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FIVE IMPORTANT CONCEPTS OF CHEMISTRY FOR JEE MAIN

1. LE CHATELIER'S PRINCIPLE AND SOLUBILITY PRODUCT

Le Chatelier's Principle and Factors Affecting Equilibria

A change in temperature, pressure and concentration alters the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium, we use the Le-Chatelier's principle.

According to this principle, "If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shift in a direction that tends to undo the effect of the change".

(i) Effect of change in concentration :

When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes. For a general reaction,

 $aA + bB \rightleftharpoons cC + dD$

$$Q_{c} = \frac{\left[C\right]^{c} \left[D\right]^{d}}{\left[A\right]^{a} \left[B\right]^{b}}$$

at equilibrium, $K_c = Q_c = \frac{\left[C\right]^c \left[D\right]^d}{\left[A\right]^a \left[B\right]^b}$

If conc. of reactants are increased, $Q_c < K_c$. Thus, to attain equilibrium again, reaction proceeds in forward direction.

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If conc. of products are increased, $Q_c > K_c$. Thus, to attain equilibrium again, reaction proceeds in backward direction.

(ii) Effect of pressure change

If the pressure is increased, then according to Le-Chatelier's principle, then the reaction proceeds in the direction where the no. of moles (or pressure) is decreased (pressure is proportional to moles of gas).

(iii) Effect of Inert Gas addition

If the inert gas is added at constant volume, the equilibrium remains undisturbed. This is because the addition of an inert gas at constant volume does not change the partial pressures or molar concentrations of the substance involved in the reaction.

When an inert gas is added to the equilibrium system at constant pressure, then the volume will increase. As a result, the number of moles per unit volume of various reactants and products will decrease. hence, the equilibrium will shift in a direction in which there is increase in number of moles of gases.

(iv) Effect of temperature change

The temperature dependence of equilibrium constant depends on the sign of ΔH for the reaction.

The equilibrium constant for an exothermic reaction (negative ΔH) decreases as temperature increases. The reaction then proceeds in backward direction.

The equilibrium constant for an endothermic reaction (+ve Δ H) increases as temperature increases. The reaction then proceeds in forward direction.

(v) Effect of a catalyst

A catalyst increases the rate of forward and backward reactions to same extent. It lowers the activation energy for forward and backward reactions by same amount thus catalyst helps in attaing equilibrium quickly and it does not affect the equilibrium composition of the reaction mixture.



Solubility Product (K_{sp}) :

At constant temperature and pressure the saturated solution of a sparingly soluble salt has an equilibrium between the excess of the solute and the ions furnished by it. e.g.

 AgCl
 AgCl $Ag^+ + Cl^-$

 Solid
 dissolved but
 ions in sol.

 undissolved not ionised
 $Ag^+ + Cl^-$

Applying law of mass action, $K = \frac{[Ag^+][Cl^-]}{[AgCl]}$

or $K[AgCl] = [Ag^+] [Cl^-], K_{sp} = [Ag^+] [Cl^-]$

The constant K_{sp} is known as solubility product. It is equal to the product of the concentration of ions in saturated solution.

When $K_{sp} > [Ag^+] [Cl^-]$ Solution is not saturatedWhen $K_{sp} < [Ag^+] [Cl^-]$ Solution is supersaturated

and precipitation takes place Solution is saturated

When $K_{sp} = [Ag^+] [Cl^-]$ For general electrolyte $A_x B_y$.

 $K_{sp} = [A^{+y}]^x [B^{-x}]^y$

- (I) K_{sp} is independent of the source of ions.
- (II) Helps to know the solubility of electrolytes.
- (III) Predicting ionic reactions.
- (IV) Qualitative analysis.

(V) Purification of common salt, salting out of soap and Solvay ammonia soda process.

- Relation between solubility product (\mathbf{K}_{sp}) and solubility (S).
- 1. For binary electrolyte e.g. AgCl, $BaSO_4$

$$S = \sqrt{K_{sp}}$$

2. For ternary electrolyte e.g. CaF_2 , PbI_2 S =

Representation of K_{sp} for various electrolytes. Mg(OH)₂ $K_{sp} = [Mg^{++}] [OH^{-}]^2$

 Ag_2S $K_{sp} = [Ag^+]^2 [S^{--}]$

 Sb_2S_3 $K_{sp} = [Sb^{3+}]^2 [S^{-1}]^3$

- *Ex.*: K_{sp} of AgCl is 2.8×10^{-10} at 25°C. Calculate the solubility of AgCl in (I) Pure Water (II) 0.1 M AgNO₃ solution (III) 0.1 M NaCl.
- **Sol.** (I) Let S mole/l be the solubility of AgCl $K = [A \alpha^{+1}|C|^{-1} = S \times S = S^{2}$.

$$\mathbf{K}_{\rm sp} = [Ag^{-}][CI] = \mathbf{S} \times \mathbf{S} = \mathbf{S}^{-};$$

$$\therefore$$
 S = $\sqrt{K_{sp}} = \sqrt{2.8 \times 10^{-10}} = 1.67 \times 10^{-5} \text{ mol}/1$

(II) AgCl $Ag^+ + Cl^ K_{sp} = [Ag^+] [Cl^-]$

Solubility of AgCl will be equal to

$$[CI^-] = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ mol}/1$$

(III)Solubility of AgCl will be equal to

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ mol}/1$$



 $\textit{Sol.:} \qquad \text{SrF}_2 \implies \text{Sr}^{++} + 2\text{F}^-$

Solubility of SrF_2 will be equal to

$$[\mathbf{Sr}^{++}] = \frac{\mathbf{K}_{\rm sp}}{[\mathbf{F}^{-}]^2} = \frac{8 \times 10^{-10}}{(0.1)^2} = 8 \times 10^{-8} \,\mathrm{mol/lit}$$

2. HYBRIDISATION

According to Pauling, the atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. It is these hybrid orbitals which are used in bond formation. The phenomenon is known as hybrid isation.

Features of Hybridisation

- (i) The number of hybrid orbitals is equal to the number of atomic orbitals that get hybridised.
- (ii) The hybridised orbitals are always equal in energy and shape.
- (iii) The hybrid orbitals are more effective in forming stable bonds than pure atomic orbitals.
- (iv) The type of hybridisation indicates the geometry of molecules.

Conditions of Hybridisation

- (i) The orbitals present in valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

Depending upon the type and number of orbitals involved in intermixing, the hybridization can be of various types namely sp, sp^2 , sp^3 , sp^3d , dsp^2 , sp^3d^2 , sp^3d^3 .

Method for Finding the Type of Hybridisation

The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation :

$$H = \frac{1}{2}(V + M - C + A)$$

where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp, sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3 respectively.

- V = Number of electrons in valence shell of the central atom,
- M = Number of monovalent atoms,
- C = Charge on cation,
- A = Charge on anion.

Shape of	Hybridisation	Atomic	Evomulos
molecule ion 📏	Туре	orbitals	Examples
Linear	sp	s + p	$BeCl_2, C_2H_2, CO_2, HgCl_2,$
Trigonal planar	sp ²	s + p(2)	$\operatorname{SnCl}_2, \operatorname{CO}_3^{2-}$
Tetrahedral	sp ³	s + p(3)	CH_4 , H_2O , NH_3
Square planar	dsp ²	d + s + p(2)	$\left[\operatorname{Ni}(\operatorname{CN})_{4}\right]^{2-}, \left[\operatorname{PtCl}_{2}\right]^{2-}$
Trigonal bipyramidal	sp ³ d	s+p(3)+d	PF_5, PCl_5
Square pyramidal	sp ³ d ²	s+p(3)+d(2)	BrF5
Octahedral	sp^3d^2 , d^2sp^3	s+p(3)+d(2), d(2)+s+p(3)	$SF_6[CrF_6]^{3-}$
Pentagonal bipyramidal	sp ³ d ³	s+p(3)+d(3)	IF ₇

3. CRYSTAL FIELD THEORY FOR OCTAHEDRAL COMPLEXES

When a ligand approaches the metal ion, the 'd' orbitals of the metal ion undergo splitting forming two sets i.e., higher energy set, e_g of $d_{x^2-y^2}$ and d_{z^2} and a lower energy set, t_{2g} of d_{xy} , d_{yz} , and d_{xz}

This is shown diagrammatically as:





The difference of energy between the two sets of d-orbitals is called crystal field splitting energy or crystal field stabilization energy (CFSE). It is usually represented by the symbol Δ_0 . For any given metal cation, the magnitude of Δ_0 depends upon the nature of the ligands

Spectro chemical series

In general, ligands can be arranged in a series in order of increasing field strength as given below: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^-$

$$< C_2 O_4^{2-} < O^{2-} < H_2 O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^{-2} < CN^- < CO$$

This series is called spectrochemical series.

Pairing of the two sets of d-orbital depends on the magnitude of Δ_0 and P ($\Delta_0 \rightarrow$, CFSE and P \rightarrow pairing energy)

If $\Delta_0 > P$, EC is $t_{2g}^{4} e_g^0$. Upto d^6 pairing will occur in the t_{2g} and e_g . will remain vacant. Ligands which produce this effect are called **strong field ligands** and form **low spin complex**.

If $\Delta_0 < P$, EC is $t_{2g}^3 e_g^1$. For d^5 configuration $t_{2g}^3 e_g^2$ ligands which produce this effect are called **weak field ligands** and form high spin complexes.

For **tetrahedral complex**, $\Delta_t = \frac{4}{9} \Delta_0$

Splitting pattern for tetrahedral complexes is just the reverse of the splitting patterns of the octahedral complexes Δ_t is so small that it is unable to force the electrons to pair up.

Here, energy of $e_g < energy of t_{2g}$. Colour of the complexes

The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of d-orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region. As the result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured.

Different complexes exhibit different colours when either metal is different or ligands are different.

In absence of ligand, crystal field splitting does not occur and hence, the substance is colourless. For ex: $CuSO_4$. $5H_2$ O is blue but anhydrous $CuSO_4$ is white.

The size of Δ depends on -

Nature of the ligand : In Spectrochemical series Δ decreases as shown below (i)

$$I^- < Br^- < Cl^- < OH^- < F^- < C_2O_4^{2-} < H_2O < CNS^- < < NH_3 < en < NO_2^- < CN^- < CO$$
weak ligands strong ligands

- (ii) **Oxidation state of the metal :** Δ is greater for M³⁺ than for M²⁺
- (iii) **Position of the metal in the periodic table:** For a given ligand and oxidation state of the metal, Δ increases going down in a group eg.

 Δ is greater in [Ru (NH₃)₆]³⁺ than in [Fe(NH₃)₆]³⁺

4. REACTION INTERMEDIATES

Free Radicals



$$\stackrel{|}{-} \stackrel{-}{-} \stackrel{-}{-} \stackrel{-}{-} X \xrightarrow{\text{Homolytic fission}} - \stackrel{|}{-} \stackrel{+}{-} \stackrel{+}{-} \stackrel{+}{-} X^{\bullet}$$

If EN of C
$$\simeq$$
 EN of X

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It is an atom or group of atoms possessing an odd or unpaired electron. It is electrically neutral and shows paramagnetism. **Stability of free radicals is due to following reasons :** (i) Resonance (ii) Hyperconjugation **Order of stability of free radicals :** t-butyl > isopropyl > ethyl > methyl **Stability on the basis of resonance :** Stability \propto Number of resonating structures **The order is :** $(\Phi)_3 C \cdot > (\Phi)_2 CH \cdot > \Phi CH_2 \cdot > CH_2 = CH - CH_2 \cdot$ $[where \phi = C_6 H_5]$ Carbonium ion or Carbocation $-C \oplus (D \oplus C) + X \oplus (D \oplus C) +$

If EN of X > EN of C

Organic species containing positively charged carbon atom is known as carbonium ion. The positively charged carbon atom contains six electrons in its valence shell.

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Stability of carbonium ions :

Stability of carbocation $\propto +I \propto \frac{1}{-I}$ e.g. (i) $CH_3 - CH_2 > CH_3 > NO_2 - CH_2$ (ii) $(C_6H_5)_3 \stackrel{\oplus}{C} > (C_6H_5)_2 \stackrel{\oplus}{CH} > C_6H_5 \stackrel{\oplus}{CH}_2$

 $CH_2 = CH - CH_2 > 3^\circ > 2^\circ > 1^\circ > CH_3$

 $\overset{\oplus}{>} CH_2 = CH - \overset{\oplus}{CH_2} > 3^\circ > 2^\circ > 1^\circ > \overset{\oplus}{CH_3}$ Stability \propto No. of resonating structures

Carbanion $\begin{bmatrix} | \\ -C : -\Theta \\ | \end{bmatrix}$: $-C - X \xrightarrow{\text{Heterolytic fission}}$

If EN of C > EN of X

An organic species containing negatively charged carbon atom is called carbanion. **Stability of carbanion is due to following reasons**

- (i) Inductive effect
- (ii) Resonance
- (iii) s-character in Hybridisation

Stability of Carbanion $\propto -I$, $\propto \frac{1}{+I}$

Ex. (i)
$$CH_3 - \ddot{C}H_2 < \ddot{C}H_3 < NO_2 - \ddot{C}H_2$$

$$(\ddot{\mathbf{u}}) \overset{\mathbf{C}}{\mathbf{CH}}_3 > \mathbf{CH}_3 \overset{\mathbf{C}}{\mathbf{CH}}_2 > (\mathbf{CH}_3)_2 \overset{\mathbf{C}}{\mathbf{CH}} > (\mathbf{CH}_3)_3 \overset{\mathbf{C}}{\mathbf{C}}$$

Note : Carbanions are nucleophiles.

5. PROPERTIES OF CARBOXYLIC ACIDS

I. Reactionsd Due to Cleavage of O–H Bond: Acid strength of acids



- (i) $2RCOOH + 2Na \longrightarrow 2RCOO^{-}Na^{+} + H_{2}$
- (ii) $RCOOH + NaOH \longrightarrow RCOO^{-}Na^{+} + H_2O$

(iii) RCOOH + NaHCO₃ \longrightarrow RCOO⁻Na⁺ + H₂O + CO₂ Note: Acids liberate $CO_2(gas)$ with NaHCO₃. This reaction is used to distinguish carboxylic acids from phenols which do not react with NaHCO₃.

(iv) $2\text{RCOOH} + \text{Ca(OH)}_2 \rightarrow (\text{RCOO})_2\text{Ca} + 2\text{H}_2\text{O}$

In water, carboxylic acids dissociate as :

$$R - C + H_2O + H_3O^+ + RCOO^-$$

$$K_{eq} = \frac{\left[H_3O^+\right]\left[RCOO^-\right]}{\left[H_2O\right]\left[RCOOH\right]}$$

$$\Rightarrow K_a = K_{eq}\left[H_2O\right] = \frac{\left[H_3O^+\right]\left[RCOO^-\right]}{\left[RCOOH\right]}$$

and $pk_a = -\log K_a$ \therefore smaller the pk_a , stronger the acid.

The acidity of carboxylic acids, phenols and alcohols follows the order:

Carboxylic acid > phenol > alcohol

Consider the resonating structures of carboxylate ion and phenoxide ion.



This is because the carboxylate ion is stabilised by two equivalent resonance structures with -ve charge at more electronegative O-atom. On the other hand, phenoxide ion has non-equivalent structures with -ve charge on less electronegative C-atom. Thus, contribution of resonating structures of phenoxide ion towards resonance is very small. Therefore, carboxylate ion is more stable than phenoxide ion so carboxylic acids are more acidic than phenols.

EWG increase the acidity of acid by stabilising the carboxylate ion whereas EDG decrease the acidity by destabilising the ion.

Note:

- More will be the electron withdrawing nature of substituent greater will be acidic strength. (i)
- (ii) More will be the number of electron withdrawing substituents greater will be acidic strength.
- (iii) As the distance between electron withdrawing substituent and COOH group increases acidic strength decreases.
- (iv) Direct attachment of phenyl or vinyl groups increase the acidity of acid due to resonance:



In general, acidity increases as the electronegativity of the carbon atom directly attached to -COOH group increases or the hybridization of the carbon atom directly attached to -COOH changes from $sp^3 \rightarrow sp^2 \rightarrow sp$.

The order of acidity of various acids is as follows:

 $CF_{3}COOH > CCl_{3}COOH > CHCl_{2}COOH > NO_{2}CH_{2}COOH > NC - CH_{2}COOH >$

 $FCH_2COOH > ClCH_2COOH$

BrCH₂COOH > HCOOH > ClCH₂CH₂COOH >

 $C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$



Note: o–Substituted benzoic acids are usually stronger acids than benzoic acid regardless of the nature of the substituent.

- II. Cleavage of C OH Bond
- (i) Anhydride Formation



Acid anhydrides can also be obtained by treating acid chlorides with carboxylic acids. (ii) Esterification

$$RCOOH + R'OH \xrightarrow{Dry HCl or}_{Conc. H_2SO_4} RCOOR' + H_2O$$

Note: As the number and size of the substituents around the –COOH or –OH group increases, the rate of esterification decreases.

(iii) Formation of Acid Chlorides.

Reaction with PCl_5 , PCl_3 and $SOCl_2$ RCOOH + $PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$ RCOOH + $PCl_3 \longrightarrow 3RCOCl + H_3PO_3$ RCOOH + $SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

Note: In this reaction, SO_2 being a gas escapes out and HCl gets absorbed by basic pyridine and pure acyl chloride is left. So it is best method for preparing acyl chloride from acid.

(iv) Reaction with NH₃

$$\mathrm{NH}_4^+ \xrightarrow{\Delta(-\mathrm{H}_2\mathrm{O})} \mathrm{RCONH}_2$$

- $RCOOH + NH_3 \implies RCOO^-NH_4^+ -$ III. Reaction Involving - COOH Group
- (i) Reduction:
 - (a) Reduction to alkanes: RCOOH



NaBH₄ does not reduce the carboxyl group B_2H_6 does not reduce groups like ester, $-NO_2$, halo, etc. (b) Reduction to alkanes:

$$R - COOH + 6HI \xrightarrow{\text{Red } P} R - CH_3 + 2H_2O + 3I_2$$

(ii) Decarboxylation

RCOONa

NaOH + CaO (soda lime)

 $R - H + Na_2CO_3$

(iii) Kolbe's electrolytic synthesis : $2RCOOK \Rightarrow 2RCOO^{-} + 2K^{+}$ At Anode : $2RCOO^{-} \longrightarrow R - R + CO_{2} \uparrow$ At Cathode : $2K^{+} + HOH \longrightarrow 2KOH + H_{2} \uparrow$ (iv) Hunsdiecker reaction :

$$O \\ \parallel \\ R - C - OAg + X_2 \xrightarrow{CCl_4} R - X + CO_2 \uparrow + AgX \downarrow \\ (X = Cl \text{ or } Br)$$







