

M.Sc-IVth Semester (Physical Chemistry) AR-7154

1. Reactions in the solid takes place only slowly in most cases

A solid state reaction is a chemical reaction in which solvents are not used. In a normal reaction, the reacting agents, also called the reactants, are placed in a solvent before the reaction can take place. A solid state reaction takes place because of diffusion process or migration of ions. In general solid state reactions takes place very slowly at low temp and high temperatures are required to accelerate the diffusion process or migration of ions. Moreover nucleation takes place slowly.

2. Normal spinel structures are usually cubic closed-packed oxides with one octahedral and two tetrahedral sites per oxide. An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions. A common example is Fe_3O_4 .
3. Which of the following halides shows less intensity in XRD and arrange in increasing order? KF, KBr, KI, KCl

KCl shows less intensity in XRD in 111 planes due to isoelectronic. $\text{KCl} < \text{KF} < \text{KBr} < \text{KI}$.

4. Which of the following plane is absent in the bcc structure?

(210) plane

5. How would you classify the transformation from quartz to cristobalite?

Rock salt type crystal quartz gives cristobalite at 1200 °C; whereas amorphous silica produces at 900 °C. These transitions are reconstructive transitions.

6. What is a displacive transition and give an example?

Displacive transition proceeds through a small distortion of bonds. The atomic displacements are reduced and specific heat is low. Ex: LiFe_2O_3 , BaTiO_3

7. Neither *P* nor *N*-type

8. An intrinsic semi conductor is chemically pure and poor conductor of electricity. It has the equal number of holes and electrons. Extrinsic semi conductors are intrinsic

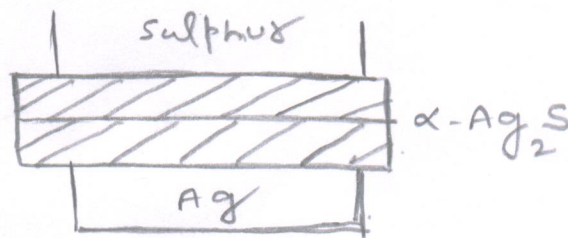
semiconductors doped with impurities. Doping process produces two types of semi conductors. *N*-type and *P*-type semi conductors.

- 9. Greater than to that of pure $NiFe_2O_4$
- 10. The hysteresis loop shows the irreversible, nonlinear response of a ferromagnetic to a magnetic field. When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed. It must be driven back to zero by a field in the opposite direction. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a hysteresis loop. The lack of retrace ability of the magnetization curve is the property called hysteresis and it is related to the existence of magnetic domains in the material.

Section-B

2a . For ionic compounds, it is assumed that the mobility of cations is relatively high, and anions are immobile and do not participate in the diffusion process. If more than one cation is diffusing, the differences in the motilities sets up a diffusion potential which controls the rate of migration; the mobility of the fast moving ions is slowed down, while the slow moving ion increased.

A silver block was separated from sulphur by two blocks of silver sulphide (Ag_2S). The temperature was raised to $220\text{ }^\circ\text{C}$ and maintained there for about an hour. Sulphur melted and reacted through the Ag_2S blocks; that the reaction took place was shown by the loss in weight of the silver block and gain in weight of Ag_2S block.



wagner's expt of reaction of sulphiding of silver.

Wagner suggested the following mechanism for the reaction:

- (a) Ag^+ ions diffused through Ag_2S blocks and arrived at the $Ag_2S(II)/S$ interface.

- (b) The electrons converted the sulphur atoms adsorbed on the Ag_2S surface into sulphide (S^{2-}) ions, which build up a frame work of the anion lattice.
- (c) The Ag^+ ions arriving at the Ag_2S (II)/S interface occupied the cations in the newly formed anion lattice.

- 2b. Laue predicted that the distances between particles in a crystal are of the same order of magnitude as the wavelength of X-rays. The diffraction pattern can be recorded by placing a photographic plate behind the crystal. On developing the film, one observes a series of spots arranged in some symmetrical way around the intense central beam.

According to Bragg, crystal is composed of a series of equally spaced atomic planes; it may be employed not only as a transmission grating as in the Laue method, but also as a reflection grating. If the reflected waves from successive layers are out of phase, then due to the destructive interference, no diffraction will be observed.

3. Zeolite synthesis: By crystallization from aqueous solutions, crystalline phases can be prepared at low temperatures, *i.e.* from 25 to 100 °C, whereas much higher temperatures would be required for a normal solid state synthesis. The starting materials for zeolite synthesis are aqueous solutions of silicate and aluminate anions which are mixed together with alkali. A gel formed by a copolymerization of the silicate and aluminate anions and on subsequent heat treatment, crystals of zeolite are produced. This may be represented, schematically, for a sodium aluminosilicate zeolite, by the following reactions:



Some general conditions for the synthesis of zeolite are:

- Reactive starting materials should be used freshly coprecipitated gels or amorphous solids
- Relatively high pH, introduced in the form of alkali metal hydroxide.
- Low temperature hydrothermal conditions
- A high degree of super saturation of the components of the gel is desirable leading to the nucleation of large number of crystals.

Effect of viscosity on glass formation: Viscosity is an important parameter in the manufacture and use of glass.

- (a) It influences the choice of melting conditions, *i.e* the temperature of melting and the time for which the mixture of raw material is heated in order to obtain a homogeneous melt.
- (b) For good quality, it is necessary to fine the melt.
- (c) After melting and fining stages, the material is cooled to form a glass.
- (d) In use, the upper temperature at which a glass retains, its characteristic properties is usually given by the onset of softening. Viscosity is an important parameter in controlling the temperatures at which these processes occur.

Zone refining: Many metals and important semiconductors such as silicon and germanium can be purified by this process. It is essential that these important semiconductors be highly pure before they are used in *p-n* junctions. Initially seed crystal is melted. As the boat is pulled through the furnace, oriented solidification onto the seed occurs and at the same time more of the charge is melts. This also forms a well known method for purification of solids, the *zone-refining* technique.

4. (a) The density of the crystal is

$$\rho = (NM)/a^3N_A$$

Here “*a*” is the unit cell length, “*M*” is the molar mass of a given crystal. N_A is the Avogadro’s number. “*N*” is the number of atoms per unit cell.

$$N = (\rho a^3 N_A) / M$$

Given density = $2.71 \times 10^3 \text{ Kg/m}^3$ and unit cell length is $563.1 \text{ pm} = 563.1 \times 10^{-12} \text{ m}$

$N_A = 6.022 \times 10^{23}$, $M = 57.74 \text{ g}$

$$N = (2.71 \times 10^3) (563.1 \times 10^{-12})^3 (6.022 \times 10^{23}) / 57.74 \times 10^{-3}$$

$N = 4$ (approximately)

4 (b) Miller indices for the given planes are (010) (110) and (101)

5. (a) The morphological study of crystals of different symmetries classified into seven crystal systems based on rotation of certain axis.

Crystal System	Parallelepiped dimensions
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Trigonal or Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$

5b Some Applications of powder XRD are:

- A) Identification of single phase materials
- B) Crystallographic structure analysis and unit cell calculation
- C) Determination of crystallite shape from study of peak symmetry
- D) Recognition of amorphous materials
- E) Determination of lattice parameter.

5 (c) Debye Scherrer equations:

By using Debye Scherrer equation, one can calculate the thickness of a crystallite by using:

$T = C\lambda / B \cos\theta$; where T is the crystallite size, λ is the wavelength of X-rays. "B" is the full width half maximum (FWHMS).

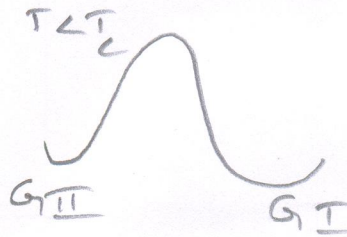
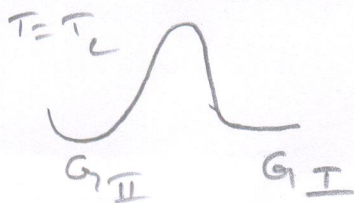
6. Phase transitions vary enormously and are controlled by several factors. Rates are slow in either direction at temperatures that are close to the equilibrium transition temperatures, (T_c). Since ΔG is nearly zero at T_c , there is little driving force for transition to occur either in the direction. At temperatures further removed from T_c , reaction rate increase.

In general, the occurrence of maximum at T_M can be obtained based on effect of temperature on reaction rates by the Arrhenius equation and relative free energies of the polymorph.

The Arrhenius equation, as applied to kinetics, is of the form:

Rate = $A \exp(-E/RT)$, where "E" is activation energy of the transition. From this equation, we predict a rapid increase in rate with increasing temperature. The usual method of analyzing results in terms of the Arrhenius equation is

$$\log_{10} \text{rate} = \log A - \frac{E}{RT} \log_{10} e.$$



The magnitude of the difference in free energy between two polymorphs gives a measure of the driving force for the transition to occur. At T_c , $G_1 = G_2$ and there is no driving force for the transition to occur in either direction. At any other temperature, $G_1 \neq G_2$ and the transition takes place only in one direction.

Martensitic Transition: Austenite, a solid solution of carbon in iron when cooled undergoes a rapid transformation to new structure known as martensite. The martensite growth rate is extremely fast (10^5 cm/s). In austenite, the carbon atoms randomly occupy the octahedral interstices formed by fcc packing of iron atoms. Martensite has a body centered tetragonal structure resembling a slightly distorted rock salt structure. Austenite to martensite does not involve any atom jump or diffusion. It occurs by a small displacement of atoms by a shear process. Such transformations are known as martensitic transformation.

8. In the case of Nickel oxide coupling of spin occurs to give rise to antiferromagnetism. The Ni^{2+} has eight d electrons. In an octahedral environment, two of these electrons singly occupy

the e_g orbitals, d_{z^2} and $d_{x^2-y^2}$. These orbitals are oriented so as to be parallel to the axes of the unit cell and point directly at adjacent oxide ions. The unpaired electrons in the e_g orbitals of Ni^{2+} ions are able to couple magnetically with electrons in the p -orbitals of O^{2-} ions. The p -orbitals of O^{2-} contain two electrons each, which are also coupled antiparallel and shows antiferromagnetism.

Whereas in the case of vanadium (V^{2+}) has 3 d electrons. The Pauli Exclusion Principle ensures that net spin of the resulting O^- will be antiparallel to the spin direction of V^+ ion. In VO, the d - orbitals overlap very strongly. The cation exchange is small compared to NiO. The number of lone pair of electrons is more and acts as a good conductors and even their conductivity is comparable to metallic conductor; whereas NiO is poor semi conductor.

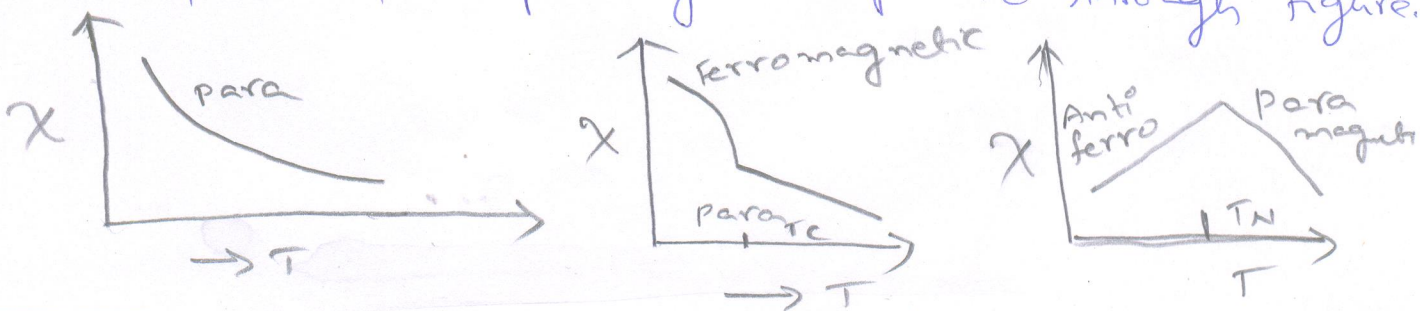
(b) Many solids exhibit magnetic effects other than diamagnetism, which is a property of all substances, are characterized by having unpaired electrons present. The unpaired electrons may be oriented at random on different atoms, in which case the material is paramagnetic. If they aligned parallel, it is ferromagnetic. Alternatively, they may be aligned in antiparallel fashion, giving zero overall magnetic moment and antiferromagnetic behavior.

In a vacuum, the magnetic field and the magnetic flux density are related by the permeability of free space, is given by $B = \mu_0 H$.

The magnetization is usually discussed in terms of the magnetic susceptibility χ , where $\chi = M/H$, "M" is magnetization.

The susceptibilities of the different kinds of magnetic material are distinguished by their different temp dependence. many paramagnetic substances obey the simple curie law, especially at high temp. This states that suscept is inversely proportional to temp. $\chi = \frac{c}{T}$, 'c' is curie constant.

The magnitude of χ in different materials and its variation with temp may be explained through figure.



Q. 7(a)

- * The difference between the electrical properties of a metal and a semiconductor is due to the difference in density of conduction e's present in each. Moreover, the density of conduction e's increases in semiconductor as temp raised.
- * Free-electron density in a metal changes little with increasing temp while its conductivity decreases because of increased thermal scattering.
- * The difference between an insulator and semiconductor can be described quantitatively with the aid of fermi distribution

$$f(E) = \frac{1}{e^{(E-E_0)/kT} + 1}$$

E is occupation of quantum state
where energy

At absolute zero, $f(E) = 1$ for $E < E_0$ " E_0 " is fermi energy

$f(E) = 0$ for $E > E_0$. " E " is energy of allowed state

Assuming that only e's occupying quantum states at the top of valence band can gain sufficient thermal energy to transfer to states at the bottom of conduction band.

- * If there are N e's per unit volume in the crystal at absolute zero, then the density of occupied states in the conduction band, N_c , at some other temp is given by

$$N_c = N(E_c) = N f(E_c) = \frac{N}{e^{(E_c - E_0)/kT} + 1}$$

"The density of states of energy occupied " E_0 " in the valence band is given by

$$N(E_0) = N f(E_0) = \frac{N}{e^{(E_0 - E_0)/kT} + 1}$$

"The density of unoccupied states of energy E_0

$$N_0 = N - \frac{N}{e^{(E_0 - E_0)/kT} + 1}$$

But the no of empty states in v.B must be equal to c.B (occupied), so

$$N_c = N_v$$

$$\frac{N}{e^{(E_c - E_0)/kT} + 1} = N \left[1 - \frac{1}{e^{(E_0 - E_c)/kT} + 1} \right]$$

divide by N on both sides, $1 = e^{(E_0 + E_c - 2E_0)/kT}$

taking natural log on both sides,

$$\log 1 = 0 = E_0 + E_c - 2E_0 / kT$$

$$E = \frac{1}{2} (E_0 + E_c)$$

Effective density states in the conduction band, n by

$$n = \int_{E_c}^{\infty} N(E) dE = \int_{E_c}^{\infty} S(E) f(E) dE$$

density of available states in conduction band

$$S(E) = \frac{8\pi m^2}{h^3} \sqrt{2m(E - E_c)}$$

(b)

$$n = \frac{8\pi m^2 k^3}{h^3} \sqrt{2mkT} e^{-(E_0 - E_c)/kT} (\pi/4)^{1/2}$$

$$= 2.52 \times 10^{19} e^{-(E_0 - E_c)/kT} \text{ (n.o of } e^{\text{'s per cm}^3 \text{)}$$