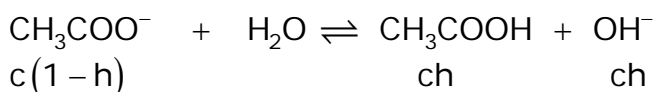
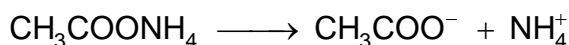
$$K_h = \frac{K_w}{K_b} = \frac{ch^2}{(1-h)}; \text{ for } h \ll 1 \quad K_h = ch^2 \quad \Rightarrow h = \sqrt{\frac{K_w}{cK_b}}$$

$$[\text{H}_3\text{O}^+] = ch = \sqrt{\frac{cK_w}{K_b}}$$

$$\Rightarrow \text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log_{10} C)$$

- Hydrolysis of Salts ( BA) of Weak Acid and Weak Base (CH<sub>3</sub>COONH<sub>4</sub>)**

Both A<sup>-</sup> (CH<sub>3</sub>COO<sup>-</sup>, ...) and B<sup>+</sup> (NH<sub>4</sub><sup>+</sup>, C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>...) will react with water and produce HA, BOH, H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} = \frac{c^2 h^2}{c^2 (1-h)^2} = \frac{K_w}{K_a \times K_b}$$

$$K_h = \frac{K_w}{K_a \times K_b}; \quad \text{and} \quad \frac{h}{1-h} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$\text{Further, } \frac{ch}{c(1-h)} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \Rightarrow \frac{h}{(1-h)} = \frac{[\text{CH}_3\text{COOH}][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]} = \frac{[\text{H}_3\text{O}^+]}{K_a}$$

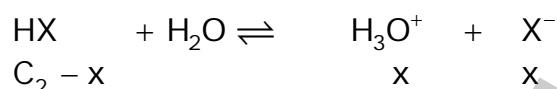
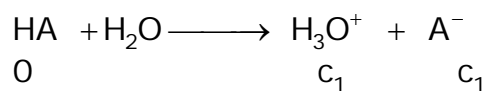
$$\text{Hence, } \frac{h}{1-h} = \frac{[\text{H}_3\text{O}^+]}{K_a} = \sqrt{\frac{K_w}{K_a K_b}} \Rightarrow [\text{H}_3\text{O}^+] = \sqrt{\frac{K_a K_w}{K_b}}$$

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \text{p}K_b)$$

Type of Salt	Examples	Ions That React with Water	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KNO <sub>3</sub> , BaI <sub>2</sub>	None	~ 7
Cation from weak base; anion from strong acid	NH <sub>4</sub> Cl, NH <sub>4</sub> NO <sub>3</sub> , [(CH <sub>3</sub> ) <sub>3</sub> NH]Cl	Cation	< 7
Small, highly charged cation; anion from strong acid	AlCl <sub>3</sub> , Cr(NO <sub>3</sub> ) <sub>3</sub> , Fe(ClO <sub>4</sub> ) <sub>3</sub>	Hydrated cation	< 7
Cation from strong base; anion from weak acid	NaCN, KF, Na <sub>2</sub> CO <sub>3</sub>	Anion	> 7
Cation from weak base; anion from weak acid	NH <sub>4</sub> CN, NH <sub>4</sub> F, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Cation and anion	< 7 if K <sub>a</sub> > K <sub>b</sub> > 7 if K <sub>a</sub> < K <sub>b</sub> ~ 7 if K <sub>a</sub> ≈ K <sub>b</sub>

- Acids giving more than one hydrogen ion per molecule are referred to as 'polybasic' or 'polyprotic' acids. e.g.  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_3\text{PO}_4$ ...
- These acids dissociates in stages, and equilibrium constant of second stage is  $\ll$  that of first stage
- To calculate hydrogen ion concentration, only the first step should be considered, as the  $\text{H}_3\text{O}^+$ , obtained from successive dissociation can be neglected, but to calculate the concentration of other ions, both equilibria stages needs to be considered
- **Mixture of strong acid and weak acids**

Let us take a mixture of strong acid HA with initial concentration  $c_1$  and HX with initial concentration  $c_2$  respectively.



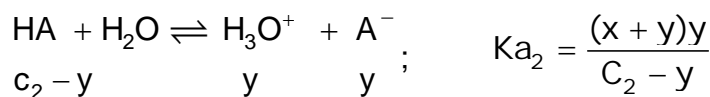
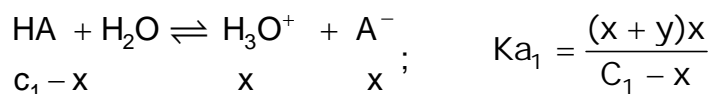
Total concentration of  $[\text{H}_3\text{O}^+] = c_1 + x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} = \frac{(c_1 + x)x}{c_2 - x}; \quad \Rightarrow x^2 + x(c_1 + K_a) - c_2K_a = 0$$

$$x = \frac{-c_1 \pm \sqrt{c_1^2 + 4K_a c_2}}{2}; \quad [\text{H}_3\text{O}^+] = c_1 + x = \frac{c_1 \pm \sqrt{c_1^2 + 4K_a c_2}}{2}$$

- **Mixture of two weak acids**

Let us take a mixture of strong acid HA with initial concentration  $c_1$  and HB with initial concentration  $c_2$  respectively.



Total concentration of  $[\text{H}_3\text{O}^+] = x + y$

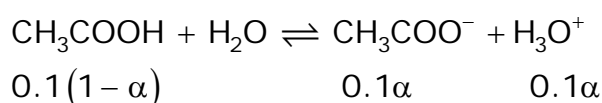


For  $x, y$  being negligible compared to  $c_1$  and  $c_2$ ;  $x = \frac{K_{a_1}c_1}{(x+y)}$  and  $y = \frac{K_{a_2}c_2}{(x+y)}$

$$\Rightarrow (x+y) = \frac{K_{a_1}c_1 + K_{a_2}c_2}{(x+y)} \Rightarrow (x+y) = \sqrt{K_{a_1}c_1 + K_{a_2}c_2}$$

### Common - Ion effect in Acid-Base Equilibria

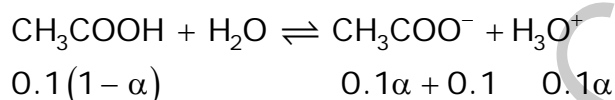
- Suppression of dissociation of weak acid / base on addition of same species
- Let us take 0.1 M  $\text{CH}_3\text{COOH}$  and assume degree of dissociation as  $\alpha$



$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 4.24 \times 10^{-2}; \quad [\text{H}_3\text{O}^+] = 0.1\alpha = 4.24 \times 10^{-3}$$

- Let us consider now a mixture of 0.1 M  $\text{CH}_3\text{COOH}$  and 0.1 M  $\text{CH}_3\text{COONa}$

now total concentration of acetate ion in solution  $[\text{CH}_3\text{COO}^-] = 0.1 + 0.1\alpha$



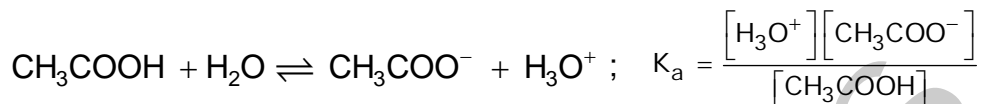
$$K_a = 1.8 \times 10^{-5} = \frac{0.1\alpha(0.1\alpha + 0.1)}{0.1(1-\alpha)} \Rightarrow 1.8 \times 10^{-4} = \alpha^2 + \alpha$$

$$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1 + 7.2 \times 10^{-4}}}{2} = 1.8 \times 10^{-4} \text{ AND } [\text{H}_3\text{O}^+] = 0.1\alpha = 1.8 \times 10^{-5}$$

### Buffer Solution

- Two component systems that alter pH only slightly when acid or base is added to that system.
- Acidic Buffer :  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  ; Basic Buffer :  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  and Salt or neutral Buffer :  $\text{CH}_3\text{COONH}_4$

- Acidic Buffer : Weak Acid ( $\text{CH}_3\text{COOH}$ ) and its Salt ( $\text{CH}_3\text{COONa}$ ) ;  
 $\text{CH}_3\text{COONa (aq)} \rightarrow \text{CH}_3\text{COO}^- \text{(aq)} + \text{Na}^+ \text{(aq)}$



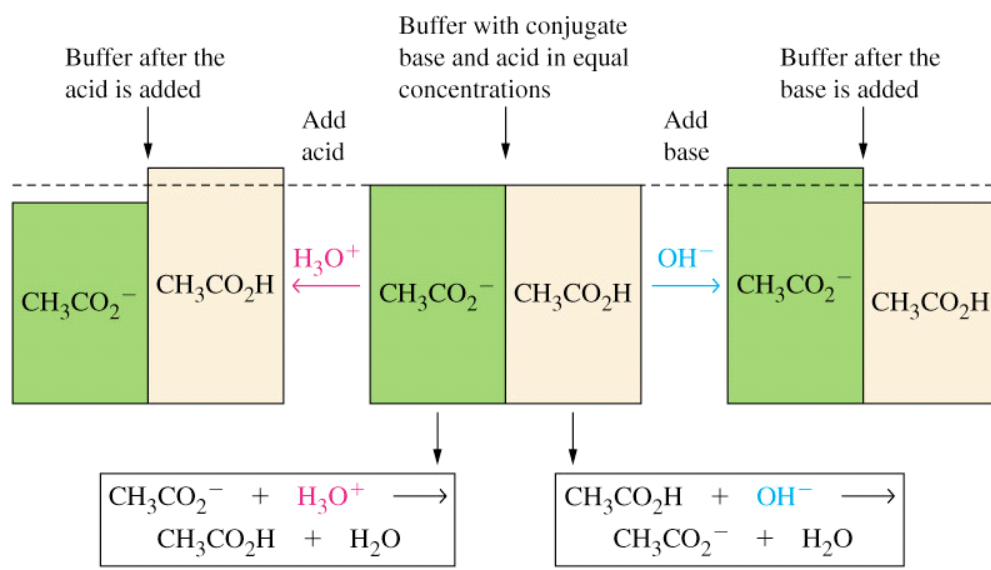
$$\Rightarrow [\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\text{Hence, } \text{pH} = \text{p}K_a - \log_{10} \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

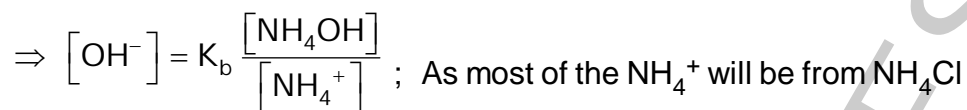
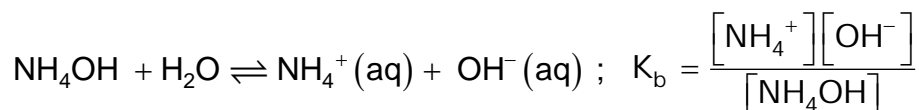
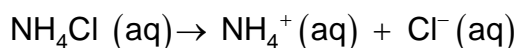
Please note that most of the acetate ions ( $\text{CH}_3\text{COO}^-$ ) will be from dissociation of salt.  
 $[\text{CH}_3\text{COO}^-] = [\text{Salt}]$  as Acetic acid dissociates feebly.

$$\therefore \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{Salt}]}{[\text{acid}]} \text{ known as Henderson - Hasselbach Equation}$$

- Mechanism of this acidic buffer :



- **Basic Buffer : Mixture of weak base(  $\text{NH}_4\text{OH}$ ) and its salt (  $\text{NH}_4\text{Cl}$ )**



$$\therefore \text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{base}]}$$

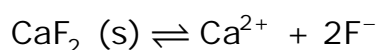
- Buffer Capacity is defined quantitatively as number of moles of acid or base added in One Litre of buffer solution leads to increase of pH by unity.

$$\text{Buffer Capacity} = \frac{\text{No. of moles of acid (or base) added to 1 L}}{\text{Change in pH}}$$

- **Solubility and solubility product**

Sparingly soluble salt will dissolve in very small amount and whatever dissolves will ionize into respective ions. At certain temperature solubility of a salt is fixed.

For example, a sat. soln. of  $\text{CaF}_2$  in contact with solid  $\text{CaF}_2$  contains constant equilibrium concentrations of  $\text{Ca}^{2+}(\text{aq})$  and  $\text{F}^-(\text{aq})$



$$\text{Equilibrium constant } K = \frac{[\text{Ca}^{2+}][\text{F}^-]^2}{[\text{CaF}_2(\text{s})]}$$

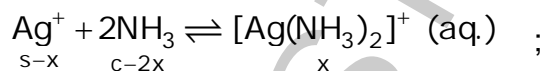
As  $[\text{CaF}_2(\text{s})]$  is constant, we may write  $K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$ , where  $K_{\text{sp}}$  is referred to as solubility product,  $[\text{Ca}^{2+}]$  and  $[\text{F}^-]$  are equilibrium concentrations (solubilities).

- The equilibrium constants for saturated solution and solid formation (precipitate) are called solubility product,  $K_{\text{sp}}$
- If at an instant, concentration of  $[\text{Ca}^{2+}]$  and  $[\text{F}^-]$  are such that product of  $[\text{Ca}^{2+}][\text{F}^-]^2$ , known as Ionic Product ( $K_i$ ) is not same as  $K_{\text{sp}}$ , the solution is either unsaturated or supersaturated. In these cases, equilibrium is reached either by more dissolution of salt or by formation of solid (precipitate).
- If  $K_i > K_{\text{sp}}$ , solution is supersaturated and precipitation occurs.
- For salt of type  $\text{AB}_2$ :  $\text{AB}_2(\text{s}) \rightleftharpoons \text{A}^{+2} + 2\text{B}^-$ ; where  $s$  is solubility of salts in  $\text{mol L}^{-1}$

$$K_{\text{sp}} = [\text{A}^{2+}][\text{B}^-]^2 = s \cdot (2s)^2 = 4s^3 ; \quad s = \sqrt[3]{\frac{K_{\text{sp}}}{4}}$$

- Solubility of salt decrease in presence of common ion.** For an example solubility of  $\text{Ag}_2\text{CrO}_4$  will decrease if  $\text{AgNO}_3$  is added to the solution.
- Solubility of salt increases due to complex formation

Let the solubility of  $\text{AgCl}$  is  $s \text{ mol L}^{-1}$



$$K_f = \frac{x}{(s-x)(c-2x)} ; \text{ where } K_f \text{ is equilibrium constant for the formation of complex.}$$

## 2002

1. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is  
(1) not a buffer solution with  $\text{pH} < 7$                       (2) not a buffer solution with  $\text{pH} > 7$   
(3) a buffer solution with  $\text{pH} < 7$                               (4) a buffer solution with  $\text{pH} > 7$
2. Species acting as both Bronsted acid and base is  
(1)  $(\text{HSO}_4)^{-1}$     (2)  $\text{Na}_2\text{CO}_3$   
(3)  $\text{NH}_3$     (4)  $\text{OH}^{-1}$
3. Let the solubility of an aqueous solution of  $\text{Mg}(\text{OH})_2$  be  $x$  then its  $K_{sp}$  is  
(1)  $4x^3$     (2)  $108x^5$   
(3)  $27x^4$     (4)  $9x$
4. Change in volume of the system does not alter the number of moles in which of the following equilibria ?  
(1)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$                       (2)  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
(3)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$                       (4)  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$
5. In which of the following reactions, increase in the volume at constant temperature does not affect the number of moles at equilibrium  
(1)  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$                       (2)  $\text{C}(\text{g}) + (1/2)\text{O}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g})$   
(3)  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$                       (4) None of these
6. For the reaction  $\text{CO}(\text{g}) + (1/2)\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ ,  $\frac{K_p}{K_c}$  is equal to  
(1)  $RT$     (2)  $(RT)^{-1}$   
(3)  $(RT)^{-1/2}$     (4)  $(RT)^{1/2}$

## 2003

7. Which one of the following statements is not true?
- (1)  $\text{pH} + \text{pOH} = 14$  for all aqueous solutions      (2) The pH of  $1 \times 10^{-8}$  M HCl is 8  
 (3) 96,500 coulombs of electricity when passed through a  $\text{CuSO}_4$  solution deposits 1 gram equivalent of copper at the cathode  
 (4) The conjugate base of  $\text{H}_2\text{PO}_4^{-1}$  is  $\text{HPO}_4^{2-}$
8. For the reaction equilibrium  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium are  $4.8 \times 10^{-2}$  and  $1.2 \times 10^{-2}$  mol  $\text{L}^{-1}$  respectively. Value of  $K_c$  for the reaction is
- (1)  $3 \times 10^{-1}$  mol  $\text{L}^{-1}$       (2)  $3 \times 10^{-3}$  mol  $\text{L}^{-1}$   
 (3)  $3 \times 10^3$  mol  $\text{L}^{-1}$       (4)  $3.3 \times 10^2$  mol  $\text{L}^{-1}$
9. Consider the reaction equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}); \Delta H^\circ = -198$  kJ. On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is
- (1) increasing temperature as well as pressure  
 (2) lowering the temperature and increasing the pressure  
 (3) any value of temperature and pressure  
 (4) lowering of temperature as well as pressure

2004

10. The conjugate base of  $\text{H}_2\text{PO}_4^-$  is
- (1)  $\text{PO}_4^{3-}$       (2)  $\text{HPO}_4^{2-}$   
 (3)  $\text{H}_3\text{PO}_4$       (4)  $\text{P}_2\text{O}_5$
11. What is the equilibrium expression for the reaction  $\text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightleftharpoons \text{P}_4\text{O}_{10}(\text{s})$ ?
- (1)  $K_c = \frac{[\text{P}_4\text{O}_{10}]}{[\text{P}_4][\text{O}_2]^5}$       (2)  $K_c = \frac{1}{[\text{O}_2]^5}$   
 (3)  $K_c = [\text{O}_2]^5$       (4)  $K_c = \frac{[\text{P}_4\text{O}_{10}]}{5[\text{P}_4][\text{O}_2]}$
12. For the reaction,  $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$  the  $\frac{K_p}{K_c}$  is equal to
- (1)  $\frac{1}{RT}$       (2) 1.0  
 (3)  $\sqrt{RT}$       (4) RT

13. The equilibrium constant for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction  $\text{NO}(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$  at the same temperature is
- (1)  $2.5 \times 10^2$  (2) 0.02  
 (3)  $4 \times 10^{-4}$  (4) 50
14. The molar solubility product of  $\text{MX}_4$  is  $K_{sp}$ . 's' is given in terms of  $K_{sp}$  by the relation
- (1)  $s = \left(\frac{K_{sp}}{128}\right)^{1/4}$  (2)  $s = \left(\frac{K_{sp}}{256}\right)^{1/5}$   
 (3)  $s = (128K_{sp})^{1/4}$  (4)  $s = (256K_{sp})^{1/5}$

## 2005

15. The solubility product of a salt having general formula  $\text{MX}_2$ , in water is:  $4 \times 10^{-12}$ . The concentration of  $\text{M}^{2+}$  ions in the aqueous solution of the salt is
- (1)  $2.0 \times 10^{-6} \text{ M}$  (2)  $1.0 \times 10^{-4} \text{ M}$   
 (3)  $1.6 \times 10^{-6} \text{ M}$  (4)  $4.0 \times 10^{-10} \text{ M}$
16. For the reaction  $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  ( $K_c = 1.8 \times 10^{-5}$  at  $184^\circ \text{C}$ )  
 ( $R = 0.0831 \text{ kJ / (mol.K)}$ )  
 When  $K_p$  and  $K_c$  are compared at  $184^\circ \text{C}$ , it is found that
- (1)  $K_p$  is greater than  $K_c$  (2)  $K_p$  is less than  $K_c$   
 (3)  $K_p = K_c$   
 (4) Whether  $K_p$  is greater than, less than or equal to  $K_c$  depends upon the total gas pressure
17. Hydrogen ion concentration in mol / L in a solution of  $\text{pH} = 5.4$  will be
- (1)  $3.98 \times 10^8$  (2)  $3.88 \times 10^6$   
 (3)  $3.68 \times 10^{-6}$  (4)  $3.98 \times 10^{-6}$
18. An amount of solid  $\text{NH}_4\text{HS}$  is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm. Pressure. Ammonium hydrogen sulphide decomposes to yield  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for  $\text{NH}_4\text{HS}$  decomposition at this temperature is
- (1) 0.30 (2) 0.18  
 (3) 0.17 (4) 0.11

## 2006

19. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel,  
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ . If total pressure at equilibrium of the reaction mixture is P

and degree of dissociation of  $\text{PCl}_5$  is "x", the partial pressure of  $\text{PCl}_3$  will be

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

(2)  $\left(\frac{2x}{1-x}\right)P$

(3)  $\left(\frac{x}{x-1}\right)P$

(4)  $\left(\frac{x}{1-x}\right)P$

20. Which of the following statements is true?

- (1)  $\text{H}_3\text{PO}_3$  is a stronger acid than  $\text{H}_2\text{SO}_3$   
 (2) In aqueous medium HF is a stronger acid than HCl  
 (3)  $\text{HClO}_4$  is a weaker acid than  $\text{HClO}_3$   
 (4)  $\text{HNO}_3$  is a stronger acid than  $\text{HNO}_2$

21. The equilibrium constant for the reaction  $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  is

$K_c = 4.9 \times 10^{-2}$ . The value of  $K_c$  for the reaction  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$  will be

(1) 416

(2)  $2.40 \times 10^{-3}$

(3)  $9.8 \times 10^{-2}$

(4)  $4.9 \times 10^{-2}$

2007

22. The  $\text{pK}_a$  of a weak acid (HA) is 4.5. The  $\text{pOH}$  of an aqueous buffered solution of HA in which 50% of the acid is ionized is

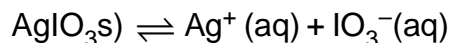
(1) 4.5

(2) 2.5

(3) 9.5

(4) 7.0

23. In a saturated solution of the sparingly soluble strong electrolyte  $\text{AgIO}_3$  (Molecular mass = 283) the equilibrium which sets in is



If the solubility product constant  $K_{sp}$  of  $\text{AgIO}_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $\text{AgIO}_3$  contained in 100 ml of its saturated solution?

(1)  $28.3 \times 10^{-2}$  g

(2)  $2.83 \times 10^{-3}$  g

(3)  $1.0 \times 10^{-7}$  g

(4)  $1.0 \times 10^{-4}$  g



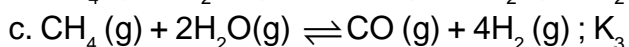
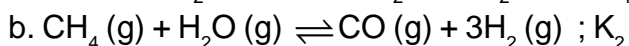
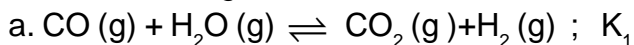
24. The first and second dissociation constants of an acid  $H_2A$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be
- (1)  $5.0 \times 10^{-5}$  (2)  $5.0 \times 10^{-15}$   
 (3)  $5.0 \times 10^{15}$  (4)  $5.0 \times 10^5$

2008

25. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  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 pressure at these equilibria is

- (1) 1 : 36 (2) 1 : 1  
 (3) 1 : 3 (4) 1 : 9

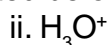
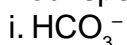
26. For the following three reactions a, b and c, equilibrium constants are given:



Which of the following relations is correct?

- (1)  $K_1 \sqrt{K_2} = K_3$  (2)  $K_2 K_3 = K_1$   
 (3)  $K_3 = K_1 K_2$  (4)  $K_3 (K_2)^3 = (K_1)^2$

27. Four species are listed below



Which one of the following is the correct sequence of their acid strength?

- (1)  $iv < ii < iii < i$  (2)  $ii < iii < i < iv$   
 (3)  $i < iii < ii < iv$  (4)  $iii < i < iv < ii$

28. The  $pK_a$  of a weak acid, HA, is 4.80. The  $pK_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be

- (1) 9.58 (2) 4.79  
 (3) 7.01 (4) 9.22

2009.

29. Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form? ( $K_{sp}$  for  $\text{BaCO}_3 = 5.1 \times 10^{-9}$ ).
- (1)  $4.1 \times 10^{-5} \text{ M}$  (2)  $5.1 \times 10^{-5} \text{ M}$   
 (3)  $8.1 \times 10^{-8} \text{ M}$  (4)  $8.1 \times 10^{-7} \text{ M}$

2010

30. Three reactions involving  $\text{H}_2\text{PO}_4^-$  are given below :
- (i)  $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$  (ii)  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$   
 (iii)  $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}_2^-$
- In which of these does  $\text{H}_2\text{PO}_4^-$  act as an acid?
- (1) (ii) only (2) (i) and (ii) only  
 (3) (iii) only (4) (i) only

31. In aqueous solution the ionization constants for carbonic acid are  $K_1 = 4.2 \times 10^{-7}$  and  $K_2 = 4.8 \times 10^{-11}$ . Select the correct statement for a saturated  $0.034 \text{ M}$  solution of the carbonic acid.
- (1) The concentration of  $\text{CO}_3^{2-}$  is  $0.034 \text{ M}$ .  
 (2) The concentration of  $\text{CO}_3^{2-}$  is greater than that of  $\text{HCO}_3^-$ .  
 (3) The concentration of  $\text{H}^+$  and  $\text{HCO}_3^-$  are approximately equal.  
 (4) The concentration of  $\text{H}^+$  is double that of  $\text{CO}_3^{2-}$

2011

32. The  $K_{sp}$  of  $\text{Cr}(\text{OH})_3$  is  $1.6 \times 10^{-30}$ , the molar Solubility of the compound in water is:

- (1)  $\sqrt[3]{1.6 \times 10^{-30}}$  (2)  $\left(\frac{1.6 \times 10^{-30}}{27}\right)^{1/4}$   
 (3)  $\left(\frac{1.6 \times 10^{-30}}{27}\right)^{1/2}$  (4)  $\left(\frac{1.6 \times 10^{-30}}{27}\right)$

33. An acid  $\text{HA}$  ionises as  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ . The pH of  $1.0 \text{ M}$  solution is 5. Its dissociation constant would be
- (1) 5 (2)  $5 \times 10^{-8}$   
 (3)  $1 \times 10^{-5}$  (4)  $1 \times 10^{-10}$

## 2011 (retest)

34. A vessel at 1000 K contains  $\text{CO}_2$  with a pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is
- (1) 3 atm (2) 0.3 atm  
(3) 0.18 atm (4) 1.8 atm

## 2012

35. The equilibrium constant ( $K_c$ ) for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction,  $\text{NO}(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  at the same temperature is :
- (1) 0.02 (2)  $2.5 \times 10^2$   
(3)  $4 \times 10^{-4}$  (4) 50

## 2013

36. How many litres of water must be added to 1 litre of an aq. solution of HCl with a pH of 1 to create an aq. solution with pH of 2 ?
- (1) 0.1 L (2) 0.9 L  
(3) 2.0 L (4) 9.0 L

## 2014

37. For the reaction  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ , if  $K_p = K_c(\text{RT})^x$  where the symbols have the usual meaning then the value of "x" is : (assuming ideality)
- (1) -1 (2)  $-\frac{1}{2}$   
(3)  $\frac{1}{2}$  (4) 1
38. Among the following oxacids, the correct order of acid strength is :
- (1)  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$  (2)  $\text{HClO}_4 > \text{HClO} > \text{HClO}_2 > \text{HClO}_3$   
(3)  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$  (4)  $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HClO}$

## 2015

39. The standard Gibbs energy change at 300 K for the reaction  $2\text{A} \rightleftharpoons \text{B} + \text{C}$  is 2494.2 J. At a given time, the composition of the reaction mixture is  $[\text{A}] = 1/2$ ,  $[\text{B}] = 2$  and  $[\text{C}] = 1/2$ . The reaction proceed in the
- (1) Forward direction because  $Q > K_c$  (2) Reverse direction because  $Q > K_c$   
(3) Forward direction because  $Q < K_c$  (4) Reverse direction because  $Q < K_c$

1. For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , the equilibrium constant  $K_p$  changes with  
(1) total pressure (2) catalyst  
(3) the amount of  $\text{H}_2$  and  $\text{I}_2$  present (4) temperature
2. The pH of  $10^{-8}$  M solution of HCl in water is  
(1) 8 (2) -8  
(3) between 7 and 8 (4) between 6 and 7
3. At  $90^\circ\text{C}$ , pure water has  $[\text{H}_3\text{O}^+]$  as  $10^{-6}$  mol  $\text{L}^{-1}$ . What is the value of  $K_w$  at  $90^\circ\text{C}$   
(1)  $10^{-6}$  (2)  $10^{-12}$   
(3)  $10^{-14}$  (4)  $10^{-8}$
4. Of the given anions, the strongest base is  
(1)  $\text{ClO}^-$  (2)  $\text{ClO}_2^-$   
(3)  $\text{ClO}_3^-$  (4)  $\text{ClO}_4^-$
5. Ammonia (pure) is placed in a vessel at a temperature where its dissociation constant ( $\alpha$ ) is appreciable. At equilibrium  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$   
(1)  $K_p$  does not change significantly with pressure  
(2)  $\alpha$  does not change with pressure  
(3) Concentration of  $\text{NH}_3$  does not change with pressure  
(4) Concentration of hydrogen is less than that of nitrogen
6. A buffer solution contains equal concentration of  $\text{X}^-$  and  $\text{HX}$ ,  $K_a$  for  $\text{X}^-$  is  $10^{-10}$ . Then pH of buffer is :  
(1) 4 (2) 7  
(3) 10 (4) 14
7. A weak acid with dissociation constant of  $10^{-4}$ , equilibrium constant of its reaction with a strong base is :  
(1)  $10^{-4}$  (2)  $10^{-10}$   
(3)  $10^{10}$  (4)  $10^{14}$
8. Indicator of end point of titration of a weak acid and strong base is :  
(1) methyl orange (3 to 4) (2) methyl red (5 to 6)  
(3) bromothymol (6 to 7.5) (4) phenolphthalein (8 to 9.6)
9. The conjugate acid of  $\text{NH}_2^-$  is :  
(1)  $\text{NH}_3$  (2)  $\text{NH}_2\text{OH}$   
(3)  $\text{NH}_4^+$  (4)  $\text{N}_2\text{H}_4$

10. Which one is not a Lewis acid:  
(1)  $\text{BF}_3$  (2)  $\text{AlCl}_3$   
(3)  $\text{BeCl}_2$  (3)  $\text{SnCl}_4$
11.  $\text{pK}_a$  of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about "8". Aspirin will be  
(1) unionised in the small intestine and in the stomach  
(2) completely ionised in the small intestine and in the stomach  
(3) ionised in stomach and almost unionised in the small intestine  
(4) ionised in small intestine and almost unionised in the stomach
12. If equal volumes of the following are mixed, precipitation of  $\text{AgCl}$  ( $K_{\text{sp}} = 1.8 \times 10^{-10}$ ) will occur only in:  
(1)  $10^{-4} \text{ M (Ag}^+) \text{ and } 10^{-4} \text{ M (Cl}^-)$  (2)  $10^{-5} \text{ M (Ag}^+) \text{ and } 10^{-5} \text{ M (Cl}^-)$   
(3)  $10^{-6} \text{ M (Ag}^+) \text{ and } 10^{-6} \text{ M (Cl}^-)$  (4)  $10^{-10} \text{ M (Ag}^+) \text{ and } 10^{-10} \text{ M (Cl}^-)$
13. Which of the following is the strongest acid?  
(1)  $\text{ClO}_3(\text{OH})$  (2)  $\text{ClO}_2(\text{OH})$   
(3)  $\text{SO}(\text{OH})_2$  (3)  $\text{SO}_2(\text{OH})_2$
14. Which of the following hydroxide has the lowest value of  $K_{\text{sp}}$  at  $25^\circ \text{C}$ ?  
(1)  $\text{Mg}(\text{OH})_2$  (2)  $\text{Ca}(\text{OH})_2$   
(3)  $\text{Ba}(\text{OH})_2$  (4)  $\text{Be}(\text{OH})_2$
15. Which of the following solution will have pH close to 1.0?  
(1) 100 ml of M/10 HCl + 100 ml of M/10 NaOH  
(2) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
(3) 10 ml of M/10 HCl + 90 ml of M/10 NaOH  
(4) 75 ml of M/5 HCl + 25 ml of M/5 NaOH
16. One mole of  $\text{N}_2\text{O}_4$  (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of  $\text{N}_2\text{O}_4$  decompose into  $\text{NO}_2$  (g). The resultant pressure is:  
(1) 1.2 atm (2) 2.4 atm  
(3) 2.0 atm (4) 1.0 atm
17. For the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  at a given temperature, the equilibrium amount of  $\text{CO}_2$  (g) can be increased by  
(1) adding a suitable catalyst (2) adding an inert gas  
(3) decreasing volume of container (4) increasing the amount of  $\text{CO}(\text{g})$

- (1)  $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$   
 (3)  $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
- (2)  $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$   
 (4)  $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
19. For the chemical reaction  $3\text{X}(\text{g}) + \text{Y}(\text{g}) \rightleftharpoons \text{X}_3\text{Y}(\text{g})$ ; the amount of  $\text{X}_3\text{Y}$  at equilibrium is affected by  
 (1) temperature and pressure  
 (2) temperature only  
 (3) pressure only  
 (4) temperature, pressure and catalyst
20. For the reversible reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  at  $500^\circ\text{C}$ , the value of  $K_p$  is  $1.44 \times 10^{-5}$  when partial pressure is measured in atmosphere. The corresponding value of  $K_c$  with concentration in mol/L is :  
 (1)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$   
 (2)  $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$   
 (3)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$   
 (4)  $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$
21. When two reactants, A and B are mixed to give products, C and D, the reaction quotient, Q at the initial stages of the reaction  
 (1) is zero  
 (2) decreases with time  
 (3) is independent of time  
 (4) increases with time
22. At constant temperature, the equilibrium constant ( $K_p$ ) for the decomposition reaction ,  
 $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , is expressed by  $K_p = \frac{4x^2p}{(1-x^2)}$ , where p = pressure, x = extent of decomposition. Which one of the following statements is true ?  
 (1)  $K_p$  increases with increase of "p"  
 (2)  $K_p$  increases with increase of "x"  
 (3)  $K_p$  increases with decrease of x  
 (4)  $K_p$  remains constant with change in "p" and "x"
23. For a sparingly soluble salt  $\text{A}_p\text{B}_q$ , the relationship of its solubility product ( $L_s$ ) with its solubility (S) is  
 (1)  $L_s = S^{p+q} \cdot p^p \cdot q^q$   
 (2)  $L_s = S^{p+q} \cdot p^q \cdot q^p$   
 (3)  $L_s = S^{pq} \cdot p^p \cdot q^q$   
 (4)  $L_s = S^{pq} \cdot (pq)^{q+p}$
24. A solution,  $10^{-3}$  M each in  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  is treated with  $10^{-16}$  M sulphide ion. If  $K_{sp}$  of  $\text{MnS}$ ,  $\text{FeS}$ ,  $\text{ZnS}$  and  $\text{HgS}$  are  $10^{-15}$ ,  $10^{-23}$ ,  $10^{-20}$  and  $10^{-54}$  respectively, which one will precipitate first ?  
 (1)  $\text{FeS}$   
 (2)  $\text{MgS}$   
 (3)  $\text{ZnS}$   
 (4)  $\text{HgS}$

25. HX is a weak acid ( $K_a = 10^{-5}$ ). It forms a salt NaX (0.1M) on reacting with caustic Soda. The degree of hydrolysis of NaX is  
 (1) 0.01% (2) 0.0001%  
 (3) 0.1% (4) 0.5%
26.  $\text{CH}_3\text{NH}_2$  (0.1 mole,  $K_b = 5 \times 10^{-4}$ ) is added to 0.08 moles of HCl and this solution is diluted to one litre, resulting hydrogen ion concentration as  
 (1)  $1.6 \times 10^{-11}$  (2)  $8 \times 10^{-11}$   
 (3)  $5 \times 10^{-5}$  (4)  $8 \times 10^{-2}$
27.  $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)^+]$  ;  $k_1 = 3.5 \times 10^{-3}$   
 $[\text{Ag}(\text{NH}_3)^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2^+]$  ;  $k_2 = 1.7 \times 10^{-3}$
- Formation constant of  $[\text{Ag}(\text{NH}_3)_2^+]$  is  
 (1)  $6.08 \times 10^{-6}$  (2)  $6.08 \times 10^6$   
 (3)  $6.08 \times 10^{-9}$  (3) None of these
28.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ; which of the following is correct?  
 (1) The equilibrium will shift to forward direction, the reason being that as per IInd law of thermodynamics, entropy must increase in the direction of spontaneous reaction  
 (2) The condition for equilibrium is  $G(\text{N}_2) + 3G(\text{H}_2) = 2G(\text{NH}_3)$ , where "G" is Gibbs free energy per mole of gaseous species measured at that partial pressure. The condition of equilibrium is not affected by the use of the catalyst, which increases the rate of both forward and backward reactions to the same extent.  
 (3) The catalyst will increase the rate of forward reaction by  $\alpha$  and that of backward reaction by  $\beta$   
 (4) Catalyst will not alter the rate of either reaction.

2006

29. The species present in solution when  $\text{CO}_2$  is dissolved in water are  
 (1)  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  (2)  $\text{H}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$   
 (3)  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  (4)  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$

2008

30. Solubility product constant ( $K_{sp}$ ) of salts of types MX,  $\text{MX}_2$  and  $\text{M}_3\text{X}_2$  at temperature "T" are  $4.0 \times 10^{-8}$ ,  $3.2 \times 10^{-14}$  and  $2.7 \times 10^{-15}$  respectively. Solubilities ( $\text{mol dm}^{-3}$ ) of the salts at temperature "T" are in order  
 (1)  $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$  (2)  $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$   
 (3)  $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$  (4)  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

2008

31. 2.5 mL of  $\frac{2}{5}$  M weak monoacidic base ( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with  $\frac{2}{15}$  M HCl in water at  $25^\circ\text{C}$ . The concentration of  $\text{H}^+$  at equivalence point is ( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ )
- (1)  $3.7 \times 10^{-13}$  M (2)  $3.2 \times 10^{-7}$  M  
 (3)  $3.2 \times 10^{-2}$  M (4)  $2.7 \times 10^{-2}$  M

2010

32. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is :  
 KCN,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{FeCl}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NH}_4\text{NO}_3$ , LiCN
- (1) 1 (2) 2  
 (3) 3 (4) 4

2009

33. The dissociation constant of a substituted benzoic acid at  $25^\circ\text{C}$  is  $1.0 \times 10^{-4}$ . The pH of 0.01 M solution of its sodium salt is
- (1) 6 (2) 7  
 (3) 5 (4) 8

2010

34. The total number of diprotic acids among the following is  
 $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{SO}_3$
- (1) 6 (2) 7  
 (3) 5 (4) 8

2011

35. In 1 L saturated solution of AgCl ( $K_{sp} = 1.6 \times 10^{-10}$ ), 0.1 mole of CuCl ( $K_{sp} = 1.0 \times 10^{-6}$ ) is added. the resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$ . The value of "x" is :
- (1) 6 (2) 7  
 (3) 5 (4) 8

2013

36. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M) at  $25^\circ\text{C}$ . The  $K_a$  of HA is
- (1)  $1 \times 10^{-4}$  (2)  $1 \times 10^{-5}$   
 (3)  $1 \times 10^{-6}$  (3)  $1 \times 10^{-3}$

37. The  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298 K. The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a



01 M  $\text{AgNO}_3$  solution is

- (1)  $1.1 \times 10^{-11}$   
(3)  $1.1 \times 10^{-12}$

- (2)  $1.1 \times 10^{-10}$   
(4)  $1.1 \times 10^{-9}$

2015

38 100 ml of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) is mixed with 100 ml 1.0 M NaOH, the pH of the solution is :

- (1) 2.8  
(3) 24.5

- (2) 4.7  
(4) 51.4

STP CLASSES

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**JEE Main / AIEEE Questions :**

1.(1)	2.(1)	3.(1)	4.(1)	5.(4)	6.(3)
7.(2)	8.(2)	9.(2)	10.(2)	11.(2)	12.(1)
13.(2)	14.(2)	15.(2)	16.(1)	17.(4)	18.(4)
19.(1)	20.(4)	21.(1)	22.(3)	23.(2)	24.(2)
25.(1)	26.(3)	27.(3)	28.(3)	29.(2)	30.(1)
31.(3)	32.(1)	33.(4)	34.(4)	35.(4)	36.(4)
37.(2)	38.(3)	39.(2)			

**JEE Advanced Single Option :**

1.(4)	2.(4)	3.(2)	4.(1)	5.(1)	6.(1)
7.(3)	8.(4)	9.(1)	10.(3)	11.(4)	12.(1)
13.(1)	14.(2)	15.(4)	16.(2)	17.(4)	18.(2)
19.(1)	20.(4)	21.(4)	22.(4)	23.(1)	24.(4)
25.(1)	26.(2)	27.(1)	28.(2)	29.(1)	30.(4)
31.(4)	32.(3)	33.(4)	34.(1)	35.(4)	36.(1)
37.(2)	38.(2)				

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STP CLASSES