SOLID STATE

Seven Crystal System :-

Name of System	Axes	Angle	Forms of Lattices
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-Centred Body Centred] 3
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Body Centred] 2
3. Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive] 1
4. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	Primitive, Face-entred Body centred End centred] 4
5. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ, \neq 120^\circ, \neq 60^\circ$	Primitive, End centred] 2
6. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive] 1
7. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Primitive] 1 Total = 14

Geometry of a cube

Number of corners = 8

Number of faces = 6

Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

Number of face diagonals = 12

Contribution of atom at different sites of cube

At corner = 1/8

at face = 1/2

at edge = 1/4

At body centre = 1

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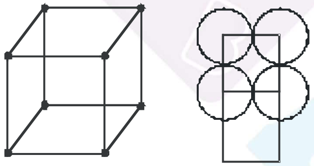
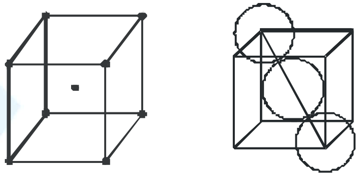
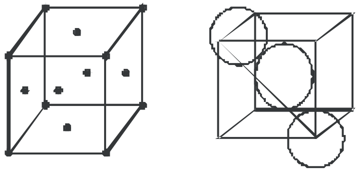
Types of unit cell (Bravais Lattice)

	Simple Cubic Cell (SCC)	**Body centred Cubic Cell (BCC) (SCC – Body centred = BCC)**	**Face centred Cubic Cell (FCC) (SCC + Face Centred = FCC)**
Geometry	 $a = 2r$	 $4r = \sqrt{3}\,a$	 $4r = \sqrt{2}\,a$
Number of atoms per unit cell (n)	$= 8 \times 1/8 = 1$ Corners	$= (8 \times 1/8) – (1 \times 1) = 2$ corners body centre	$= (8 \times 1/8) – (6 \times 1\ 2) = 4$ corner face centre
Co - Ordination No.	6	8	12
Relation between a and r	$a \quad 2r$	$4r = \sqrt{3}\,a$	$4r = \sqrt{2}\,a$
Packing efficiency $\text{P.E.} = \frac{n \times 4/3\pi r^3}{V = a^3}$	$\frac{\pi}{6}$ or 52.4%	$\frac{\sqrt{3}\pi}{8}$ or 68%	$\frac{\pi}{3\sqrt{2}}$ or 74%

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Density of the unit cell = $\frac{n \times M}{V \times N_A} \text{ g cm}^{-3}$

Where M = Molecular weight or atomic weight

Three dimensional close packing

Contents	BCC	CCP/FCC	HCP
Type of packing	ABAB……… Packing but not close packing	ABCABC……. Close Packing	ABAB………. Close Packing
No. of Atoms	2	4	6
Co- Ordination No.	8	12	12
Packing efficiency	68%	74%	74%
Examples	IA, BA V & Cr group Fe	Ca, Sr, Al Co Group, Ni group, Copper group All inert gases Except helium	Remaining d-Block Elements Be & Mg

Note : Only Mn crystallizes in S.C.C.

Voids in close packing structure :

$$\text{per atom}\left\langle\begin{array}{l}2\text{ Tetrahedral void}\\ 1\text{ Octahedral void}\end{array}\right.$$

Limiting Radius Ratio = r/R	Coordination Number of Cation	Structural Arrangement (Geometry of Voids)	Example
0.155 – 0.225	3	Plane Trigonal	Boron Oxides (B_2O_3)
0.225 – 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 – 0.732	6	Octahedral	NaCl, MgO_2
0.732 – 1.000	8	Cubic	CsCl

NaCl Type :

For NaCl : Distance between two nearest ions $(r^+ + r^-)$:-

$$2r^+ + 2r^- = a$$

i.e. $r^+ + r^- = \frac{a}{2}$

CsCl Type :

For CsCl : Distance between two nearest ions $(r^+ + r^-)$:-

$2r^+ + 2r^- = \sqrt{3}a$ i.e. $r^+ + r^- = \frac{\sqrt{3}a}{2}$

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Defects or Imperfections in Solids :

Schottky defect	Frenkel defect	F-Centre
Equal number of cations and anions are missing from their respective position leaving behind a Pair of holes	This type of defect is created when an ion levels its appropriate site in the lattice and occupies an interstitial site	A compound may have excess metal in ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron
Density decreased C. No. is high L.R.R. is high Electrically neutral Ex. NaCl. CsCl, KCl, KBr	Density unchanged C. No. is low L.R.R. is low Electrically neutral Ex. ZnS, AgBr, AgCl etc.	Ex. NaCl – Yellow KCl – Voilet

B. TYPES OF IONIC CRYSTAL

Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples
NaCl (1 : 1) (Rock Salt Type)	C.C.P. – Cl^- - every element of C.C.P. Na^+ - at every OHV	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II - A (Some exception) AgF, AgCl, AgBr, NH_4X
CsCl Type (1 : 1)	B.C.C. – Cl^- - at every corner Cs^+ - at body centre or at cubic void	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS
ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. – S^{-2} - every element of C.C.P. Zn^{+2} – at 50% of T.H.V. or at alternate tetrahedral void	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P. – Ca^{+2} - every element of C.C.P. F^- - at every T.H.V.	$4Ca^{+2}$, $8F^-$ 4 : 8	$4Ca^{+2} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2 $CaCl_2$, CaF_2
Na_2O Type (2 : 1) (Antifluorite)	C.C.P. – Na^+ - at every T.H.V. O^{-2} - every element of C.C.P.	$8Na^+$, $4O^{-2}$ 8 : 4	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S
ZnS Type (1 : 1) (Wurtzite another geometry of ZnS	C.C.P. – S^{-2} - every element of H.C.P. Zn^{+2} - 50% of T.H.V. or (at alternate T.H.V.)	4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite

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SOLUTION

1. % by wt. = $\frac{\text{Wt. of the solute (in g)}}{\text{Wt. of the solution (in g)}} \times 100$

2. % by wt./vol. = $\frac{\text{Wt. of solute (in g)}}{\text{Vol. of solution (in cc)}} \times 100$

3. % by volume = $\frac{\text{Vol. of solute (in cc)}}{\text{Vol. of the solution (in cc)}} \times 100$

4. Molarity = $\frac{\text{Moles of solute (in gm)}}{\text{Vol. of the solution (in litre)}}$

where moles = $\frac{\text{Mass of the solute (in g)}}{\text{Molecular mass of the solute}}$

5. Normality = $\frac{\text{Gram equivalents of the solute}}{\text{Vol. of the solution in cc}} \times 1000$

where gm eq. = $\frac{\text{Mass of the solute (in g)}}{\text{Eq. mass of the solute}}$

6. Molality = $\frac{\text{Moles of solute}}{\text{Mass of the solvent (in g)}} \times 1000$

7. Mole fraction of solute in solution (x_2) = $\frac{n_2}{n_1 + n_2} = \frac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2}$

Mole fraction of solvent in solution (x_1) = $\frac{n_1}{n_1 + n_2} = \frac{w_1 / M_1}{w_1 / M_1 + w_2 / M_2}$

where w_1, M_1 are mass and molecular mass of solvent and w_2, M_2 for the solute. $x_1 + x_2 = 1$. In general, for a solution containing many components (A, B, C.....), mole fraction of A

$(x_A) = \frac{n_A}{n_A + n_B + n_C + \dots\dots}$ and so on. $x_A + x_B + \dots\dots\dots\dots = 1$.

Strength (g/L) = N × eq. wt.

Strength (g/L) = M × mol. wt.

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8. Mass fraction of component A (x_A) = $\frac{w_A}{w_A + w_B}$

Mass fraction of component B (x_B) = $\frac{w_B}{w_A + w_B}$

$x_A + x_B = 1$

9. Parts per million (ppm) = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6 \simeq \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 10^6$

10. Normality equation (for dilution of a solution or for a complete reaction between two solutions) $N_1V_1 = N_2V_2$

11. Molarity equation (for dilution of a solution) $M_1V_1 = M_2V_2$

12. If V_1 cc of a solution with normality N_1 is mixed with V_2 cc of the solution with normality N_2, then normality N_3 of the final solution can be calculated using.
$N_1V_1 + N_2V_2 = N_3 (V_1 + V_2)$.

13. Molality mole fraction and mass fraction do not change with temperature because they involve weights, Normality and molarity change with temperature because they involve volume.

14. One molar (1M) aqueous solution is more concentrated than one molal aqueous (1m) solution of the same solute. This is because 1M solution contains 1 mole of the solute in 1000cc of the solution which includes the solute i.e., mass of solvent is less than 1000g (as density of H_2O = 1g / cc). However, in case of non aqueous solution 1M > < 1m or 1M = 1m depending upon the density of the solutions

15. Alloys are solution of solids in solids.

16. According to Raoult's law, for solution containing volatile components A and B
$p_A = x_A p^\circ_A$ and $p_B = x_B p^\circ_B$
$P_{Total} = p_A + p_B = x_A p^\circ_A + x_B p^\circ_B = (1 - x_B)\, p^\circ_A + x_B p^\circ_B = (p^\circ_B - p^\circ_A)\, x_B + p^\circ_A$

17. Raoult's law for non-volaltile solute containing solution.

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \text{ (if solution is dilute i.e., < 5 \%)}$$

$$= \frac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2} \approx \frac{w_2 / M_2}{w_1 / M_1} \text{ (if solution is dilute)}$$

18. Osmotic pressure P or π = C.RT
C = molar conc. T = temp. in K, R = 0.082 L atm K^{-1} mol^{-1} (if P is in atm and vol. of solution in litres) or 8.314 JK^{-1} mol^{-1} (if P is in Nm^{-2} or Pascals and vol. in m^3)

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19. Isotonic solutions have same osmotic pressure and same molar concentIsotonic solutions have same osmotic pressure and same molar concentrations. If one solution has lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution. The more concentrated solution is said to be hypertonic with respect to the dilute solution. $\pi_1 = \pi_2$ Isotonic solution.rations. If one solution has lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution. The more concentrated solution is said to be hypertonic with respect to the dilute solution. $\pi_1 = \pi_2$ Isotonic solution.

20. Elevation in boiling point, $\Delta T_b = K_b m$ where K_b = molal elevation constant and m = molality of the solution.

21. Depression in freezing point, $\Delta T_f = K_f m$ where K_f = molal depression constant and m = molality of the solution.

22. $K_b = \dfrac{RT_b^2}{1000 l_v} = \dfrac{M_1 RT_b^2}{1000\,\Delta H_v}$

where T_b = boiling point of the liquid (pure solvent)
l_v = latent heat of vaporisation per g of the solvent
ΔH_v = latent heat of vaporisation per mole of the solvent
M_1 = molecular mass of the solvent
R = gas const. 8.314 $JK^{-1}\,mol^{-1}$ if l_v or ΔH_v is in joules or 1.987 cal $K^{-1}\,mol^{-1}$ if l_v or ΔH_v is in calories.

23. $K_f = \dfrac{RT_f^2}{1000 l_f} = \dfrac{M_1 RT_f^2}{1000\,\Delta H_f}$

where T_f = freezing point of the liquid (pure solvent)
l_f = latent heat of fusion per g of the solvent
ΔH_f = latent heat of fusion per mole of the solvent

24. The lowering of vapour pressure on adding a non volatile solute to a solvent is due to converting up partially the surface of the solution by solute particles which are non - volatile.

25. Osmotic pressure method is the best method for determination of molecular masses of polymers because for polymer solutions, observed value of any other colligative property is too low to be measured accurately.

26. Van't Hoff factor (i) = $\dfrac{\text{Observed value of Colligative property}}{\text{Calculated value of colligative property}}$

$$= \frac{\text{Calculated mol. mass}}{\text{Observed mol. mass}} = \frac{M_{cal.}}{M_{obs.}}$$

$$\left(\because \text{Mol mass} \propto \frac{1}{\text{Colligative property}}\right)$$

27. For solutions undergoing dissociation / association

$$\Delta T_b = iK_b\,m,\ \Delta T_f = i\,K_f m,\ \pi = i\frac{n}{V}RT \qquad \left\{\therefore C = \frac{n}{v}\right\}$$

28. For an electrolyte, A_xB_y undergoing dissociation with degree of dissociation α.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$i = 1 - \alpha + n\alpha \ (n = x + y)$$

$$i = 1 + (n-1)\alpha \text{ or } \alpha = \frac{i-1}{n-1}$$

29. For a solute A undergoing association

$$nA \rightleftharpoons A_n$$

$$i = 1 - \alpha + \frac{\alpha}{n} \quad \text{or} \quad \alpha = \frac{1-i}{1-\frac{1}{n}}$$

30. Van't Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association.

31. Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called anti-freeze.

32. Common salt (NaCl) or anhydrous $CaCl_2$ are used to clear snow on the roads. This is because they decrease the freezing point of water to such an extent it cannot freze to form ice.

33. According to Henry's law $\Rightarrow$
mass of gas dissolved $\propto$ pressure of gas above the solution
(i.e. $m \propto p$ or $m = k_H p$ where k_H is called Henry's constant)
or for a mixture of gases.
Solubility in terms of mole fraction $\propto$ partial pressure (i.e., $x_A = k_H p_A$ where k_H is in atm^{-1} or bar^{-1} or $p_A = k_H x_A$ where k_H is in atm or bar).

34. Raoult's law is a special case of Henry's law (Idea).

35. **Konowaloff's rule.** At any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase. In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

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SURFACE CHEMISTRY

Classification Based on Interaction of Phases :-

Lyophilic and Lyophobic sols

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols. (solvent -liking).

For example - Dispersion of gelatin, Starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called lyophobic collidal (Solvent hating) Solutions.

Comparison of Lyophobic and Lyophilic sols

Property	**Lyophilic Sol. [Liq. Loving Solution] (Emulsoid)**	**Lyophobic sol [Solvent hating colloid] (Suspensoid)**
1. Preparation	Can be easily prepared by Shaking or warming the substance with solvent	Can not be prepared Easily special methods are required
2. Stability	are more stable	are less stable
3. Reversibility	are reversible	are irreversible
4. Viscosity	viscosity is much higher than that of solvent	viscosity is nearly same as that of the solvent
5. Surface tension	Surface tension is usually low	Surface tension is almost same as that of solvent
6. Hydration or Solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7. Charge	The particles have little Charge or no charge at all	The particles carry a characteristic charge either positive or negative
8. Visibility	Particles can not be seen under microscope	Particles can be seen Under microscope
9. Coagulation or Precipitation	Precipitated by high concentration of electrolytes	precipitated by low concentration of electrolytes
10. Tyndall Effect	Less scattering	More scattering
11. Migration in electric field	may or may not migrate as they may or may not carry charge.	migrate towards anode or cathode as these particles carry charge.
12. General example	Mostly of organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose solution	Mostly of Inorganic nature Ex. Transiton metal Salt in water. Gold, As etc.

Peptization :

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The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is called **Peptizing agent.**

Hardy Schulze Rule :

This rule state that the precipitating effect of an ion on dispersed phase of oposite charge increasing with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its precipitating power of As_2S_3 sol (negative), the precipitating power of Al^{3+}, Ba^{2+} and Na^+ ion is in the order

$Al^{3+} > Ba^{2+} > Na^+$.

Similarly for precipitating $Fe(OH)_3$ sol (positive), the precipitating power of $[Fe(CN)_6]^{3-}$, SO_4^{2-} and Cl^- ions is in the order.

$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$

The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

$$\text{Flocculation value} \propto \frac{1}{\text{Flocculation Power}}$$

Gold Number :

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 100% NaCl solution is know as Gold Number of that protector (Lyophillic colloid).

The precipitation of the gold solution is indicated by a colour change from red to blue when the particle size just increases.

The smaller the gold number of a protective Lyophilic colloid, Greater is its protection power.

$$\text{Protection capacity} \propto \frac{1}{\text{Protection Number}}$$

(Gold Number)

$$\text{G.N.} = \frac{\text{Wt. of lyophilic sol. in mg}}{\text{Vol. of gold solution in mL}} \times 10$$

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Note : Gelatin is best protecting colloid because it has least gold number.

Types of colloids according to their size		
Multi Molecular	**Macro Molecular**	**Associated colloids**
Formation by Aggregation a large number of atoms or smaller molecules of substance. Ex. – **Gold Sol (Au), Sulphur sol. (S_8)**	Macromolecules having size in the colloidal range These are polymers with high molecular mass. Ex. – **Starch,** Cellulose, Protein etc.	These are the substances of which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal. These Associated particlesare Also called micelles. Ex. Sodium stearate.

Comparison of physisorption and chemisorption	
Physical adsorption	**Chemical Adsorption (Activated ad.)**
1. It is caused by intermolecular Vander waal's forces.	It is caused by chemical bond Formation.
2. It is not specific.	It is highly specific.
3. It is reversible.	It is irreversible.
4. Heat of adsorption is low. 20 to 40 kJ/mol	Heat of adsorption is high 80 to 240 kJ/mol
5. No appreciable activation energy is involved.	High activation energy is involved.
6. It forms multimolecular layers on adsorbent surface under high pressure	It forms unimolecular layer.

General Characteristics of Catalysts :

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.
(ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.
(iii) A catalyst does not initiate a reaction.
(iv) Solid catalyst is more efficient when used in finaly divided state.
(v) Generally catalyst does not change the nature of products.
(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.
(vii) The catalyst is generally specific in nature.
(viii) Change rate constant of reaction.
(ix) Does not change free energy of reaction.
(x) Participate in mechanism of reaction.

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