



## Document Information

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## Sources included in the report

<b>SA</b>	<b>PRACTICAL INORGANIC CHEMISTRY_VIVA VOCE_SMALL_SIZE.pdf</b> Document PRACTICAL INORGANIC CHEMISTRY_VIVA VOCE_SMALL_SIZE.pdf (D110660621)		<b>1</b>
<b>J</b>	<b>14_annexure.pdf</b> URL: 2b8a2b9c-6a2b-4cc1-9ebd-fc01b41778ff Fetched: 2022-08-20 02:44:59		<b>1</b>

## Entire Document

Printed in accordance with the regulations of the Distance Education Bureau of the University Grants Commission. FirstPrint:November,2021 Netaji Subhas Open University Under Graduate Degree Programme Choice Based Credit System (CBCS) Subject: Honours in Chemistry (HCH) Course : Practical Paper - II Course Code - CC-CH-02 40 \_\_\_\_\_ NSOUCC-CH-02 flask, dilute up to the mark with distilled water and then shake to form a uniform solution. Strength of prepared oxalic acid solution 1 Actual weight of oxalic acid taken N = S (N) 0.7879 20 (3) Standardise the ~ (N/20) KMnO 4 solution:

**59%**

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PRACTICAL INORGANIC CHEMISTRY\_VIVA VOCE\_SMALL\_... (D110660621)

Pipette out an aliquot of 25mL standard oxalic acid solution in a 500mL conical flask, add 25mL 4(N) H 2 SO 4 , heat

nearly to 70 o -80 o C and then titrate the solution with the ~(N/ 20) KMnO 4 solution in hot condition until a faint pink colour stable for 30 sec is obtained. Record the titre value. The titration is repeated twice. (4) Estimation of Iron: Iron can be directly titrated with standard KMnO 4 solution in the following way.

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**MATCHING BLOCK 2/2**

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Pipette out 25mL of the stock solution in a 500mL conical flask. Add 20mL

conc. HCl (A. R.). Heat just to boiling and reduce Fe<sup>3+</sup> ion with SnCl<sub>2</sub> solution adding dropwise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap to room temperature. Add 10mL 5% HgCl<sub>2</sub> solution at a time with vigorous shaking and dilute to 300mL with water. Add 25mL Z-R reagent. Titrate with the standard ~ (N/20) KMnO<sub>4</sub> solution until the solution just turns pale pink colour. Record the titre value. (5) Estimation of Calcium (Ca<sup>2+</sup>) after the separation of iron: Step1: Separation of iron 25 ml aliquot of the stock solution is pipetted out into a 500 ml beaker 1-2 ml of conc. HNO<sub>3</sub> is added, boiled for 3 minutes to oxidise Fe<sup>2+</sup> to Fe<sup>3+</sup>, diluted to 100 mL distilled water; 1-2 gms of NH<sub>4</sub>Cl is added, heated to boiling, (1:1) NH<sub>4</sub>OH is added drop-wise with stirring by a glass-rod until the smell of ammonia persists. The precipitate of Fe(OH)<sub>3</sub> is allowed to settle on a hot asbestos board (colourless supernatant liquid indicates complete precipitation). The precipitate is filtered while hot, by a Whatman No.-41 filter paper, washed by decantation 3-4 times with hot water till free from chloride (a drop of the filtrate is to be tested with HNO<sub>3</sub> and AgNO<sub>3</sub>). The filtrate with the washings is collected in another 500 ml beaker.

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<b>1/2</b>	<b>SUBMITTED TEXT</b>	<b>20 WORDS</b>	<b>59% MATCHING TEXT</b>	<b>20 WORDS</b>
	Pipette out an aliquot of 25mL standard oxalic acid solution in a 500mL conical flask, add 25mL 4(N) H <sub>2</sub> SO <sub>4</sub> , heat			
<b>SA</b>	PRACTICAL INORGANIC CHEMISTRY_VIVA VOCE_SMALL_SIZE.pdf (D110660621)			
<b>2/2</b>	<b>SUBMITTED TEXT</b>	<b>15 WORDS</b>	<b>78% MATCHING TEXT</b>	<b>15 WORDS</b>
	Pipette out 25mL of the stock solution in a 500mL conical flask. Add 20mL		pipette out 10 ml of the mixed solution into a 250 ml conical flask. 3. Add 25-50 ml	
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## Sources included in the report

<b>SA</b>	<b>UGCHE-103-English-234.pdf</b> Document UGCHE-103-English-234.pdf (D146862396)		45
<b>W</b>	URL: <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a> Fetched: 11/9/2021 2:04:30 AM		58
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<b>W</b>	URL: <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a> Fetched: 12/3/2021 6:08:15 PM		8
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1 PREFACE In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. core, discipline specific, generic elective, ability and skill enhancement for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade "A". UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme. Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs. I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar Vice-Chancellor

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5 Netaji Subhas Open University UG : CHEMISTRY (HCH) Unit – 1 Chemical Energetic 7-21 Unit – 2 Chemical Equilibrium 22-33 Unit – 3 Ionic Equilibrium 34-54 Unit – 4 Kinetic Theory of Gases 55-73 Unit – 5 Liquids 74-84 Unit – 6 Solids 85-104 Unit – 7 Solutions 105-124 Unit – 8 Chemical Kinetics 125-151 Course : Basic Physical Chemistry Course Code : GE-CH-11

Unit 1 ????? Chemical Energetic Contents 1.0. Objectives 1.1. Introduction 1.2. Brief review of thermodynamics and the Laws of Thermodynamics 1.2.1. System and surrounding 1.2.2. State of a system 1.2.3. Properties of a system: 1.2.4. Types of processes 1.2.5. Work, heat and heat capacity 1.2.6. The Zeroth law of thermodynamics 1.2.7. The First law of thermodynamics 1.2.8. Internal energy 1.2.9. Enthalpy 1.3. Important principles and definitions of thermochemistry 1.3.1. Energy changes accompanying chemical reactions 1.3.2. Thermochemical equations 1.3.3. Standard enthalpy of reactions 1.3.4. Hess's law of constant heat summation 1.4. Standard enthalpies of formations 1.5. Enthalpies of solution and dilution 1.6. Bond energy, bond dissociation energy and resonance energy 1.7. Variation of enthalpy of a reaction with temperature - Kirchhoff's equation 1.8. Third Law of thermodynamics and calculation absolute entropies of substances 1.9. Summary 1.10. Questions  
1.0 Objectives

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After reading this unit, we will be able to: ? define the commonly used terms in thermodynamics

and laws of thermodynamics; ? state important principles of thermochemistry; ? explain standard state and standard enthalpies of formations; ? explain enthalpies of solution and dilution; ? solve numerical problems based on the enthalpy changes; ? define bond enthalpy and bond dissociation enthalpy and resonance energy; ? variation of enthalpy of a reaction with temperature – Kirchhoff's equation; ? state the third law of thermodynamics and calculate the absolute entropies of substances. 1.1 Introduction

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When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose,  $C_6H_{12}O_6$  by the process of photosynthesis requires the absorption of light energy from the sun. Thus,

various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. In this unit we will review some of the fundamental concepts of energy and heat and the relation between them. We will begin the study of thermodynamics, which treats the energetic aspects of change in general, and will finally apply this specifically to chemical change. 1.2. Brief review of thermodynamics and the Laws of Thermodynamics

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In this lesson we would come across some frequently used terms. Let us understand the meaning of these terms first.  
8 ? NSOU ? GE-CH-11 1.2.1 System and surrounding

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System is the part of the physical universe which is under study, while the rest of the universe is surroundings. The system

and surroundings are separated by a boundary. The system can be of three different types – open, closed and isolated system. An

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open system is a system which can exchange both energy and matter with surroundings.

A closed system

is a system which can exchange energy but not matter with the surroundings. An isolated system is a system which can exchange neither matter nor energy with the

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surroundings. 1.2.2 State of a system We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system 1.2.3

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Properties of a system The measurable properties of a system are called state variables. They may be further divided into two main types –

extensive

properties and intensive properties. Extensive properties are those whose value depends upon the size or mass of the system. Examples of extensive properties are energy, enthalpy, entropy, heat capacity etc. Intensive properties are those whose value is independent of the size or mass of the system, like temperature, refractive index, density, solubility etc., are the examples of intensive property. 1.2.4 Types of processes

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The method of bringing about a change in state is called process. Processes could be of different types. The different types of processes are explained below.

a)

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Isothermal process: When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.

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b) Adiabatic Process:

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In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature.

c) Isobaric process: It is a process in which the pressure of the system remains constant. Heating of water in an open vessel is an example of isobaric process. d) Isochoric process: It is a process in which the volume of the system remains constant. e) Reversible and irreversible Process: A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

**1.2.5 Work, heat and heat capacity** Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other? Work is a quantity of energy that flows across the boundary of a system by means of a force during a change in its state and is completely convertible into lifting of a mass in the surroundings. So, work appears in only at the boundary of the system and it appears only during change in the state of the system. The SI unit of work is joule (J). Heat is a form of energy that is exchanged at the boundary between a system and its surroundings by virtue of a difference in temperature between them and flows from a point of higher to a point of lower temperature and causes a change in the state of the system. Since heat is also a form of energy, so its SI unit is joule (J). Heat is said to be positive when energy is transferred to a system from its surroundings and negative when energy is transferred from system to surroundings. Heat Capacity (C) is defined as the amount of energy as heat needed to raise the temperature of the system by 1 o C. So, SI unit of heat capacity is joule per Kelvin (J K<sup>-1</sup>). Heat capacity is proportional to the amount of substance. So the molar heat capacity or specific heat capacity is defined as the quantity of the

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heat required to raise the temperature of one unit mass of the substance.

Now, the transfer of heat to system can be done under 10 ? NSOU ? GE-CH-11 different condition. If the transfer of heat is done under the conditions of constant volume, the associated heat capacity is called as the heat capacity at constant volume (C<sub>v</sub>) and if the transfer of heat is done under the conditions of constant pressure, the associated heat capacity is called as the heat capacity at constant pressure (C<sub>p</sub>). The values of C<sub>p</sub> and C<sub>v</sub> for a given solid or liquid systems are not much different. However for gaseous systems the difference in their values is significant and for an ideal gas it is given by the following expression C<sub>p</sub> – C<sub>v</sub> = R where R is the gas constant.

**1.2.6 The Zeroth law of thermodynamics**

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The Zeroth law of thermodynamics is states that, if two thermodynamic systems, A and B are in thermal equilibrium with

a third thermodynamic system, C then the two thermodynamic system (A and B) are also in thermal equilibrium with each other.

**1.2.7 The First law of thermodynamics**

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You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows: Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant. Mathematically the first law of thermodynamics is stated as:  $\Delta U = q + w$  where  $\Delta U$  = change in internal energy,  $q$  = heat absorbed by the system, and  $w$  = work done on the system. 1.2.8 Internal energy (U) Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei. The internal energy may be defined as the sum of the energies of NSOU ? GE-CH-11 ? 11 all the atoms, molecules or ions contained in the system. It is a state variable. It is not possible to measure the absolute values of internal energy. However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is  $U_1$  and that in the final state is  $U_2$ , then change in internal energy  $\Delta U$  is independent of the path taken from the initial to the final state. We can write this change as:  $\Delta U = U_2 - U_1$  The internal energy of the system can be changed in two ways: (i) either by allowing heat to flow into the system or out of the system; and (ii) by work done on the system or by the system. 1.2.9

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Enthalpy (H) For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by  $H = U + pV$

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Where, U is the internal energy, p is the pressure and V is the volume of the system.

Enthalpy change,  $\Delta H$ , is given by  $\Delta H = \Delta U + p \Delta V$  (at constant pressure) =

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$q$  (at constant pressure) We denote  $q$  at constant pressure by  $q_p$  hence  $\Delta H = q_p$  So, by measuring heat lost or gained at constant pressure

by the system, we can measure enthalpy change for any process. 1.3. Important Principles and Definitions of Thermochemistry 1.3.1 Energy changes accompanying chemical reactions Majority of chemical reaction are performed under the conditions of constant pressure, so the measured heat changes refer to the enthalpy change for the reaction. Such an enthalpy change associated with a given chemical reaction is termed as the enthalpy of reaction ( $\Delta_r H$ ).

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Let us denote total enthalpy of reactants as  $H_{\text{reactants}}$  and total enthalpy of 12 ?

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products as  $H_{\text{products}}$ . The difference between these enthalpies,  $\Delta$

r



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$\Delta_r H$  is the enthalpy of the reaction  $\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$ . When  $H_{\text{products}}$  is greater than  $H_{\text{reactants}}$  then  $\Delta_r H$

r

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$\Delta_r H$  is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ ;  $\Delta_r H = 52.5 \text{ kJ}$ . When  $H_{\text{products}}$  is less than  $H_{\text{reactants}}$  then  $\Delta_r H$  is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example,  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ;  $\Delta_r H = -890.4 \text{ kJ}$ . Enthalpy of a reaction changes with pressure and temperature. 1.3.2

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Thermochemical equations You are familiar with equations for chemical reactions

as the symbolic representation of a given reaction that consists of chemical formulae of the reactant(s) and product(s) and the reaction condition. If

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we write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below:  
(i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) alongside the chemical formulae respectively. For example, to represent burning of methane in oxygen, we write  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{heat}$  (

ii)

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In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol

$\Delta_r H$ .

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The amount of heat evolved or absorbed is written after the equation followed by semicolon.

$\Delta_r H$

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is negative for exothermic reactions and it is positive for endothermic reactions. For example: An exothermic reaction is written as  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ;  $\Delta_r H = -891 \text{ kJ}$ . Whereas an endothermic reaction is written as  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ ;

$\Delta_r H = 52.2 \text{ kJ}$  NSOU ? GE-CH-11 ? 13  
(iii)

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Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the  $\Delta_r H$  values given correspond to these quantities of substances. (iv) In case, if the coefficients are multiplied or divided by a factor,

$\Delta_r H$

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value must also be multiplied or divided by the same factor. In such cases, the

$\Delta_r H$

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value will depend upon the coefficients. For example, in equation  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ ;  $\Delta_r H = -242 \text{ kJ}$  If coefficients are multiplied by 2, we would write the equation  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ ;

$\Delta_r H = 2(-242) = -484 \text{ kJ}$  (v)

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When a chemical equation is reversed, the value of  $\Delta_r H$  is

reversed in sign. This is known as Lavoisier – Laplace law. For example  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ;  $\Delta_r H = -91.8 \text{ kJ}$

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$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ ;  $\Delta_r H = +91.8 \text{ kJ}$  1.3.3

Standard enthalpy of reactions Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The

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standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. It is denoted by  $\Delta_r H^\ominus$ .

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K. 1.3.4

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Hess's law of constant heat summation Hess's law

can be stated as follows: The standard enthalpy change for a reaction is the sum of standard enthalpies of a sequence of reactions (at the same temperature and pressure); the overall reaction should be capable of being represented by the given sequence of reactions. Hess's law is a direct consequence of the law of conservation of energy i.e. first law of thermodynamics. It is not necessary that every reaction in the given sequence should be 14 ? NSOU ? GE-CH-11 conducted in a laboratory. A particular reaction can also be imaginary. The only requirement is that the individual chemical reactions in the sequence must balance and add up to the equation for a particular reaction. Also Hess's law enables arithmetic operations of chemical equations. This law is helpful in calculating enthalpies of reactions which cannot be experimentally determined; what is required is to select a correct sequence of reactions. We give below the use of Hess's law in calculating the enthalpy of conversion of graphite to diamond which is very difficult to determine. C (

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graphite) + O<sub>2</sub> (g) → CO<sub>2</sub> (g); Δ<sub>r</sub> H<sub>1</sub> = - 393.5 kJ C (diamond) + O<sub>2</sub> (g) → CO<sub>2</sub> (g); Δ<sub>r</sub> H<sub>2</sub> = -395.4 kJ

Then subtracting, we get C (graphite) - C (diamond) = Δ<sub>r</sub> H<sub>3</sub> =

Δ<sub>r</sub> H<sub>1</sub> - Δ<sub>r</sub> H<sub>2</sub> = -393.5 kJ - (-395.4 kJ) = 1.9 kJ Hence, we can write C (graphite) → C(Diamond) Δ<sub>r</sub> H<sub>3</sub> = 1.9 kJ 1.4.

Standard enthalpies of formations

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The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by Δ<sub>f</sub> H<sub>0</sub>. When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by Δ<sub>f</sub> H<sub>0</sub>. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero. For example: C(Graphite) + O<sub>2</sub> (g) → CO<sub>2</sub> (g); Δ<sub>f</sub> H<sub>0</sub> = - 393.5 kJ This means that carbon dioxide is formed from its elements in their most stable states, carbon in the form of graphite at room temperature and gaseous O<sub>2</sub> and CO<sub>2</sub> being at 1 bar. 1.5. Enthalpies of

solution and dilution Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy NSOU ? GE-CH-11 ? 15 change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible. When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These ions are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s) The enthalpy of solution of AB(s), Δ<sub>sol</sub> H<sub>0</sub>, in water is, therefore, determined by the selective values of the lattice enthalpy, Δ<sub>lattice</sub> H<sub>0</sub> and enthalpy of hydration of ions, Δ<sub>hyd</sub> H<sub>0</sub> as Δ<sub>sol</sub> H<sub>0</sub> = Δ<sub>lattice</sub> H<sub>0</sub> + Δ<sub>hyd</sub> H<sub>0</sub> For most of the ionic compounds, Δ<sub>sol</sub> H<sub>0</sub> is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. For water HCl (g) + 10 aq. → HCl.10 aq. ΔH = -69.01 kJ / mol Let us consider the following set of enthalpy changes: (S-1) HCl (g) + 25 aq. → HCl.25 aq. ΔH = -72.03 kJ / mol (S-2) HCl (g) + 40 aq. → HCl.40 aq. ΔH = -72.79 kJ / mol (S-3) HCl (g) + ? aq. → HCl. ? aq. ΔH = -74.85 kJ / mol 16 ? NSOU ? GE-CH-11

The values of  $\Delta H$  show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of  $\Delta H$  is given above in equation (S-3). If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain  $\text{HCl}_{.25 \text{ aq.}} + 15 \text{ aq.} \rightarrow \text{HCl}_{.40 \text{ aq.}}$   $\Delta H = [ -72.79 - (-72.03)] \text{ kJ / mol} = -0.76 \text{ kJ / mol}$  This value ( $-0.76 \text{ kJ/mol}$ ) of  $\Delta H$  is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

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In a chemical reaction, we have seen that energy is either absorbed or evolved. The origin of this

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energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only. At high temperature, hydrogen molecules dissociate into atoms as  $\text{H}_2 (\text{g}) \rightarrow \text{H} (\text{g}) + \text{H} (\text{g}); \Delta_r H^\circ = 435 \text{ kJ/mol}$  The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the  $\text{H}_2$  molecules. For a diatomic molecule like  $\text{H}_2 (\text{g})$ , we define bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms. Now, let us consider a polyatomic molecule like  $\text{CH}_4 (\text{g})$ . The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in  $\text{CH}_4 (\text{g}) \rightarrow \text{CH}_3 (\text{g}) + \text{H} (\text{g}); \Delta_r H^\circ = 431.8 \text{ kJ/mol}$   $\text{CH}_3 (\text{g}) \rightarrow \text{CH}_2 (\text{g}) + \text{H} (\text{g}); \Delta_r H^\circ = 471.1 \text{ kJ/mol}$

$\text{CH}_2 (\text{g}) \rightarrow \text{CH} (\text{g}) + \text{H} (\text{g}); \Delta_r H^\circ = 421.7 \text{ kJ/mol}$

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$\text{CH} (\text{g}) \rightarrow \text{C} (\text{g}) + \text{H} (\text{g}); \Delta_r H^\circ = 338.8 \text{ kJ/mol}$

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We can observe here that each of these equation represent the dissociation of C-H bond but the energies required for them are different. Though all the C-H bond in  $\text{CH}_4$  are equivalent, the dissociation energies are not same. This is due to the fact that once a C- H bond dissociated, the remaining species has different electronic distributions. We can add these four equations to get  $\text{CH}_4 (\text{g}) \rightarrow \text{C} (\text{g}) + 4\text{H} (\text{g}); \Delta_r H^\circ = 1663.4 \text{ kJ/mol}$  In this reaction

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the methane molecule has got converted into its constituent atoms therefore the enthalpy change is called enthalpy of atomization of methane. If we divide the enthalpy of atomization of methane by 4, we get an average value ( $1663.4/4 = 415.9 \text{ kJ/ mol}$ ) for the bond enthalpy for C-H bond. Now if we want to determine the bond enthalpy in ethane ( $\text{C}_2\text{H}_6$ ), here two types of bond exist, C-H and C-C. We assume that the bond enthalpy for C-H bond in ethane is same as that of methane. The atomization of ethane is given by the expression  $\text{C}_2\text{H}_6 (\text{g}) \rightarrow 2\text{C} (\text{g}) + 6\text{H} (\text{g}); \Delta_r H^\circ = 1411.2 \text{ kJ/mol}$

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$\text{H}_6(\text{g}) \rightarrow 2\text{C}(\text{g}) + 6\text{H}(\text{g}); \Delta_r H^\circ = 2842.4 \text{ kJ/mol}$  The

enthalpy of atomization of ethane would be equal to the bond enthalpies of six C-H bond and one C-C bond. If we subtract the bond enthalpies of six C-H bonds from the enthalpy of atomization we can get the bond enthalpy for C-C bond. Thus, bond enthalpy for a given bond refers to the average bond dissociation energy for the same bond in a number of molecules having the said bond. Using Hess's law, bond enthalpies can be calculated. Again

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bond enthalpy data can be used to calculate  $\Delta_r H^\circ$  for a chemical reaction occurring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products.  $\Delta_r H^\circ = \sum \text{B.E. (reactants)} - \sum \text{B.E. (products)}$ .

Using bond energy and enthalpy of formation data resonance energy in a molecule can be calculated. When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally. Resonance energy = Experimental or actual heat of formation - Calculated heat of formation. For example the resonance energy of  $\text{N}_2\text{O}$  can be calculated if observed  $\Delta_f H^\circ(\text{N}_2\text{O})$  is  $82 \text{ kJ mol}^{-1}$ , B.E of N-N is  $946 \text{ kJ mol}^{-1}$ , B.E of N-O is  $418 \text{ kJ mol}^{-1}$ , B.E of O=O is  $498 \text{ kJ mol}^{-1}$ ; B.E of N=O is  $607 \text{ kJ mol}^{-1}$ . 18 ? NSOU ? GE-CH-11

So we can write,  $2\text{N}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g})$  In another way we can write,  $\text{N}_2(\text{g}) + \text{O}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g})$  So, calculated  $\Delta_f H^\circ(\text{N}_2\text{O}) = [\text{B.E}(\text{N}=\text{N}) + \text{B.E}(\text{O}=\text{O})] - [\text{B.E}(\text{N}=\text{N}) + \text{B.E}(\text{N}=\text{O})] = 498 + 946 - [418 + 607] = +170 \text{ kJ/mole}$  Hence, Resonance energy = observed  $\Delta_f H^\circ$  - calculated  $\Delta_f H^\circ = 82 - 170 = -88 \text{ kJ/mol}$  1.7. Variation of enthalpy of a reaction with temperature – Kirchhoff's equation We have learnt that the enthalpy of different types of reactions can be calculated with the help of enthalpy of formation of different compounds. However, most of the data available on enthalpy of reaction or enthalpy of formation of compounds are at 298 K. If the enthalpy of reaction required at some other temperature, we need to know the temperature dependence of the enthalpy of reaction. The enthalpy of reaction at a desired temperature can be obtained from the enthalpy of reaction at some other temperature with the help of Kirchhoff's equation. Let us derive Kirchhoff's equation. We know that:  $\Delta_r H^\circ = H^\circ(\text{products}) - H^\circ(\text{reactants})$  Differentiating with respect to temperature we get,  $\frac{d(\Delta_r H^\circ)}{dT} = \frac{dH^\circ(\text{products})}{dT} - \frac{dH^\circ(\text{reactants})}{dT}$  As  $\frac{dH^\circ}{dT} = C_p$  we can write  $\frac{d(\Delta_r H^\circ)}{dT} = C_p(\text{products}) - C_p(\text{reactants})$  NSOU ? GE-CH-11 ? 19 ? ? ? ? ? Writing the equation in differential form ? ? ? ? ?

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Integrating the equation between temperature  $T_1$  and  $T_2$ ,  $\int_{T_1}^{T_2} \frac{d(\Delta_r H^\circ)}{dT} dT = \int_{T_1}^{T_2} [C_p(\text{products}) - C_p(\text{reactants})] dT$

$\Delta_r H^\circ(T_2) - \Delta_r H^\circ(T_1) = \int_{T_1}^{T_2} [C_p(\text{products}) - C_p(\text{reactants})] dT$  Rearranging,  $\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} [C_p(\text{products}) - C_p(\text{reactants})] dT$  This is the Kirchhoff's equation that gives the temperature dependence of enthalpy change for a reaction. 1.8. Third Law of thermodynamics and calculation absolute entropies of substances

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The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This

is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing  $q_{rev}/T$  increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation. 1.9. Summary In this unit we have started our discussion by revisiting the important terms and laws 20 ? NSOU ? GE-CH-11

of thermodynamics. Then we have focused our discussion on thermochemistry – the study of the heat changes associated with chemical reactions. We have discussed about important principles and definitions of thermochemistry. We have highlighted the concept of standard state and standard enthalpies of formations, enthalpies of solution and dilution. We have shown how to calculate bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature is discussed and Kirchhoff's equation was derived. Finally third law of thermodynamics was stated and calculation absolute entropies of substances were discussed. 1.10. Questions 1. What is standard enthalpy of a reaction? 2. Why the formation enthalpy of Graphite is taken as zero? 3. What is an exothermic and endothermic reaction? 4. Describe Hess's law and explain. 5. Derive the Kirchhoff's equation relating to the effect of temperature on the reaction enthalpy of a reaction. 6. Calculate  $\Delta_r H^\circ$  for the reaction  $C(\text{graphite}) + O_2(g) \rightarrow CO(g)$  at 298 K., using the following thermochemical equations:

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$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = -393.5 \text{ kJ}$   
 $CO(g) + 1/2O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = -283.5 \text{ kJ}$

Ans. -110 kJ)

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Unit 2 ????? Chemical Equilibrium Contents 2.0. Objectives 2.1. Introduction 2.2. Free energy change in a chemical reaction 2.3. Law of mass action 2.4. Thermodynamic derivation of the law of chemical equilibrium 2.5. Distinction between  $\Delta_r G$  and  $\Delta_r G^\circ$  2.6. Relationships between  $K_p$ ,  $K_c$  and  $K_x$  for reactions involving ideal gases 2.7.

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Le Chatelier's principal 2.7.1. Effect of change of concentration 2.7.2. Effect of change of pressure 2.7.3. Effect of change of temperature 2.7.4.

Effect of catalyst 2.8. Summary 2.9. Questions 2.0. Objectives After going through this unit, we will be able to know about ? reversible and irreversible reactions. ? free energy change in a chemical reaction. ? law of mass action. ? relation between free energy and equilibrium constant ? express the equilibrium constant in different ways ? Le Chatelier's principle and its applications. 2.1. Introduction In general, chemical reactions can be divided into two types - reversible and irreversible.

Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. So in the irreversible reactions, the same reactants cannot be formed back from the products under normal set of experimental conditions. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available are reversible reactions.

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This stage of the system is the dynamic equilibrium and the rates of the forward and

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reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture.

The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy. 2.2. Free energy change in a chemical reaction While discussing about the criteria for reversible and irreversible reactions in thermodynamics, it was concluded that if the free energy change of a chemical reaction is negative, the reaction can take place spontaneously, that is it is feasible. If the free energy change is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed. By definition,  $G = H - TS$  so that, at constant temperature,  $\Delta G = \Delta H - T\Delta S$  (1)

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where,  $\Delta G$  is the change in free energy of the reaction,  $\Delta H$  is the change in enthalpy of the reaction and  $\Delta S$  is the change in entropy of the

reaction. From the above equation it is evident that the spontaneity of the reaction is dependent on the overall value of the two factors - energy factor  $\Delta H$  and the entropy factor,  $T\Delta S$ . For a reaction to be spontaneous,  $\Delta G$  value should be negative. For this,  $\Delta H$  should be negative and  $T\Delta S$  should be positive. When both factors are favourable then the value of  $\Delta G$  will have large negative value, and the reaction will be highly feasible. Now suppose the energy factor is favourable, i.e.,  $\Delta H$  is negative, but the entropy factor is not favourable i.e.,  $T\Delta S$  is also negative. In such case, the feasibility of the reaction will be determined by the factor which predominates. So if the numerical value of  $\Delta H$  is greater than  $T\Delta S$ , then the reaction is feasible. Again, if the energy factor does not favour, i.e.,  $\Delta H$  has a positive value but the entropy factor favours the reaction, i.e.,  $T\Delta S$  is positive then the reaction will occur if  $T\Delta S$  is numerically greater than  $\Delta H$ . NSOU ? GE-CH-11 ? 23

If neither energy factor nor entropy factor predominates then  $\Delta H$  is numerically equal to  $T\Delta S$ . Then the value of  $\Delta G$  will be zero. Under these circumstances, the reaction will be in a state of equilibrium, i.e., no net reaction will occur in any direction. Standard free energy change ( $\Delta\Delta\Delta\Delta\Delta G^\circ$ ): The standard free energy change of a reaction is defined as the free energy change of

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a reaction when the reactants and products are in their standard states (25

o C, 1 atm pressure). At this condition the equation 1 may be written as  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  (2) where  $\Delta H^\circ$  is the standard enthalpy change of the reaction and  $\Delta S^\circ$  is the standard entropy change of the reaction at the temperature T. 2.3. Law of mass action Our experimental observations tell us that most of the chemical reactions when carried out in closed vessels do not go to completion. The reactants may still be present but they do not appear to change into products. In this situation

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the rate of the back reaction becomes equal to the rate of the forward reaction. The composition of the reaction

mixture at a given temperature is the same irrespective of the initial state of the system, i.e., irrespective of the fact whether we start with the reactants or the products. The reaction is said to be in a state of equilibrium. The attainment of equilibrium can be recognised by noting constancy of observable properties such as pressure, concentration, density or whichever may be suitable in a given case. The relationship between the quantities of the reacting substances and the products formed can be correlated readily with the help of the law of mass action.

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The law of mass action may be stated as follows: The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is

directly proportional to the product of the active masses of the reacting substances. If we consider a general chemical reaction  $aA + bB \rightleftharpoons mM + nN$  According to the law of mass action, assuming that active masses are equivalent to the molar concentration, the rate of the forward reaction,  $r_f = k_f [A]^a [B]^b$  i.e.  $r_f = k_f [A]^a [B]^b$  and the rate of the reverse reaction,  $r_r = k_r [M]^m [N]^n$  i.e.  $r_r = k_r [M]^m [N]^n$  where  $k_f$  and  $k_r$  are proportionality constants and square brackets represent the molar concentration of the entities enclosed. The constant  $k_f$  is rate constant of the forward reaction and  $k_r$  is the rate constant of the reverse or backward reaction. Now at equilibrium,

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the rate of forward reaction is equal to the rate of the reverse reaction, that is, a

$k_f [A]^a [B]^b = k_r [M]^m [N]^n$  (3) The constant  $K_{eq}$  is called the equilibrium constant of the reaction. Equilibrium constant being the ratio of the concentrations raise to the stoichiometric coefficients. Therefore, the unit of the equilibrium constant =  $\text{mole}^{-\Delta n} \text{L}^{\Delta n}$  where,  $\Delta n = (\text{sum of stoichiometric coefficients of products} - \text{sum of stoichiometric coefficients of reactants})$  Equation 3 represents the law of chemical equilibrium. The equilibrium concentrations in equation 3 can be written in terms of activities ( $a_i$ ), partial pressure ( $p_i$ ), molar concentrations ( $c_i$ ) or mole fraction ( $x_i$ ) of the species involved in the reaction. Consequently,  $K_{eq}$  will have different numerical values for a given chemical reaction. Example 1: Calculate  $K_c$  for the reaction,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ , if the reaction had been started with 1 mole of  $H_2(g)$  and 3 mole of  $I_2(g)$ . At the equilibrium the moles of  $HI$  formed is 1.5 moles. The volume of the reaction vessel is 2 litre. Solution:  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  Initially moles 1 3 0 Moles at eqm.  $1 - x$   $3 - x$   $2x$  Conc. of eqm. From question,  $2x = 1.5$   $x = 0.75$  NSOU ? GE-CH-11 ? 25  
 $[H_2] = (1-x)/2 = 0.25/2$   $[I_2] = (3-x)/2 = 2.25/2$   $[HI] = 1.5/2$  Therefore  $K_c$  for the reaction =  $\frac{[HI]^2}{[H_2][I_2]}$  By putting the values we get  $K_c = 0.8$  2.4. Thermodynamic Derivation of the Law of Chemical Equilibrium Consider once again the general reversible chemical reaction  $aA + bB \rightleftharpoons mM + nN$  where the reactants and the products are assumed to be ideal gases. We know that chemical potential (i.e., Gibbs free energy) of reactants consisting of  $a$  moles of  $A$  and  $b$  moles of  $B$  is given by the expression  $G_{\text{reactants}} = a\mu_A + b\mu_B$  (4) where  $\mu$

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$A$  and  $\mu_B$  are the chemical potentials of the species  $A$  and  $B$ , respectively.

Similarly, for the products we have  $G_{\text{products}} = m\mu_M + n\mu_N$  (5) In each case, pressure and temperature are constant. The free energy of the reaction is equal to the difference between the free energy of the products and that of the reactants. So  $(\Delta G)_{\text{reaction}} = G_{\text{products}} - G_{\text{reactants}} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$  (6) Now at equilibrium, the free energy change  $\Delta G = 0$ . So the equation 6 becomes  $(m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0$  (7) The chemical potential of the  $i$ th species in the gaseous state is given by  $\mu_i = \mu_i^\ominus + RT \ln p_i$  (8) where,  $p_i$  is the partial pressure of the  $i$ th component and the  $\mu_i^\ominus$  is its standard chemical potential. NSOU ? GE-CH-11



potential (i.e., when the partial pressure of the  $i$ th component is unity). So from equation 7 and 8 we can obtain  $\mu_i = \mu_i^\ominus + RT \ln p_i$  (9) or  $\mu_i = \mu_i^\ominus + m_i RT \ln p_i$  (10) or  $\mu_i = \mu_i^\ominus + m_i RT \ln \frac{p_i}{p^\ominus}$  (11) Since  $\Delta G^\ominus$  depends only on temperature and  $R$  is the gas constant, hence the right hand side of equation 11 is a constant at constant temperature. Thus  $\mu_i = \mu_i^\ominus + m_i RT \ln p_i$  (12) This is the law of chemical equilibrium. It can be easily shown that if the chemical potentials of the various species are expressed in terms of mole fractions ( $x_i$ ), then  $\mu_i = \mu_i^\ominus + RT \ln x_i$  (13) So we obtain similar equation like equation 12  $\mu_i = \mu_i^\ominus + m_i RT \ln x_i$  (14) NSOU ? GE-CH-11 ? 27

If the chemical potentials of the various species are expressed in terms of molar concentrations ( $c_i$ ), then  $\mu_i = \mu_i^\ominus + RT \ln c_i$  (15) From which we obtain the following expression  $\mu_i = \mu_i^\ominus + m_i RT \ln c_i$  (16) Equation 12, 14 and 16 are the expressions of  $K_p$ ,  $K_x$ , and  $K_c$  respectively. van't Hoff reaction isotherm: From equation 11 and 12 we can have  $\Delta G = RT \ln K_p$  (17) or  $\Delta G = RT \ln K_c$  (18) The equation 18 is called van't Hoff reaction

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isotherm. It may be used to calculate the change in free energy of a reaction in the standard condition ( $\Delta G^\ominus$ ) from the equilibrium constant and vice-versa. 2.5.

Distinction between  $\Delta G^\ominus$  and  $\Delta G$  For a reaction  $\Delta G^\ominus$  is the difference in the free energy of products and reactants when all of them are in their standard states. This does not refer to the actual reaction at equilibrium.  $\Delta G$ , however, refers to the difference in the free energy of products and reactants at the actual measured concentrations (or partial pressures) of the components. When  $\Delta G=0$ , the reaction is at equilibrium and the concentrations (or the partial pressures) of the components are those which appear in the equilibrium constant expression. 2.6. Relationships between  $K_p$ ,  $K_c$  and  $K_x$  for reactions involving ideal gases Relation between  $K_p$  and  $K_c$ : For an ideal gaseous mixture we can write 28 ? NSOU ? GE-CH-11

$p_i V = n_i RT$  Where,  $c_i (=n_i/V)$  is the molar concentration of the  $i$ th component in the mixture of total volume  $V$ . For the reaction  $aA + bB \rightleftharpoons mM + nN$

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We can write,  $p_A = c_A RT$ ,  $p_B = c_B RT$ ,

$p_M = c_M RT$ ,  $p_N = c_N RT$  So from equation 12 we get  $\Delta G = RT \ln \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$

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$\Delta G = RT \ln K_c$

$\Delta G = RT \ln K_p$  where  $\Delta n = (m + n) - (a + b)$  Relation between  $K_p$  and  $K_c$ : In an ideal gaseous mixture, each component obeys Dalton's law of partial pressure, i.e., where,  $P$  is the total pressure and  $p_i$  is the partial pressure of the  $i$ th component with mole fraction  $x_i$  in the mixture. For the reaction  $aA + bB \rightleftharpoons mM + nN$  we have  $p_A = x_A P$ ,  $p_B = x_B P$ ,  $p_M = x_M P$ ,  $p_N = x_N P$   $\Delta G = RT \ln K_p$

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$\Delta G = RT \ln K_c$

$\Delta G = RT \ln K_p$  (20) where  $\Delta n = (m + n) - (a + b)$  NSOU ? GE-CH-11 ? 29  
So from equation 19 and 20 we can write  $\Delta G = RT \ln K_p$  (21) This is the relation between different equilibrium constants. If  $\Delta n = 0$ ,  $(m + n) = (a + b)$  (i.e.,

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the number of moles of products equals to the number of moles of

reactants),

then  $K_p = K_c = K \times 2.7$ . Le Chatelier's principal The equilibrium expressions derived so far are very useful to perform numerical computations to check the effects of change in pressure, temperature or volume for a system under equilibrium. We can find out the effect of such factors on the system under equilibrium with the help of expressions such as, Eq. 12, 14 and 16. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium. The effect of concentration, temperature and pressure on a system in equilibrium can be predicted with the help of a generalization first proposed by a French chemist Le-Chatelier in 1884. After his name, this generalization is known as Le-Chatelier's principle. It states as follows: If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible). The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these, changes is neutralised. We shall consider the effect of each one of these factors on equilibrium.

**2.7.1 Effect of change of concentration** Let us consider the following reaction at equilibrium,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  Now, if we add some  $H_2$  to the equilibrium mixture, it will disturb the equilibrium. According to Le Chatelier's principle,

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the equilibrium would shift in such a way so as to oppose the effect of

this excess  $H_2$ . It can

do so by using up this excess  $H_2$  to react with more  $I_2$  to give more of  $HI$ . We describe this process by saying that the final position of 30 ? NSOU ? GE-CH-11

equilibrium has shifted to the right of the equation. In this final state of equilibrium, then, more amount of  $HI$  is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of  $H_2$  some  $HI$  is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the value of the equilibrium constant remains the same.

**2.7.2 Effect of change of pressure** If we consider the above reaction again and suppose that the pressure of the system is increased by reducing the volume of the container, the system should react

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in such a way so as to reduce the effect of the

increase in pressure. However there is no way - by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products. However, the situation changes if we consider

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the synthesis of ammonia:  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  If the

pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles, so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus, if we want to produce ammonia in the industry, it is preferable to carry out the reaction at high pressures. Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total numbers of moles of the reactants are different from the total number of moles of the products.

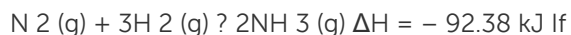
2.7.3 Effect of change of temperature Consider once again

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the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction.

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the temperature of the system is increased at equilibrium then according to Le Chatelier's principle, the

system should react in such a way so as to neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of  $\text{N}_2$  and  $\text{H}_2$  and decrease the amount of  $\text{NH}_3$  at equilibrium. We can generalise this observation as with the increase of the temperature of the system the amount of the products will decrease and the amount of the reactants will increase for an exothermic reaction. Just the opposite will be true for all endothermic reactions. The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of  $\text{N}_2$  and  $\text{H}_2$  will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic. However, we cannot carry out the reaction at a very low temperature because the rate of the reaction becomes too slow at lower temperatures. Hence the reaction is performed at pressures of several megapascals and at optimum temperatures between 650 and 750 K in presence of finely divided iron as catalyst.

2.7.4 Effect of catalyst There is no effect on addition of a catalyst on the equilibrium state. This is because catalyst increases the rate of forward reaction as well as rate of backward reaction to the same extent. It simply helps to achieve the equilibrium quickly. It may be further noted that catalyst has no effect on the equilibrium concentration of a reaction mixture.

2.8. Summary In this unit we have discussed reversible and irreversible reaction and the free energy change in a chemical reaction. Then we have discussed the meaning of chemical equilibrium and the law of mass action. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression

NSOU ? GE-CH-11 were then utilised in understanding the equilibrium. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure in the system.

2.9. Questions

1. Describe the Law of mass action.
2. Derive the relation between  $K_p$  and  $K_c$ .
3. Write a short note on Le Chatelier's principle.
4. Explain the effect of pressure and temperature in the following reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ ;  $\Delta H = -43.2 \text{ kJ}$
5. At 20 °C the  $K_p$  of

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the reaction  $2\text{NO (g)} + \text{Cl}_2 \text{(g)} \rightleftharpoons 2\text{NOCl (g)}$  is  $1.9 \times 10^{-3} \text{ atm}^{-1}$ . Calculate the value of  $K_c$  at

that temperature. (Ans.  $45649.4 \text{ L mol}^{-1}$ ) 6.

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At equilibrium, the concentrations of  $\text{N}_2 = 3.0 \times 10^{-3} \text{ M}$ ,  $\text{O}_2 = 4.2 \times 10^{-3} \text{ M}$  and  $\text{NO} = 2.8 \times 10^{-3} \text{ M}$  in a sealed vessel at 800

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K. What will be  $K_c$  for the reaction  $\text{N}_2 \text{(g)} + \text{O}_2 \text{(g)} \rightleftharpoons 2\text{NO (g)}$  (

Ans. 0.622) NSOU ? GE-CH-11 ? 33

Unit 3 ????? Ionic Equilibrium Contents 3.0. Objectives 3.1. Introduction 3.2. Strong and weak electrolytes 3.3. Degree of ionization 3.4. Ionization of weak acids and bases 3.5. Ionization constant and ionic product of water 3.6. pH scale 3.7. Common ion effect 3.8. Salt hydrolysis - hydrolysis constant, degree of hydrolysis and pH for different salts 3.9. Buffer solutions 3.10. Solubility and solubility product of sparingly soluble salts 3.11. Summary 3.12. Questions 3.0. Objectives After going through this unit, we will be able to know about ? Strong and weak electrolytes. ? Degree of ionization. ? Ionic product of water. ? pH scale and pH calculation. ? Common ion effect and its applications. ? Salt hydrolysis. ? Buffer solution and buffer action.

? Solubility and solubility product of sparingly soluble salts. ? Application of solubility product in precipitation reaction. 3.1. Introduction

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There are numerous equilibria that involve ions only. In the following sections we will study the equilibrium involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (NaCl) is added to water it conducts electricity. Also, the conductance of electricity increases with increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not

conduct electricity

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are, referred to as non electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is

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established between ions and unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium. 3.2.

Strong and weak electrolytes An electrolyte is defined as a compound whose aqueous solution or molten state conducts electricity. On the other hand, a compound whose aqueous solution or molten state does not conduct electricity is called a non electrolyte. The conductance by an electrolyte is due to the presence of ions produced by the dissociation of the substance. However, different electrolytes dissociate to different extents. Acids, bases and salts come under the category of electrolytes. Depending upon the degree of dissociation or ionization, the electrolytes are divided into two categories, called 'strong electrolytes' and 'weak electrolytes'. Strong Electrolytes: These are the substances which dissociate almost completely into ions in aqueous solution and hence are a very good conductor of electricity. NSOU ? GE-CH-11 ? 35

Examples: Acid: HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> etc. Base: NaOH, KOH, Ba(OH)<sub>2</sub> etc. Salt: NaCl, KCl, CaCl<sub>2</sub>, KNO<sub>3</sub>, CuSO<sub>4</sub> etc. Weak Electrolytes: These are the substances which dissociate to a small extent in aqueous solution and hence conduct electricity also to a small extent. Examples: Acids: H<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COOH, HCN etc. Base: NH<sub>4</sub>OH, Al(OH)<sub>3</sub>, Zn(OH)<sub>2</sub> etc. Salt: MgCO<sub>3</sub>, PbCl<sub>2</sub>, BaCO<sub>3</sub> etc. 3.3. Degree of ionization As we know that the weak electrolytes do not ionize completely, so an equilibrium will reach between the ionized and unionized species in the solution.

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The degree of ionisation may be defined as the fraction of total amount of a weak electrolyte that exists in the ionized form. It is denoted by a Greek letter 'α'.

So, Number of molecules dissociated at equilibrium Total number of molecules taken ? ? (1) Consider a weak electrolyte AB, which dissociates in water and forms A<sup>+</sup> and B<sup>-</sup>. So an equilibrium will be established in solution. Let the initial concentration of the weak electrolyte, AB is c mol/L and α is the degree of dissociation. Then at equilibrium the concentration of A<sup>+</sup> and B<sup>-</sup> will be αc mol/L and concentration of AB will be (c- αc) mol/L. AB ? A<sup>+</sup> + B<sup>-</sup> Initial concentration: c 0 0 Equilibrium concentration: c(1-α) αc αc 36 ? NSOU ? GE-CH-11

So according to the law of mass action the equilibrium constant can be written as ? ? A B K AB ? ? ? ? ? ? ? ? where K is the dissociation constant or ionization constant. So, 2 c c c K c(1 - α) 1 ? ? ? ? ? ? ? ? (2) As for a weak electrolyte α >> 1; we can take (1 - α) = 1. 2 K

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K c or, c ? ? ? ? (3) So if we know the value of the dissociation constant of the weak electrolyte and the concentration of the weak electrolyte we can find its degree of dissociation or

ionization. Factors affecting

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degree of ionization: The degree of ionization of a weak electrolyte depends on the following factors: 1. Nature of electrolytes: The degree of

ionization depends upon the nature of electrolytes. Strong electrolytes have a high degree of ionization (value of  $\alpha$  is equal to 1) while weak electrolytes have a low degree of ionization. 2. Nature of solvent: The ionizing power of the solvent depends upon its dielectric constant. The greater the value of the dielectric constant greater will be ionizing power of solvent and the greater will be the degree of ionization. 3. Dilution: From equation 3, we can observe that degree of ionization is inversely proportional to the concentration i.e.  $\alpha \propto \frac{1}{c}$ . This is known as the Ostwald's dilution law. So, the degree of ionization increases with an increase in dilution. At infinite dilution, even the weak electrolytes are almost completely ionized. 4. Temperature: The degree of ionization increases with the increase in temperature. NSOU ? GE-CH-11 ? 37

5. Common ion effect: Due to the common ion effect, the degree of ionization of weak electrolytes is decreased or suppressed. The suppression of

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degree of ionization of weak electrolyte by the addition of strong electrolyte having common ion is called common ion effect. 3.4. Ionization of

weak acids and bases Ionization of weak acid: Weak acids are dissociated to a very small extent in the solution and the ions produced on dissociation are in equilibrium with the undissociated molecules in solution If HA represents any weak acid, we can write the dissociation reaction as,  $HA \rightleftharpoons H^+ + A^-$  and the corresponding dissociation constant expression as,  $K_a = \frac{[H^+][A^-]}{[HA]}$  (4)  $K_a$  is the dissociation constant of the acid. If the initial concentration of the acid is  $c$  and  $\alpha$  is the degree of dissociation, then the equilibrium concentrations would be,  $HA \rightleftharpoons H^+ + A^-$  Initial concentration:  $c \quad 0 \quad 0$  Equilibrium concentration:  $c(1-\alpha) \quad \alpha c \quad \alpha c$  Substituting these values in equation 4, we get  $K_a = \frac{\alpha^2 c}{1-\alpha}$  (5) for a weak acid  $\alpha \ll 1$ ; we can take  $(1 - \alpha) \approx 1$ .  $K_a \approx \alpha^2 c$  (6) From this equation we can

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calculate the degree of dissociation of a weak acid. 38 ? NSOU ? GE-CH-11 Now the concentration of  $H^+$  ion in the solution

can be calculated using equation 6  $\alpha = \sqrt{\frac{K_a}{c}}$  (7) Ionization of weak base: Similarly for a weak base BOH, we can write the dissociation reaction as,  $BOH \rightleftharpoons B^+ + OH^-$  and the corresponding dissociation constant expression as,  $K_b = \frac{[B^+][OH^-]}{[BOH]}$  (8)  $K_b$  is the dissociation constant of the weak base. If the initial concentration of the base is  $c$  and  $\alpha$  is the degree of dissociation, then the equilibrium concentrations would be,  $BOH \rightleftharpoons B^+ + OH^-$  Initial concentration:  $c \quad 0 \quad 0$  Equilibrium concentration:  $c(1-\alpha) \quad \alpha c \quad \alpha c$  Substituting these values in equation 8, we get  $K_b = \frac{\alpha^2 c}{1-\alpha}$  (9) for a weak base  $\alpha \ll 1$ ; we can take  $(1 - \alpha) \approx 1$ .  $K_b \approx \alpha^2 c$  (10) From this equation we can calculate the degree of dissociation of a weak base. Now the concentration of  $OH^-$  ion in the solution can be calculated using equation 10  $[OH^-] = \alpha c = \sqrt{K_b c}$  (11) NSOU ? GE-CH-11 ? 39

3.5. Ionization constant and ionic product of water Pure water is poor conductor of electricity. This shows that water is weak electrolyte i.e., it is ionized to a very small extent as  $H_2O \rightleftharpoons H^+ + OH^-$  (12) or  $2H_2O \rightleftharpoons H_3O^+ + OH^-$  (13) Although eqs. 12 and 13 are representations of the same equilibrium, eq. 13 is a better representation in the sense that a free proton having a high charge density and extremely small size is incapable of free existence in solution and, therefore, gets attached to a molecule of water. However, since our calculations on equilibrium constant will not be different in case of either representation, for simplicity sake, we represent the water equilibrium by eq 12.

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Applying law of chemical equilibrium, its dissociation constant  $K$ , is given by ? ? 2

$K_w = [H^+][OH^-]$  (14) In pure water the concentration of  $H_2O$  molecules is approximately 55.4 M and since the dissociation of  $H_2O$  is negligibly small in comparison with its concentration, we can safely assume that the concentration of  $H_2O$  at equilibrium is a constant quantity. Thus,  $K_w$  in eq. 14 can be replaced by a new constant.  $K_w = [H^+][OH^-]$  (16) where  $K_w$  is called the dissociation constant of water or, more commonly, the ionic product of water. Hence ionic product of water may be defined as the product

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of the molar concentration of  $H^+$  and  $OH^-$  ions. The value of  $K_w$  at 298 K (25 °C) is

experimentally determined as  $K_w = 1.0 \times 10^{-14}$ . Hence,  $[H^+][OH^-] = 1.0 \times 10^{-14}$  (17) Since the amount of  $H^+$  and  $OH^-$  produced by the dissociation of pure water is equal, concentration of each ion in solution is given by 40 ? NSOU ? GE-CH-11

$K_w = 1.0 \times 10^{-14}$  (for pure water) (18) Like any equilibrium constant,  $K_w$  also depends on temperature as with increase of temperature degree of dissociation of water increases. So the concentration of  $H^+$  and  $OH^-$  also increases. The following table shows the variation of  $K_w$  with temperature. T (°C)  $K_w$  (mol<sup>2</sup> dm<sup>-6</sup>) 0  $0.114 \times 10^{-14}$  25  $1.008 \times 10^{-14}$  50  $5.476 \times 10^{-14}$  100  $51.3 \times 10^{-14}$  3.6. pH scale From the above discussion we have seen that the equilibrium of water is given by equation 14 ? ?  $H_2O \rightleftharpoons H^+ + OH^-$  Now suppose that we add a small quantity of an acid to water, thereby increasing the concentration of  $H^+$  ions at equilibrium. The equilibrium will immediately shift back to oppose the effect of this increase by the combination of the added  $H^+$  ions with some  $OH^-$  ions to form undissociated water till eq.14 is satisfied. Once the equilibrium is re-established, the concentration of the hydrogen ion will be more than the concentration of the hydroxyl ion in solution. Hence, at 298 K, whenever the concentration of hydrogen ion in water is greater than  $1.0 \times 10^{-7}$  M, we call the solution to be acidic and whenever it is less than  $1.0 \times 10^{-7}$  M, we call it a basic solution.

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It is quite inconvenient to express these concentrations by using powers of 10. In 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called pH scale) for expressing the concentrations of  $H^+$  ions. He defined pH as the negative logarithm of the molar concentration of hydrogen ions. That is,  $pH = -\log_{10} [H^+]$  (19)

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$[H^+] = 10^{-pH}$  (20) where  $H^+$  ion concentration is expressed in  $\text{mol dm}^{-3}$ . The concept of negative logarithm can be used for defining the concentration of other ions also. For example,  $pOH$  represents the concentration of  $OH^-$  ion in solution and  $pM$  represents the concentration of the metal ion,  $M$ , in solution. Pure water, where  $H^+$  ion and  $OH^-$  ion concentration are both equal to  $1.0 \times 10^{-7}$  (at 298 K), will thus have a pH value of 7. An acidic solution means that the pH should be less than 7 and a basic solution should have pH greater than 7. Let us consider a few simple calculations to see quantitatively as to what happens to the self-ionisation equilibrium of water when we add a small quantity of a strong acid to it. Consider a solution containing 0.010 mole of HCl in one  $\text{dm}^3$  of water. The concentration of hydrogen ion due to HCl will be  $1.0 \times 10^{-2}$  M. This addition of acid will disturb the water equilibrium and this equilibrium will shift to left so that dissociation of water is suppressed. Thus, the concentration of  $H^+$  ions produced by the self-ionisation of water ( $10^{-7}$  M) is negligible in comparison with the  $H^+$  ion produced by the added acid ( $10^{-2}$  M). Hence, the contribution due to water dissociation can be neglected in such a case and the pH of the solution will be 2. The concentration of  $OH^-$  will then be given by,  $10^{-12}$  M. We can state this in a different way that, in  $10^{-2}$  M acid solution, the concentration of  $OH^-$  ion ( $10^{-12}$  M in the above example) is less than the concentration of  $H^+$  ion ( $10^{-2}$  M) and, the product of the two is always constant, and is equal to  $1.0 \times 10^{-14}$ . This can be expressed as,  $pH + pOH = 14 = -\log K_w$  (21) Thus, in pure water or a dilute solution of an acid or a base, we can express the concentration of  $H^+$  or  $OH^-$  by simply stating the pH of the solution. We have also studied that the contribution due to self-ionisation of water is negligible in cases of solution of strong acids and bases as well as of moderately concentrated solutions of weak acids and weak bases. However, dealing with very dilute solutions of weak acids and bases, we cannot neglect the contributions due to self-ionisation equilibrium of water.

### 3.7. Common ion effect

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In the previous unit we have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.

Let us consider the

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dissociation of a weak acid such as acetic acid,  $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

the equilibrium constant for which can be represented as,  $K_a$

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$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$  (22) or,  $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$  (23)

Now, suppose that we add some acetate ions in the form of solid sodium acetate to the above solution. Sodium acetate is added in the solid form so as not to cause any change in the volume of the solution. Sodium acetate being a strong electrolyte will dissociate almost completely to give  $Na^+$  ions and  $CH_3COO^-$  ions in solution. The acetate ions so added will disturb the equilibrium of acetic acid. The equilibrium will, therefore, shift to left producing more of undissociated acetic acid in order to counteract the effect of added acetate ions according to Le Chatelier's principle. The net result is that the dissociation of the acid has been suppressed by the addition of a common ion (acetate ion in this case) at equilibrium. Thus any ion which is involved in a chemical equilibrium and comes from two different sources in solution is known as 'common ion' and its effect finds great use in the study of buffer solutions and the solubility of sparingly soluble salts which we will discuss in the next few sections.

### 3.8. Salt Hydrolysis - Hydrolysis Constant, Degree of Hydrolysis and pH for Different Salts



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The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a

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reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts. (i) Salt of strong acid

and strong base (eg.  $\text{HCl} + \text{NaOH}$ )  $\text{NaCl}$  (ii)

Salt of strong acid and

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weak base (e.g.  $\text{HCl} + \text{NH}_4\text{OH}$ )  $\text{NH}_4\text{Cl}$  (iii) Salt of weak acid

and

strong base (e.g.  $\text{CH}_3\text{COOH} + \text{NaOH}$ )  $\text{CH}_3\text{COONa}$  (iv)

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Salt of weak acid and weak base (e.g.  $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$ )  $\text{CH}_3\text{COONH}_4$  Let us consider the acid base behaviour of the different type of salts. (i) Salt of strong acid and strong base: The cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore the salts of this category do not show any acid-base behaviour and are neutral. (ii) Salt of strong acid

and

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weak base: the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid. For example,  $\text{NH}_4\text{Cl}$  dissociates as:  $\text{NH}_4\text{Cl}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$  The anion

from the strong acid

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does not get hydrolysed but the cation get hydrolysed as per the following equation:  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{OH} + \text{H}^+(\text{aq})$

which produces a weak base

and excess of hydrogen ions in solution, thus rendering the solution acidic. Hence, we can say that

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the salt of a weak base and a strong acid



two ions. If  $\text{NH}_4^+$  hydrolyses to a greater extent than  $\text{CH}_3\text{COO}^-$  ion, the solution will be acidic and, if the reverse is true, then the solution will be basic. If the extent of hydrolysis is exactly equal, then the solution should be neutral as if no hydrolysis is taking place. By considering the similar method we can establish that if  $c$  mol/litre is the concentration of the  $\text{CH}_3\text{COONH}_4$  and  $h$  is its degree of hydrolysis then We can get

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$w$   $h$   $a$   $b$   $K$   $K$   $K$   $K$   $?$  (32)  $w$   $a$   $b$   $K$   $h$   $K$   $K$   $?$   $?$  (33)

$a$   $b$   $1$   $1$   $\text{pH}$   $7$   $\text{pK}$   $2$   $2$   $?$   $?$   $?$  (34) NSOU ? GE-CH-11 ? 47  
From the equation 34,

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we can see that the pH of the solution is independent of the concentration of the

salt. If  $\text{pK}_a = \text{pK}_b$  then the pH of the solution is 7. When  $\text{pK}_a < \text{pK}_b$  then the pH  $< 7$ , so the solution will be basic. When  $\text{pK}_a > \text{pK}_b$  then the pH  $> 7$ , so the solution will be acidic. 3.9. Buffer solutions In section 3.7 we have seen that

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that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids / bases and a salt of common ion are important in a yet another way. These act as buffer solutions. Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base. In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemoglobin in our blood and activity of the enzymes in our cells depends very strongly on the pH of our body fluids. pH of the blood is very close to 7.4 and pH of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in pH by the presence of buffers. There are two kinds of commonly used buffer-solutions i) A weak acid and a soluble ionic salt of the weak acid

forms a buffer with pH less than 7 are called acidic buffers

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e.g. acetic acid and sodium acetate. ii) A weak base and a soluble ionic salt of the weak base

forms a buffer with pH above 7 are called basic buffers. e.g. ammonium hydroxide and ammonium chloride.

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Let us consider a buffer solution containing acetic acid,  $\text{CH}_3\text{COOH}$  and sodium acetate  $\text{CH}_3\text{COONa}$  to understand

about how buffer resist the change of pH in the solution. In acetic acid - sodium acetate buffer  $\text{CH}_3\text{COOH}$  acts as acid reserve while  $\text{CH}_3\text{COONa}$  (or  $\text{CH}_3\text{COO}^-$  ions) works as the base reserve. In the solution mixture the 48 ? NSOU ? GE-CH-11 added

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components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation.  $\text{CH}_3\text{COOH (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{CH}_3\text{COO}^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)}$   $\text{CH}_3\text{COONa (aq)} \rightarrow \text{Na}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$  If we add a strong acid such as HCl to this solution, it produces  $\text{H}_3\text{O}^+$ . These added  $\text{H}_3\text{O}^+$  (acid) react with an equivalent amount of the base reserve  $[\text{CH}_3\text{COO}^-]$  to generate undissociated acetic acid. The reaction being  $\text{CH}_3\text{COO}^- \text{(aq)} +$

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$\text{H}_3\text{O}^+ \text{(aq)} \rightarrow \text{CH}_3\text{COOH (aq)} + \text{H}_2\text{O (l)}$  The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being  $\text{CH}_3\text{COO}^- \text{(aq)} + \text{HCl (aq)} \rightarrow \text{CH}_3\text{COOH (aq)} + \text{Cl}^- \text{(aq)}$  Similarly, when small amount of a strong base like NaOH is added, it generates  $\text{OH}^-$  ions. These additional  $\text{OH}^-$  neutralize some of the  $\text{H}_3\text{O}^+$  ions present in the solution.

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Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of  $\text{CH}_3\text{COOH}$  to re-establish the equilibrium.

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The net result is the neutralization of  $\text{OH}^-$  by  $\text{CH}_3\text{COOH}$ . In other words we can say that the added  $\text{OH}^-$  ions (base) react with the acid reserve to produce  $\text{CH}_3\text{COO}^-$  ions.  $\text{OH}^- \text{(aq)} + \text{CH}_3\text{COOH (aq)} \rightarrow \text{CH}_3\text{COO}^- \text{(aq)} + \text{H}_2\text{O (l)}$  The effective reaction is the reaction of the added base with acid reserve.  $\text{NaOH (aq)} + \text{CH}_3\text{COOH (aq)} \rightarrow \text{CH}_3\text{COONa (aq)} + \text{H}_2\text{O (l)}$  The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve. So we can observe that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the hydronium ions and thereby the pH does not change significantly. Now the pH of a buffer solution

can be calculated from the Henderson's equation.

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Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is  $\text{CH}_3\text{COOH (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{CH}_3\text{COO}^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)}$  NSOU ? GE-CH-11 ? 49 which is characterized by the acid dissociation constant,  $K_a$

$K_a$

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$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$  Rearranging, we get  $[\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$  The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [Salt]. Thus the above equation may be re written as  $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

a [Acid]

$H^+ O K [Salt] \dots$  Taking logarithm and multiplying by (-1) in both side we get 3 a [Acid]  $\log H^+ O \log K \log [Salt] \dots$   
 $\dots$  or a [Acid]  $pH = pK + \log \frac{[Acid]}{[Salt]}$  or, a [Salt]  $pH$

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$pK + \log \frac{[Acid]}{[Salt]}$  (35) This equation is known as Henderson's equation. A similar expression can be derived for a basic buffer (e.g., ammonium hydroxide and ammonium chloride). The expression is  $pOH = pK + \log \frac{[Base]}{[Salt]}$  (36) 50 ?

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3.10. Solubility and Solubility Product of Sparingly Soluble Salts When a solute is added gradually to an amount of solvent, at a particular temperature, there comes a point when no more solute can be dissolved. This point gives a saturated solution. A solution which remains in contact with undissolved solute is said to be saturated. At the saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature. Consider in general, the electrolyte of the type  $A_x B_y$  which is dissociated as:  $A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$  Applying law of mass action we can write  $x y x x y A B K A B \dots$  (37) When the solution is saturated,  $[A^{y+}] = K'$  (constant) So we can write the equation 37 as  $[A^{y+}]^x [B^{x-}]^y = K[A_x B_y] = K \cdot K' = K_{sp}$  (constant) (38)  $K_{sp}$  is the solubility product constant or simply solubility product. Thus, solubility product is defined as

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the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation

representing the dissociation of the electrolyte at a given temperature when the solution is saturated. Relationship between solubility and solubility product: Salts like  $AgCl$ ,  $BaSO_4$ ,  $PbSO_4$ ,  $PbI_2$ , etc. are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolytes contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i.e., it is completely dissociated. The equilibrium for a saturated solution of a sparingly soluble salt  $A_x B_y$  of solubility  $S$  mol/L may be expressed as: NSOU ? GE-CH-11 ? 51  
 $A_x B_y (s) \rightleftharpoons xA^{y+} (aq) + yB^{x-} (aq)$  At equilibrium,  $[A^{y+}] = xS$  mol/L and  $[B^{x-}] = yS$  mol/L So,

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$K_{sp} = [A^{y+}]^x [B^{x-}]^y = [xS]^x [yS]^y = x^x \cdot y^y \cdot (S)^{x+y}$  (39)

Special Cases: (i) 1: 1 type salts: Examples:  $AgCl$ ,  $AgI$ ,  $BaSO_4$ ,  $PbSO_4$ , etc.  $K_{sp} = S \cdot S = S^2$  (ii) 1: 2 or 2: 1 type salts: Examples:  $Ag_2CO_3$ ,  $Ag_2CrO_4$ ,  $PbCl_2$ ,  $CaF_2$ , etc.  $K_{sp} = S \cdot (2S)^2 = 4S^3$  (iii) 1: 3 type salts: Examples:  $AlCl_3$ ,  $Fe(OH)_3$ ,  $Cr(OH)_3$ ,  $Al(OH)_3$ , etc.  $K_{sp} = S \cdot (3S)^3 = 27S^4$  Example 1. At 298 K, the solubility of silver chloride is  $1.37 \times 10^{-5}$  M. Calculate its solubility product. Solution: The equilibrium of silver chloride is  $AgCl \rightleftharpoons Ag^+ + Cl^-$  Here  $x = 1$  and  $y = 1$ , So,  $K_{sp} = S^2 = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$  Effect of common ion on solubility of sparingly soluble salt:

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What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt? We may reason out that according to Le Chatelier's principle, the common-ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us

extend the problem in example 1 as, what will be the solubility of AgCl in 0.01 M AgNO<sub>3</sub> solution? Addition of 0.01 M concentration of AgNO<sub>3</sub> will provide 0.01 M of Ag<sup>+</sup> ions in the solution as AgNO<sub>3</sub> is a strong electrolyte. Assuming this contribution to be much larger in comparison with Ag<sup>+</sup> ion concentration due to dissolved AgCl (solubility S mol/L), we can write. [Ag<sup>+</sup>] = 0.01 and [Cl<sup>-</sup>] = S So,  $K_{sp} = 1.88 \times 10^{-10} = [Ag^+][Cl^-] = 0.01 \times S$  or,  $S = 1.88 \times 10^{-8}$  52 ? NSOU ? GE-CH-11

We can see that, as compared to the solubility of AgCl in water ( $1.37 \times 10^{-5}$  M), its solubility in presence of 0.01 M AgNO<sub>3</sub> is almost 10<sup>3</sup> times less.

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Application of solubility product in qualitative analysis: The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon selective precipitation of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the  $K_{sp}$  of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of H<sub>2</sub>S. The dissociation of H<sub>2</sub>S can be written as  $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$  Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions. We know that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the S<sup>2-</sup> ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out. 3.11.

Summary In summary we have started the discussion explaining electrolytes and non electrolytes. Then we focused our discussion on strong and weak electrolytes followed by degree of dissociation for weak electrolytes and the factors affecting the degree of dissociation. Ionization of weak acid and weak bases are discussed. After that, ionic product of water was explained and the concept was extended for establishing the concept of pH scale. We have found the effect of common ion in dissociation of weak acid and bases. We have learned about the salt hydrolysis and calculated the hydrolysis constant, degree of hydrolysis and pH for different types of salts. We have seen that

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the presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called Henderson'

s equation. After that we have discussed that

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the product of the concentration of the ions in the solubility equilibrium is a constant called solubility product ( $K_{sp}$ ) and is proportional to the solubility of the sparingly soluble

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salt. We have found that

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the presence common ion decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis. 3.12.

Questions 1. Write a short note on pH scale. 2. What is degree of ionization? 3. What are sparingly soluble salts? 4. What will happen if we pass HCl gas in a saturated solution of NaCl? 5. What is buffer? Give example of one acidic and one basic buffer. 6. Why the pH of a buffer remains constant upon addition of small amount of acid or base? 7. Why the solution of FeCl<sub>3</sub> is acidic? 8. If the solubility of Zinc phosphate in water is S mol/L, then find the expression for the solubility product of the salt. (Ans.  $108 S^5$ ) 9. Calculate the pH of 0.1 M NaOH solution. (Ans. 13) 10. If in 1 L of buffer solution 0.2 mol of NH<sub>4</sub>Cl and 0.1 mol of NH<sub>4</sub>OH is dissolved then what will be the pH of the solution? Given that K<sub>b</sub> of NH<sub>4</sub>OH is  $1.8 \times 10^{-5}$ . (Ans. 8.96) 54 ? NSOU ? GE-CH-11

Unit 4 ????? Kinetic Theory of Gases Contents 4.0. Objectives 4.1. Introduction 4.2. Postulates of kinetic theory of gases 4.3. Kinetic gas equation 4.4. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies 4.5. Average, root mean square and most probable velocities 4.6. Collision Parameters 4.7. Viscosity of gases 4.8. Deviation of real gases from ideal behavior 4.9. Critical phenomena 4.10. Summary 4.11. Questions 4.0. Objectives After studying this unit, we will be able to: ? state the postulates of kinetic theory of gases ? derive the kinetic gas equation  $PV = \frac{1}{3} nmc^2$  ? explain the distribution of molecular speeds and energies ? calculate the most probable speed, the average speed and the root mean square speed ? derive an expression to calculate the collision number between gas molecules ? calculate the mean free path of molecules ? explain the origin and factors responsible for viscosity of gases ? differentiate between ideal gas and real gas and reasons for deviation from ideal behaviour ? explain the critical phenomenon and critical constants. 4.1. Introduction The kinetic theory describes a gas as a large number of sub microscopic particles (atoms or molecules), all of which are in constant, and random motion. The rapidly moving particles constantly collide with each other and with the walls of the container. Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity, and volume, by considering their molecular composition and motion. The theory depicts that gas pressure is due to the impacts, on the walls of a container, of molecules or atoms moving at different velocities. 4.2. Postulates of kinetic theory of gases The kinetic molecular theory of gases explains the laws that describe the behaviour of gases. This theory developed during the mid-19 th century by several physicists, including the Boltzmann, Clausius and Maxwell. The kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following postulates: i. Every gas consists of large number of tiny particles called point masses i.e.

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the actual volume of molecules is negligible when compared to the total volume of the gas.

ii. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel. iii. A molecule moves in a straight line with uniform velocity between two collisions. iv. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls

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of the vessel. v. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one

another. 56 ? NSOU ? GE-CH-11

vi.

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The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained. vii. The average kinetic energy of gas molecules is directly proportional to absolute temperature.

viii.

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This means that the average kinetic energy of molecules is the same at a given temperature. 4.3.

**Kinetic gas equation** Suppose a definite amount gas is placed in a cubic closed vessel of length  $l$ . Let the mass of the each gas molecule is  $m$ . The gas consists of total  $n$  molecules and each molecule is moving randomly with a velocity  $c$  (root mean square velocity). This velocity  $c$  can be divided into three components of  $u$ ,  $v$  and  $w$  along  $X$ ,  $Y$  and  $Z$  direction respectively.  $c^2 = u^2 + v^2 + w^2$  Now, we consider the movement of a molecule along  $X$  axis (figure 4.1). If the velocity of the molecule along  $X$  axis is  $u$  then the momentum is  $mu$ . Now when the molecule collides perpendicular to the wall of the container with velocity  $u$ , it will revert back to the opposite direction with same velocity as the collision is an elastic collision. The velocity after the collision will be  $-u$ . As the collision between the molecules and walls are elastic, so the momentum will be same before and after the collision. So the change in momentum after a collision with the wall =  $mu - (-mu) = 2mu$  Figure 4.1. Velocity of a gas molecule along  $X$ -axis placed in a cubic container. NSOU ? GE-CH-11 ? 57

Now after collision with the  $A$  side of the wall it will reflect and will collide with the opposite wall at a distant of  $2l$ . Hence, the number of collision per second for a gas molecule moving along  $X$ -axis with a velocity  $u$  is  $\frac{u}{2l}$ . So for  $u$  component of velocity of a molecule change in momentum per second is  $2mu \times \frac{u}{2l} = \frac{mu^2}{l}$ . For the same molecule the change of momentum per second for the  $v$  and  $w$  component of the velocity will be  $2mv \times \frac{v}{2l} = \frac{mv^2}{l}$  and  $2mw \times \frac{w}{2l} = \frac{mw^2}{l}$  respectively. Total change of momentum for a molecule per second is  $\frac{m}{l}(u^2 + v^2 + w^2) = \frac{mc^2}{l}$ . For  $n$  number of molecules rate of change of momentum is  $2mnc \times \frac{c}{2l} = \frac{mnc^2}{l}$ . From the Newton's second law we know that rate of change of momentum is equal to the force. As the pressure ( $P$ ) is equal to the force acting per unit area and the total surface area of the container =  $6l^2$ . So we can write,  $\frac{mnc^2}{l} = P \times 6l^2$  or,  $\frac{1}{3}PV = mnc^2$  (1) This is known as kinetic gas equation. NSOU ? GE-CH-11

**4.4. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies** In a given mass of gas, the velocities of all molecules are not the same, even when bulk parameters like pressure, volume and temperature are fixed. Collisions change the direction and the speed of molecules. However in a state of equilibrium, the distribution of speeds is constant or fixed. If at a particular temperature  $T$ ,  $dN$  number of molecules are present in between the velocity  $c$  and  $(c + dc)$  among total  $N$  number of molecules then the Maxwell's equation of distribution of molecular velocity is given by the following equation-  $\frac{dN}{N} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} dc$  (2) Where,  $dN$  is the number of molecules having velocity between  $c$  to  $c + dc$ ,

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$m$  is the mass of the each gas molecule,  $N$  is the total number of

gas molecules present,  $k$  is Boltzmann constant and  $T$  is absolute temperature of the gas. Also the equation can be written as  $\frac{dN}{N} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} dc$

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$\frac{dN}{N} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} dc$  (3)

Where  $R$  = universal gas constant,  $M$  = Molecular weight of the gas. Figure 4.2. Plot of Maxwell's distribution of molecular velocities. NSOU ? GE-CH-11 ? 59



The Maxwell distribution is customarily plotted with the function  $c \, dN / N \, dc$  in the y-axis and  $c$  as the x-axis. The fraction of the molecules in the speed range  $c$  to  $c + dc$  is  $c \, dN / dc$ ; dividing this by  $dc$  gives the fraction of the molecules in this speed range per unit width of the interval. The Maxwell's distribution of molecular velocities is plotted in figure 4.2. We can see from the plot that the fraction of molecules having velocities greater than zero increases with an increase in velocity, reaches a maximum and then falls off towards zero at higher velocities. The important features of the curves are as follows: i) The fraction of molecules with too low or too high velocities is very small. ii) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity. Effect of temperature on distribution of molecular velocities for a particular gas: Effect of temperature on distribution of molecular velocities for a  $N_2$  gas is plotted in figure 4.3. The important features are: i) The entire distribution curve shifts to the right and becomes broader with increase in temperature Figure 4.3. Maxwell distribution for nitrogen at two temperatures. 60 ? NSOU ? GE-CH-11

ii) With increase of temperature fraction of the molecules having high velocities increases considerably. iii) The most probable velocity increases with increase in temperature but the number of molecules present at that velocity decreases. Distribution of molecular energies: The Maxwell's speed distribution, eq. 2, can be converted to an energy distribution. The kinetic energy of a molecule is  $\frac{1}{2} m c^2$ . Then,  $\frac{1}{2} m c^2 = \epsilon$ . Thus equation 2 can be converted to energy distribution equation as  $\frac{1}{2} m c^2 = \epsilon$  (4) where  $dN$  is the number of molecules having kinetic energies between  $\epsilon$  and  $\epsilon + d\epsilon$ . Figure 4.4. Energy distribution at 300 K. Energy distribution curve is distinctly different shape compared to that of the speed distribution (figure 4.4). In particular, the energy distribution curve rises sharply at the beginning and thus it rises much more quickly than the velocity distribution. After passing the maximum, the energy distribution falls off more slowly than does the velocity distribution. As usual, the distribution is broadened at higher temperatures, a greater proportion of the NSOU ? GE-CH-11 ? 61

molecules having higher energies. As before, the areas under the curves for different temperatures must be the same. 4.5. Average, root mean square and most probable velocities Mean or Average velocity ( $C_{av}$ ) The average speed is the sum of all the velocities ranging from 0 to  $\infty$  divided by total number of molecules present ( $n$ ). If for a gas  $n_1, n_2, n_3, \dots$  number of molecules has the velocity of  $c_1, c_2, c_3, \dots$  respectively then the average velocity will be  $\frac{1}{n} (n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots)$  From Maxwell's equation of distribution of velocity, it can be shown that the average velocity for a gas with molecular mass  $M$  is  $C_{av} = \sqrt{\frac{8RT}{\pi M}}$  (5) where,  $R$  is universal gas constant and  $T$  is temperature of the gas. Root Mean Square Velocity ( $C_{rms}$ ) The root mean square velocity or rms velocity is the square root of the sum of all the squared velocities ranging from 0 to  $\infty$  divided by total number of molecules  $N$ . If for a gas  $n_1, n_2, n_3, \dots$  number of molecules has the velocity of  $c_1, c_2, c_3, \dots$  respectively then the root mean square velocity of the gas molecules will be  $\sqrt{\frac{1}{n} (n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots)}$  From Maxwell's equation of distribution of velocity, it can be shown that the root mean square velocity for a gas with molar mass  $M$  at temperature  $T$  is  $C_{rms} = \sqrt{\frac{3RT}{M}}$  (6) 62 ? NSOU ? GE-CH-11

Most Probable Velocity ( $C_{mp}$ ) The most probable velocity is the velocity possessed by maximum number of molecules at a particular temperature. From Maxwell's equation of distribution of velocity, it can be shown that the most probable velocity ( $c_{mp}$ ) for a gas with molar mass  $M$  at temperature  $T$  is  $C_{mp} = \sqrt{\frac{2RT}{M}}$  (7) 4.6. Collision parameters

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Collision diameter: The kinetic theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which

the repulsion between the molecules (resulting from electronic and nuclear repulsion) becomes so strong that it causes reversal of the direction of their motion. The distance between the centres of the two molecules at the point of their closest approach is known as collision diameter ( $\sigma$ ). Evidently, a gaseous molecule can be regarded as a hard sphere of radius ' $\sigma/2$ '. It can be imagined that if the distance between the centres of two molecules is less than  $\sigma$ , there would be a collision between them. Thus, collision is an event in which the centres of two identical molecules come within a distance between  $d$  from each other. Figure 4.5. The zigzag motion of a gas molecule. Collision cross section: The model of gaseous molecules as hard non-interacting spheres of diameter  $\sigma$  can NSOU ? GE-CH-11 ? 63

satisfactorily account for various gaseous properties such as viscosity, diffusion, thermal conductivity, mean free path, number of collision the molecules undergo. It can be imagined that when two molecules collide, the effective area of the target is  $\pi\sigma^2$ . The quantity  $\pi\sigma^2$  is called the collision cross-section of the molecule because it is the cross-sectional area of an imaginary sphere surrounding the molecule into which the centre of another molecule cannot penetrate. Collision number: Collision number is the number of collisions suffered by a single molecule per unit time per unit volume of the gas. It can be imagined that a gas molecule having diameter  $\sigma$  will collide with the molecules present in the area of  $\pi\sigma^2$ . Now if the molecule is moving with an average velocity of  $c$  and  $n'$  number of molecules are present in unit volume then in one second total number of collisions suffered by the molecule will be  $2cn'$ . Now as all the gas molecules are moving this velocity should be considered as relative velocity  $\sqrt{2}c$ . So,

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the number of molecules with which a single molecule will collide per unit time is given by  $2cn'$

This is the expression of collision number. Now as  $n'$  number of molecules are present per unit volume of the gas, total number of collisions per unit time per unit volume is  $= 2cn'$ . Since each collision involves two molecules, the number of collisions of like molecules occurring per unit time per unit volume of the gas is given by  $Z = \frac{1}{2} \times 2cn' = cn'$ . This number  $Z$  represents the number of molecular collisions occurring per unit time per unit volume of the gas, which is known as collision frequency.

Mean free path of molecules: Mean free path of a gas molecule ( $l$  or  $\lambda$ ) is defined as

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the mean distance travelled by a gas molecule between two successive collisions.

Now we already know that if a molecule has the average velocity  $c$  then the molecule will face  $2cn'$  number of collisions while travelling  $c$  distance. So, Mean free path,  $l = \frac{c}{2cn'}$  where,  $\sigma$  = collision diameter and  $n'$  = number of molecules present per unit volume.

4.7. Viscosity of gases The viscosity of a fluid is a measure of its resistance to deformation at a given rate. Viscosity can be conceptualized as quantifying the internal frictional force that arises between adjacent layers of fluid that are in relative motion. Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The viscosity coefficient ( $\eta$ ) is the force that must be applied to hold the lower layer stationary if the velocity gradient between the two layers is unity and the plate has unit area. It can be shown from the kinetic theory that the relation between viscosity coefficient ( $\eta$ ) and mean free path ( $l$ ) of a gas molecule can be given by the following equation-  $\eta = \frac{1}{3} mn'c$  where,  $c$  is average velocity,  $n'$  is the number of gas molecules present in unit volume and  $m$  is the mass of the gas molecules.

Effect of temperature and pressure on coefficient of viscosity: Effect of pressure: The viscosity of gas is independent of pressure. With increase of pressure though more number of molecules changes between the layers, but they travel shorter distance due to higher number of collisions. So the change of pressure does not affect the viscosity for gases. Effect of temperature: Viscosity in gases arises from molecules traversing layers of flow and transferring momentum between layers. The momentum transfer is caused by

free motion of gas molecules between collisions. So, increase of thermal agitation of the molecules results in a larger viscosity. Hence, gaseous viscosity increases with increase of temperature. We know,  $\eta \propto \sqrt{M}$  and  $\eta \propto \sqrt{T}$ . So,  $\eta \propto \sqrt{M T}$ . From the above equation we can see that,  $\eta \propto \sqrt{M T}$ . Deviation of real gases from ideal behaviour We know that ideal gases obey ideal gas equation ( $PV = RT$ , for one mole gas) at any pressure and temperature. But real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures. However they show deviations from ideality at low temperatures and high pressures. Compressibility factor and Boyle temperature: The deviations of real gases from ideal behaviour are best represented in terms of the compressibility factor ( $Z$ ). Compressibility factor is the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It correlates the deviation of a real gas from ideal gas behaviour. To display the deviations clearly, the ratio of the observed molar volume  $V$  to the ideal molar volume  $V_{id} (= RT/P)$  is plotted as a function of pressure at constant temperature. This ratio is called the compressibility factor ( $Z = PV/RT$ ). For the ideal gas,  $Z = 1$  and is independent of pressure and temperature. For real gases  $Z$  is a function of both temperature and pressure. The graphs plotted for the compressibility factors determined for a number of gases over a range of pressure at a constant temperature are shown in Figure 4.6. At extremely low pressure all the gases are known to have  $Z$  close to unity which means that the gases behave almost ideally. At very high pressure, all the gases have  $Z$  is greater than unity indicating that the gases are less compressible than an ideal gas. This is due to the fact that at high pressure, the molecular repulsive force is dominant. At moderately low pressure carbon monoxide, methane and ammonia are more compressible than ideal gas ( $Z > 1$ ). The compressibility factor  $Z$  goes on decreasing with increase of pressure passes through a minimum at a certain stage and then begins to increase with increase in pressure for these gases. For hydrogen and helium,  $Z$  is greater than unity (the ideal value) at all pressures.

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Figure 4.6. Compressibility factor  $Z$ , plotted against pressure for  $H_2$ ,  $N_2$  and  $CO_2$  at constant temperature.

From the plot of plot of  $Z$  versus  $p$  (figure 4.7) for nitrogen at different temperatures varying between  $-70^\circ C$  and  $50^\circ C$  it is seen that as the temperature is raised the dip in Figure 4.7. Plot of  $Z$  against  $P$  at different temperature for  $N_2$ . NSOU ? GE-CH-11 ? 67

the curve becomes smaller and smaller. At  $50^\circ C$ , the curve seems to remain almost horizontal ( $Z=1$ ) at the low pressure region. So it can be said that at this region  $PV$  remain constant and thus it obeys the Boyle's law within this range of pressure at  $50^\circ C$ . This temperature is called Boyle temperature. The Boyle temperature is different for different gases. Causes of deviation and Van der Waals equation of state for real gases: In order to explain deviations from ideal behaviour, it is necessary to modify the kinetic theory of gases. Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable. The kinetic theory assumes that gas particles occupy a negligible fraction of the total volume of the gas. It also assumes that the force of attraction between gas molecules is zero. The first assumption works at pressures close to 1 atm. But something happens to the validity of this assumption as the gas is compressed. Imagine for the moment that the atoms or molecules in a gas were all clustered in one corner of a cylinder. At normal pressures, the volume occupied by these particles is a negligibly small fraction of the total volume of the gas. But at high pressures, this is no longer true. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures. Figure 4.8. Excluded volume in case of real gas. Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures by subtracting a term from the volume of the real gas before we substitute it into the ideal gas equation. He therefore introduced a constant ( $b$ ) into the ideal gas equation that was equal to the volume actually occupied by a mole of gas particles. Because

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the volume of the gas particles depends on the number of moles of gas in the container,

the term that is subtracted from the real volume of the gas is equal to the product of number of moles of gas and  $b$ .  $P(V - nb) = nRT$  When the pressure is relatively small, and the volume is reasonably large, the  $nb$  term is too small to make any difference in the calculation. But at high pressures, when the volume of the gas is small, the  $nb$  term corrects for the fact that the volume of a real gas is larger than expected from the ideal gas equation. The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would never condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together. This force of attraction has two consequences: (i) gases condense to form liquids at low temperatures and (ii) the pressure of a real gas is sometimes smaller than expected for an ideal gas. To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals added a term to the pressure in this equation. This term contained a second constant ( $a$ ) and has the form:  $\frac{n^2 a}{V^2}$ . The complete van der Waals equation is therefore written as follows.  $\left(\frac{P}{V} + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$  (10) This is the van der Waals equation for  $n$  moles of gas which contains a pair of constants ' $a$ ' and ' $b$ '. The quantities ' $a$ ' and ' $b$ ' are called the van der Waals constants or parameters. It may be pointed that ' $b$ ' is a measure of the molecular size and ' $a$ ' is related to the intermolecular interaction. The SI unit of  $a$  is  $\text{N m}^4 \text{mol}^{-2}$  and the unit of  $b$  is  $\text{m}^3 \text{mol}^{-1}$ .

#### 4.9. Critical phenomena

When the molecules of a gas are brought closer to each other due to increase in the attractive forces a stage may be reached when the gas changes its phase to liquid. Obviously, an ideal gas cannot be liquefied as there are no interactions in that case. For the liquefaction of real gases, we can do either of the following: i) increase the pressure NSOU ? GE-CH-11 ? 69 on the gas or ii) decrease the temperature of the gas. Both these processes will tend to bring the molecules closer and liquefaction may take place. But it is observed practically that temperature is the dominant factor for liquefaction and pressure assumes a secondary role. For every real gas a temperature is observed above which it cannot be liquefied even on the application of very high pressures. This characteristic temperature of a real gas above which it cannot be liquefied is called "Critical Temperature" represented by  $T_c$ . The importance of critical temperature of a gas was first discovered by Andrew in his experiments on pressure-volume relationships (isotherms) of carbon dioxide gas at a series of

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temperatures. The isotherm of carbon dioxide determined by him at different temperatures

is shown in figure 4.9. Figure 4.9. P-V isotherms of carbon dioxide. 70 ? NSOU ? GE-CH-11

We observe from the plot that: i. At high Temperatures ( $> 31.1^\circ \text{C}$ ), the isotherms look just like those of ideal gas. ii. At low temperatures the curve is entirely different. For example, curve ABCD at temperature  $13.1^\circ \text{C}$ , as the pressure increases the volume of the gas decreases from point A to B. Then there is a sudden reduction in volume without much increase in pressure of the gas from B to C. In this portion liquefaction is taking place at constant pressure and due to the difference in the properties of gas and liquid the volume is reducing so much. And after C even on increasing pressure there is no appreciable decrease in volume as now only liquid is present. So, AB represents gaseous phase, BC represents liquid-gas coexistence and CD represents liquid phase. iii. On carrying out the same process at a higher temperature we observe that the width of the horizontal portion decreases and the pressure at which liquefaction takes place also becomes higher. The horizontal portion decreases because at higher temperatures the properties of liquid approach that of a gas. iv. At temperature  $31.1^\circ \text{C}$  ( $T_c$ ) the horizontal portion reduces to a mere point at which liquefaction takes place. Point X is called critical point; at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics. v. Above this temperature there is no liquefaction of gases and gas behaves almost ideally. At critical point X the tangent is horizontal, so that,  $dP/dV$  at critical point will be zero. Thus, the point X is also called the point of deflection. Critical constants: Critical temperature,  $T_c$  is the maximum temperature at which a gas can be liquefied that is a temperature above which liquid cannot exist. Critical Pressure,  $P_c$  is the minimum pressure required for liquefaction to take place at the critical condition.

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Critical volume,  $V_c$  is the volume occupied by one mole of the gas at critical temperature and critical pressure.

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It can be shown that the values of these parameters are given by the following expressions:  $C_p = \frac{5}{2}R$ ,  $C_v = \frac{3}{2}R$  where R is the universal gas constant. These critical constants are related by the following relation  $\frac{C_p}{C_v} = \frac{1 + \alpha}{1 - \alpha}$  where  $\alpha = \frac{a}{RT} + \frac{b}{P}$  (11) 4.10. Summary In this unit, we have discussed some characteristic microscopic features of gases. It has been shown how a simple kinetic molecular model of the gas can be used to derive an equation to calculate the pressure exerted by a gas. This equation can be used further to derive the ideal gas equation. This model is useful in showing how the constant collisions between molecules are responsible for a distribution of the speed of molecules. Further, this model helps us in deriving expressions for various kinds of speeds. We have also evolved a method of calculating the total collision frequency and the mean free path assuming hard sphere model for the molecules. We have discussed the viscosity of gases and effect of temperature on the viscosity. The deviation of real gas from ideal behaviour was explained and van der Waals equation was derived. Finally the critical phenomenon and critical constants were explained for real gases. 4.11. Questions 1. Write down the postulates of kinetic theory of gases. 2. Derive the expression of pressure for an ideal gas using kinetic molecular theory of gases. 3. Write down the expression for Maxwell distribution of molecular velocities. 72 ? NSOU ? GE-CH-11

4. What is mean free path of a gas? What is the relation between mean free path and collision diameter? 5. How does the viscosity of gas vary with temperature? 6. What is compressibility factor of a gas? 7. What are the reasons for deviation of real gases from ideal behaviour? 8. Write down the definitions of critical constants. 9. Calculate the average velocity of CO<sub>2</sub> molecule present in 1 gm of CO<sub>2</sub> gas at 27 °C. (Ans.  $3.8 \times 10^4$  cm/s) 10. If  $T = 304.2$  K and  $P = 72.8$  atm for a gas, then calculate the value of van der Waals constants. (Ans.  $a = 3.63$  atm L<sup>2</sup> mol<sup>-2</sup>,  $b = 0.0428$  L mol<sup>-1</sup>) NSOU ? GE-CH-11 ? 73

Unit 5 ???? Liquids Contents 5.0. Objectives 5.1. Introduction 5.2. Surface tension 5.3. Determination of surface tension using stalagmometer 5.4. Viscosity of a liquid 5.5. Determination of coefficient of viscosity using Ostwald viscometer 5.6. Summary 5.7. Questions 5.0. Objectives After studying this unit, we will be able to ? the surface tension and origin of surface tension of a liquid ? effect of temperature in the surface tension ? determine the surface tension of a liquid ? explain the viscosity of a liquid and effect of temperature on viscosity ? determine the viscosity by using Ostwald viscometer. 5.1. Introduction Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as surface tension and viscosity.

5.2. Surface Tension It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid? Why does an iron needle float in the water? All these phenomena are caused due to the characteristic property of liquids, called surface tension. If we consider the forces between the molecules of a liquid then we can understand these phenomena easily. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecules therefore do not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Figure 5.1), due to the molecules below it, since there are no molecules or very less number of molecules as vapour above it.

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These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, liquids tend to

have minimum number of molecules at their surface.

A sphere has a minimum surface for a given volume. As a result of the tendency to contract, surface of a liquid behaves as if it were in a state of tension. The force that tends to contract the surface of a liquid is known as surface tension.

Figure 5.1. Forces acting on a molecule on liquid surface and on a molecule inside the liquid. NSOU ? GE-CH-11 ? 75

Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is represented by Greek letter  $\gamma$  (Gamma). It has dimensions of  $\text{kg s}^{-2}$  and in SI unit it is expressed as  $\text{Nm}^{-1}$ . Surface Energy: The effect of surface tension is to reduce the area of the surface to a minimum. If we wish to increase the area of the surface of a liquid, we have to work against the force of surface tension. The energy required to increase the surface area of the liquid by one unit is defined as surface energy of the liquid. Its SI unit is  $\text{Jm}^{-2}$ . Effect of Temperature on Surface Tension: The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large.

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Increase in temperature increases the kinetic energy of the molecules

and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised. Some Effects of Surface Tension: Some important effects can be explained by surface tension. 1. Due to presence of surface tension in liquids every liquid try to reduce the area of the surface to a minimum. Hence drops of a liquid or the drops of rain are spherical in shape as sphere has minimum surface area for a given volume. 2. As the surface of a liquid tries to contract due to tension, so it behaves like a membrane. Also the distances between the surfaces of molecules are less. So an iron needle can float in the water. 3. Capillary action of a liquid is a well known phenomenon which can be explained in terms of surface tension. If the liquid in the glass tube is water, the water is drawn slightly up the walls of the tube by adhesive forces between water and glass. The interface between the water and the air above it, called a meniscus, is concave, or curved in. With liquid mercury, the meniscus is convex, or curved out. Cohesive forces in mercury, consisting of metallic bonds between Hg atoms, are strong; mercury does not wet glass. The effect of meniscus formation is greatly magnified in tubes of small diameter, called capillary tubes. In the capillary action, the water level inside the capillary tube is noticeably higher than outside. The soaking action of a sponge depends on the rise of water into capillaries of a fibrous material, such as cellulose. The penetration of water into soils also depends in part on capillary action. Conversely, mercury- with its strong cohesive forces and weaker adhesive forces- does not show a capillary rise. Rather, mercury in a glass capillary tube will have a lower level than the mercury outside the capillary. 76 ? NSOU ? GE-CH-11

Figure 5.2. Capillary action of liquid. 4. When a drop of liquid spreads into a film across a surface, we say that the liquid wets the surface. Whether a drop of liquid wets a surface or retains its spherical shape and stands on the surface depends on the strengths of two types of intermolecular forces. The forces exerted between molecules holding them together in the drop are cohesive forces, and the forces between liquid molecules and the surface are adhesive forces. If cohesive forces are strong compared with adhesive forces, a drop maintains its shape. If adhesive forces are strong enough, the energy requirement for spreading the drop into a film is met through the work done by the collapsing drop. Water wets many surfaces, such as glass and certain fabrics. This characteristic is essential to its use as a cleaning agent. If glass is coated with a film of oil or grease, water no longer wets the surface and water droplets stand on the glass. Adding a detergent to water has two effects: The detergent solution dissolves grease to expose a clean surface, and the detergent lowers the surface tension of water. Lowering the surface tension means lowering the energy required to spread drops into a film. Substances that reduce the surface tension of water and allow it to spread more easily are known as wetting agents. They are used in applications ranging from dish washing to industrial processes. NSOU ? GE-CH-11 ? 77



5.3. Determination of surface tension using Stalagmometer Stalagmometer is a simple apparatus and is frequently employed when the values of surface tension of two or more different liquids are to be compared. It consists of a bulb capillary tube, the end of which is flattened and rounded carefully so that there is a large dropping surface. There are two marks, A and B, on the wall of it which are arbitrarily etched; one of them is above the bulb and the other is below the bulb. A liquid is sucked up to the level A and then allowed to flow at a slower rate drop by drop until it reaches the level B. The speed of the drop formation can be adjusted by attaching a piece of rubber tube with a screw pinch cock at the upper end of the tube. When a liquid is allowed to flow through a capillary tube, a drop begins to form at its lower end, and increases in size to a certain extent, and then falls off. The size of the drop will depend on the radius of the capillary and the surface tension of the liquid. The total surface tension supporting the drop is  $2\pi r\gamma$ , where  $r$  is the outer radius of the capillary tube, see Fig. 5.3 The drop will fall when its weight 'w', just exceeds the force of surface tension acting along the circumference. Therefore,  $w = 2\pi r\gamma$  (1) Figure 5.3. Drawing of a stalagmometer and the formation of liquid drop from a capillary tube in a stalagmometer. 78 ? NSOU ? GE-CH-11

where  $w$ , is the weight of the drop and  $2\pi r$  is the outer circumference of the capillary tube. From the above expression, it is clear that the surface tension of a liquid can be determined if the weight of a single drop 'w' and the outer radius of the dropping tube, 'r' are known. If, we have two liquids, such that  $w_1 = 2\pi r\gamma_1$  and  $w_2 = 2\pi r\gamma_2$  then, we can say that  $\frac{w_1}{w_2} = \frac{\gamma_1}{\gamma_2}$  (2) If  $\gamma_1$  for one of the liquids is known,  $\gamma_2$  for other liquid can be determined without needing a measurement of  $r$ , the outer radius of the dropping end of the capillary, provided the weights of the individual drops of two liquids are known. This method of determination is also known as Drop Weight Method. Alternatively, the surface tension can also be determined using the Drop Number Method as given below. Instead of finding the weights of individual drops, it is easier to count the number of drops formed by equal volumes of two liquids. With two different liquids, the weights of equal volumes are proportional to their densities. If  $n_1$

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and  $n_2$  are the number of drops formed by the same volume  $V$  of the two liquids, then;  $v_1$ , the volume of a single drop of first liquid (i.e., liquid one) =  $V/n_1$ . Thus, weight of the single drop of the first liquid =  $w_1 = V/n_1 \cdot d_1 \cdot g$ ,

where  $d_1$  is the density of the first liquid. And the weight of the single

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drop of the second liquid =  $w_2 = V/n_2 \cdot d_2 \cdot g$ , where  $d_2$  is the density of

the second liquid. Substituting the above values of  $w_1$  and  $w_2$  in equation 2, we get  $\frac{V/n_1 \cdot d_1 \cdot g}{V/n_2 \cdot d_2 \cdot g} = \frac{\gamma_1}{\gamma_2}$  (3) where,  $\gamma_1$  and  $\gamma_2$  are the surface tensions of two individual liquids, and  $d_1$  and  $d_2$  are their densities, respectively. Thus, for the determination of surface tension of any liquid, NSOU ? GE-CH-11 ? 79

the number of drops produced from equal volume of two liquids and their densities must be known, in addition to the surface tension of the reference liquid (e.g. water). 5.4. Viscosity of a liquid Viscosity is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another. Viscosity can be defined as the force of friction between two layers of a liquid moving past one another with different velocities. Figure 5.4. Gradation of velocity in the laminar flow. When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. If we choose any layer in the flowing liquid (Fig.5.4), the layer above it accelerates its flow and the layer below this retards its flow. If the velocity of the layer at a distance  $dz$  is changed by a value: 'du' then velocity gradient is given by the amount  $du/dz$ . A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.  $F \propto A \cdot du/dz$  (A is the area of contact)  $du/dz$  (where,  $du/dz$  is velocity gradient; the change in velocity with distance) 80 ? NSOU ? GE-CH-11

du F A dz ? ? du F A dz ? ? (4) 'η' is proportionality constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 Newton second per square metre (N s m<sup>-2</sup>) = pascal second (Pa s = 1kg m<sup>-1</sup> s<sup>-1</sup>). In CGS system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille). 1 poise = 1 g cm<sup>-1</sup> s<sup>-1</sup> = 10<sup>-1</sup> kg m<sup>-1</sup> s<sup>-1</sup> Greater the viscosity, the more slowly the liquid flows. The viscosity is very much influenced by the shape, size and the chemical nature of the liquid molecules. The greater the size of the molecules and the higher the molar mass, the higher will be the viscosity because the greater will be the intermolecular interactions. The hydrogen bonds also enhance the coefficient of viscosity to a large extent. It is, indeed, the presence of a network of hydrogen bonds which accounts for the very high viscosity of glycerol. Incidentally, the larger the number of hydroxyl groups in a molecule, the more complex will be the network of hydrogen bonds and the greater will be the resistance of a liquid to flow. In long chain hydrocarbons or polymeric compounds the viscosity increases with the increase in the length of the molecular chain. Due to this reason, heavy hydrocarbon oil and grease (which are used as lubricants) have fairly high viscosity values. Effect of Temperature on viscosity of Liquids: In liquids, as the temperature raises, the kinetic energy of the molecules increases and the intermolecular forces of attraction become weak, resulting in the subsequent decrease in the viscosity. The value of the coefficient of viscosity appreciably drops as the temperature of liquid increases such that for each degree rise in temperature there is about two percent decrease in the viscosity. The viscosity and temperature are related to each other by the following expression:  $A \log B T$  ? ? ? where A and B are constants for a given liquid and T is the absolute temperature. NSOU ? GE-CH-11 ? 81

5.5. Determination of Coefficient of Viscosity using Ostwald Viscometer For the measurement of coefficient of viscosity of liquids having a laminar or streamlined flow through a tube or pipe, Poiseuille derived an expression, known as Poiseuille's equation. This expression is given below.  $4 \pi r^4 t \rho V g$  ? ? ? (5) where η = coefficient of viscosity of the liquid V = volume of the liquid flowing out of the tube t = time in which the volume V flows r = radius of the tube l = length of the tube p = driving pressure necessary to maintain uniform rate of flow of volume V, of the liquid. Figure 5.5. Diagram of a Ostwald viscometer. 82 ? NSOU ? GE-CH-11

This involves the use of Ostwald Viscometer (Figure 5.5) in which a fixed volume of a liquid is allowed to fall under its own weight or the force of gravity, and the time required for a given volume of the liquid to flow is noted. Obviously the driving pressure p is replaced by h.d.g, where h is the height of the liquid and d is its density and g is the acceleration due to gravity. Therefore,  $p = h.d.g$  Substituting h.d.g. for p in Poiseuille's Equation 5, we get,  $4 \pi .h.d.g.t$   $8Vl$  ? ? ? (6) If equal volumes of the two liquids (1 and 2) are allowed to fall through the same capillary tube under identical conditions of temperature and pressure then, from Eq. 5.6 by comparison, we have  $1 \eta_1 \eta_2$   $1 \eta_2$   $2 \eta_1$   $2 \eta_2$   $d_1 . t_1$   $d_2 . t_2$  ? ? ? (7) where η<sub>1</sub>, d<sub>1</sub> and t<sub>1</sub> are, respectively, the coefficient of viscosity, density and time of flow for the liquid 1 under examination and η<sub>2</sub>, d<sub>2</sub> and t<sub>2</sub> the corresponding values for the reference liquid (liquid 2). Thus, by knowing η<sub>2</sub>, d<sub>2</sub>, t<sub>2</sub> and d<sub>1</sub> and t<sub>1</sub> the coefficient of viscosity of first liquid, could be determined.

5.6. Summary In this unit we have discussed about the characteristics of liquids. Surface tension and viscosity of liquids were explained and the dependence of these characteristics on intermolecular forces was highlighted. Also the theory behind experimental determination of surface tension and viscosity were discussed. 5.7. Questions 1. What is surface tension? How the surface tension of a liquid varies with Temperature? 2. What is surface energy? What is its unit? 3. Why the drop of a liquid is spherical? NSOU ? GE-CH-11 ? 83 4. Write down the theory for determination of surface tension using stalagmometer by drop count method. 5. Why the viscosity of water is higher than alcohol? 6. How viscosity coefficient of a liquid does vary with temperature? 7. Write down the theory for determination of viscosity of a liquid using Ostwald viscometer. 8. If 10 ml of water and ether forms 29 and 86 drops respectively in a viscometer at 293 K, then calculate the surface tension of ether. Given that surface tension of water is 7.2 x 10<sup>-2</sup> N/m and density of ether is 0.7 gm/cc at 293 K. (Ans. 1.6995 x 10<sup>-2</sup> N/m) 9. In an Ostwald viscometer the flow time for water and toluene of equal volume is 102.2 second and 68.9 second respectively. Find out the viscosity coefficient of toluene if the viscosity coefficient of water is 0.01009 dyne s cm<sup>-2</sup>. (Ans. 5.9 x 10<sup>-3</sup> dyne s cm<sup>-2</sup>) 84 ? NSOU ? GE-CH-11

Unit 6 ? ? ? ? ? Solids CONTENTS 6.0. Objectives 6.1. Introduction 6.2. Forms of solids 6.3. Symmetry elements 6.4. Unit cell 6.5. Crystal systems 6.6. Bravais lattice types 6.7. Law



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of Crystallography 6.7.1. Law of constancy of interfacial angles 6.7.2. Law of symmetry 6.7.3. Law of rational indices 6.8. Miller indices 6.9. X-Ray diffraction

by crystals and Bragg's law 6.10. Structure of NaCl, KCl and CsCl 6.11. Defects in crystals 6.12. Summary 6.13. Questions 6.0. Objectives After studying this Unit, we will be able to ? describe general characteristics of solid state ? distinguish between amorphous and crystalline solids ? identify the symmetry elements in a solid ? define lattice, basis, unit cell, primitive and nonprimitive cells ? describe the seven crystal systems and the fourteen Bravais lattices ? state the laws of crystallography ? state the crystal planes in terms of Miller indices, ? state Bragg's law ? describe the structure of NaCl, KCl and CsCl ? describe the imperfections in solids and types of defects in a crystal 6.1. Introduction We are mostly surrounded by solids and we use them more often than liquids and gases. For different applications we need solids with widely different properties. These properties depend upon the nature of constituent particles and the binding forces operating between them. In gaseous state we have studied that

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if thermal energy is much greater than the forces of attraction then we have matter in gaseous state.

Molecules in gaseous state move with very large speeds and because of very small attraction forces, the gas molecules move practically independent of one another.

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In the liquid state the forces of attraction are greater than the thermal energy. We have also studied that molecules in liquid state too have kinetic energy, they cannot move very far away because of the larger forces of attraction amongst them. Because of this property, liquids have definite volume, but they do not have definite shape. Liquids also resemble gases in their ability to flow. Gaseous and liquid states are, therefore, both classified as fluids.

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The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them.

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A true solid possesses the following characteristics (a) A sharp melting point (b) A characteristic heat of fusion (c) General incompressibility (d) A definite three-dimensional arrangement Hence solids are characterised by high density and low compressibility compared to those of the gas phase. In solids, atoms, ions and molecules are held together by relatively 86 ?

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strong chemical forces- ionic bond, covalent bond, or by intermolecular Van der Waal's forces. They do not translate although they vibrate to some extent on their fixed positions. This explains why solids are rigid and have definite shape. 6.2.

Forms of solids

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Solids can generally be classified into two broad categories: (i) Crystalline solids (ii) Amorphous solids

Figure 6.1. Two dimensional structure of (a) quartz and (b) quartz glass.

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A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the crystal lattice.

Examples

of crystalline solids are sugar, salt, quartz etc. An amorphous solid (Greek amorphos = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. Examples of amorphous solids are rubber, plastics and quartz

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glass. In their disordered structure, amorphous solids are regarded as super-cooled liquids with high viscosity. The

structures of quartz NSOU ? GE-CH-11 ? 87

(crystalline) and quartz glass (amorphous) are shown in Fig. 6.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no long range order.

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Anisotropy and isotropy: Amorphous substances differ from crystalline solids and resemble liquids in another important aspect. Their properties such as electrical conductivity, thermal conductivity mechanical strength and refractive index are same in all directions. Amorphous substances are said to isotropic. Liquids and gases are also isotropic.

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Figure 6.2. Anisotropy in crystals is due to different arrangement of particles along different directions.

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Crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. For example the velocity of light through a crystal varies with the direction in which it is measured. Thus, a ray of light enter such a crystal may split up into two components each following different velocity.

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This phenomenon is known as double refraction. This can be shown in fig 6.2 in which simple two-dimensional arrangement of only two different kinds of atoms is depicted if the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case; each row is made up of one type of atoms only. In amorphous solids, atoms or molecules

are arranged at random

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and in a disorderly manner and, therefore all directions are identical and all properties are alike in all directions. 88 ?

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6.3. Symmetry elements In crystallography, symmetry is used to characterize crystals, identify repeating parts of molecules. An object is described as symmetric with respect to a transformation if the object appears to be in a state that is identical to its initial state, after the transformation. In crystallography, most types of symmetry can be described in terms of an apparent movement of the object such as some type of rotation or translation. The apparent movement is called the symmetry operation. The locations where the symmetry operations occur such as a rotation axis, a mirror plane or an inversion center are described as symmetry elements. Figure 6.3. Symmetry elements. Plane of symmetry When an imaginary plane can divide by

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a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry. Axis of symmetry An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of  $360^\circ$ . Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.

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Centre of Symmetry It is a found at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distance on either side. It may be pointed out that a crystal may have number of planes or axis of symmetry but it has only one centre of symmetry.

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6.4. Unit cell The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, a regular three dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 6.4. Figure 6.4. Crystal lattice and unit cell of a solid. Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice. A unit cell is characterised by: (i) its dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular. (ii) angles between the edges,  $\alpha$  (between b and c)  $\beta$  (between a and c) and  $\gamma$  (between a and b). Thus, a unit cell is characterised by six parameters, a, b, c,  $\alpha$ ,  $\beta$  and  $\gamma$ . Unit cells can be of following types; (a) Simple or primitive unit cell (P): The simplest unit cell which has the lattice points at the corners is called a simple or primitive unit cell. It is denoted by P. 90 ? NSOU ? GE-CH-11

(b) Non primitive or multiple unit cell: When unit cell contains more than one lattice points, it is called non primitive or multiple unit cell. It is further divided into the following three categories: (i) Face centred unit cell (F): When a unit cell, besides the points present at the corners of the unit cell, there is one point at the centre of each face, it is called face centred arrangement or face centred unit cell. It is denoted by F. (ii) Body centred unit cell (I): When in a unit cell, besides the points at the corners of the cell, there is one point at the centre with in its body, it is called body-centred arrangement or body-centred with cell. It is denoted by I. (iii) Side centre or end face unit cell: When in a unit cell, besides the points at the corners of the cell, the points are located at the centre of any two parallel faces of the unit cell, it is called side-centred or end face unit cell. It is denoted by c. 6.5. Crystal systems It can be shown from geometrical considerations that, theoretically, there can be 32 different combinations of elements of symmetry of crystal. These are called 32 point Figure 6.5. Seven crystal system. NSOU ? GE-CH-11 ? 91

group or 32 crystal systems. Some of the systems, however, have been grouped together so that we have only seven different categories, known as the seven basic crystal systems. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral or trigonal (figure 6.5). Crystal systems differ in length of the unit cell edges and the angles between the unit cell edges. 6.6. Bravais lattice types These seven different kinds of crystal systems in combination with four different kinds of centerings (primitive, base-centered, body-centered, face-centered) can yield 14 distinct lattice types which are called Bravais lattices. However, not all of the combinations of crystal systems and centerings are unique; some of the combinations are equivalent while other combinations are not possible due to symmetry reasons. This reduces the number of unique lattices to the 14 Bravais lattices. The distribution of the 14 Bravais lattices into lattice systems and crystal families is given in the figure 6.6. Figure 6.6. The Fourteen Bravais lattices. 92 ? NSOU ? GE-CH-11

6.7. Law of Crystallography There are three laws of crystallography which deal with the interfacial angles and the rational indices. 6.7.1. Law of constancy of interfacial angles Crystals are bound by surface which is usually planner. These surfaces are called faces and where two faces intersect an edge is formed. The angle between the normals to the two intersecting faces is the interfacial angle or the angle between any two faces is called interfacial angle. Although the size of the faces or even shapes of crystals of one and the same substances may vary widely with the condition of formation or other factors, yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is shown in fig 6.7. Now it is clear that although the external shape is different yet the interfacial angles are the same. Figure 6.7. Constancy of interfacial angles. 6.7.2. Law of symmetry The law of symmetry states that,

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all crystals of the same substance possess the same elements of symmetry. Symmetry in crystals may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal

which was described earlier. NSOU ? GE-CH-11 ? 93



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Each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The maximum intensity of reflection occurs at the glancing angle of  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$  for 100, 110 and 111 planes, respectively for first order reflection.

From this x-ray diffraction data it can be shown that the NaCl crystal has a face centred cubic (FCC) lattice structure. Figure 6.10. Structure of NaCl crystal. The structure of KCl crystal is similar (isomorphous) to that of NaCl. But investigating

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the KCl crystal, the maximum reflection of x-rays, corresponding to first order reflections

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are observed to occur at the glancing angles of  $5.38^\circ$ ,  $7.61^\circ$  and  $9.38^\circ$  for (100), (110) and (111) faces, respectively

which corresponds to

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a simple cubic lattice structure. The explanation for this apparent anomaly is very simple and can be explained on the basis that the x-rays scattering power for an atom or ion is governed by the number of electrons or atomic number. The atomic numbers of potassium (K=19) and chlorine (Cl=17) are not very different and the x-rays are unable to detect any difference between the two kinds of atoms. If we imagine all the atoms to be identical, it is evident that face-centred arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face-centred, but the face-centred characteristics are marked by the fact that the two types of atoms composing the substance have nearly the same atomic numbers and atomic weights (K=39, Cl=35.5). But in the case of sodium chloride the atomic numbers differ considerably (Na=11, Cl=17), and so their scattering powers are different and hence the true structure as two interpenetrating face-centred lattices become apparent.

Cesium chloride, CsCl, has a body centred cubic (BCC)

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structure. In its crystal lattice, each Cs<sup>+</sup> ion is surrounded by 8 Cl<sup>-</sup> ions and its coordination number is 8. The value of distance between Cs<sup>+</sup> ion and Cl<sup>-</sup> ion as determined by Bragg's spectrometer is  $3.510 \text{ \AA}$  (figure 6.11).

Figure 6.11. Structure of cesium chloride crystal lattice. 98 ? NSOU ? GE-CH-11

6.11. Defects in crystals Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, point defects and line defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects. Point defects can be classified into three types: (a) stoichiometric defects, (b) impurity defects and (c) non-stoichiometric defects.

(a) Stoichiometric Defects: These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types, vacancy defects and interstitial defects.

(i) Vacancy Defect: When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 6.12 i). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

(ii) Interstitial Defect: When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect (Fig. 6.12 ii). This defect increases the density of the substance.

Figure 6.12. Stoichiometric defects: (i) vacancy defect and (ii) interstitial defect. Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Schottky and Frenkel defects.

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(iii) Schottky Defect: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig 6.13a) in the crystal. Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately  $10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In  $1 \text{ cm}^3$  there are about  $10^{22}$  ions. Thus, there is one Schottky defect per  $10^{16}$  ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For examples, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

Figure 6.13. Schottky defect and Frenkel defect in a crystal lattice.

(iv) Frenkel Defect: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 6.13b) of the crystal. So it creates a vacancy defect at its original site and an interstitial defect at its new location. Frenkel defect is also called dislocation defect. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  ions.

(b) Impurity Defects: If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$  (Fig 6.14). Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and AgCl.

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Figure 6.14. Impurity defect in NaCl crystal by presence of  $\text{Sr}^{2+}$  ion as impurity.

(c) Non-Stoichiometric Defects: The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of nonstoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect: This type of defects in crystals can be formed by absence of anion in the lattice site or by the presence of extra cation in the interstitial position. Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The  $\text{Cl}^-$  ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form  $\text{Na}^+$  ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig 6.15). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called F-centres. They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

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Figure 6.15. Metal excess defect and F-centres. Metal excess defect due to the presence of extra cations at interstitial sites: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow. heating  $2 \text{ ZnO} \rightarrow 2 \text{ Zn} + \text{O}_2$ . Now there is excess of zinc in the crystal and its formula becomes  $\text{Zn}_{1+x}\text{O}$ . The excess  $\text{Zn}^{2+}$  ions move to interstitial sites and the electrons to neighbouring interstitial sites (Fig 6.16). (ii) Metal Deficiency Defect: There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. In this case some of the metal ions possess higher valences to maintain the electroneutrality of the crystal. A typical example of this type is FeO which is mostly found with a composition of  $\text{Fe}_{0.95}\text{O}$ . NSOU ? GE-CH-11

It may actually range from  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of FeO some  $\text{Fe}^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $\text{Fe}^{3+}$  ions. Figure 6.17. Metal deficiency defect in crystals. Figure 6.16. Metal excess defect due to the presence of extra cations at interstitial sites. NSOU ? GE-CH-11 ? 103

6.12. Summary In this unit, we have briefly described different forms of solid substances and found that they can be distinguished as crystalline and amorphous. We have studied the terms- lattice, basis and unit cell of crystalline solids. Symmetry elements present in the different crystal lattice were discussed. Seven crystal systems and fourteen Bravais lattices were explained. Different laws of crystallography were discussed and indexing of crystal planes was explained. Diffraction method and its utility in crystal structure determination were emphasised on the basis of Bragg's law. Finally different types of crystal defects were highlighted. 6.13. Questions 1. Define the term amorphous. Give a few examples of amorphous solids. 2. What is lattice? 3. Give definition of unit cell. 4. What are the symmetry elements present in a crystal? 5. What is the Miller indices of a crystal plane which makes intercepts  $3a/2, 2b, c$ ? [Ans. (4, 3, 6)] 6. What are the separations of the planes with Miller indices (2, 2, 1) for a cubic lattice of side length  $3\text{Å}$ ? [Ans.  $1\text{Å}$ ] 7. If an X-ray (wavelength =  $1.539\text{Å}$ ) gets reflected at an angle of  $22.5^\circ$  from a set of crystal planes, then find out the distance between the crystal planes. [Ans.  $2.01\text{Å}$ ] 8. Write down the differences in structure between the crystals of NaCl and KCl. 9. What are Frenkel and Schottky defects? Explain with examples. 104 ? NSOU ? GE-CH-11

Unit 7 ???? Solutions Contents 7.0. Objectives 7.1. Introduction 7.2. Units for the expression of concentration of solution 7.3. Ideal Solution 7.4. Raoult's law 7.5. Non-ideal solution and deviation from Raoult's law 7.6. Vapour pressure-composition curves of ideal and non-ideal solutions 7.7. Temperature-composition curves of ideal and non-ideal solutions 7.8. Partial miscibility of liquids 7.9. Critical solution temperature 7.10. Principle of steam distillation 7.11. Nernst distribution law and its applications 7.12. Solvent extraction 7.13. Summary 7.14. Questions 7.0. Objectives After studying this unit, we

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will be able to ? describe the formation of different types of solutions; ? express concentration of solution in different

units; ? state and explain Raoult's law; ? distinguish between ideal and non-ideal solutions; ? explain deviations of real solutions from Raoult's law; NSOU ? GE-CH-11 ? 105

? describe partial miscibility of liquids and critical solution temperature; ? explain steam distillation and solvent extraction process. 7.1. Introduction Solutions are homogeneous mixtures of two or more than two components. By homogeneous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes. Depending upon the nature of solvent and solute, solutions can be of different types.

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On the basis of physical state of solute and solvent



it can be categorized in the following ways: Type of Solution Solute Solvent Common Examples Gaseous Solutions Gas Gas Mixture of oxygen and nitrogen gas (Air) Liquid Gas Chloroform mixed with nitrogen gas Solid Gas Camphor in nitrogen gas Liquid Solutions Gas Liquid Oxygen dissolved in water Liquid Liquid Ethanol dissolved in water Solid Liquid Glucose dissolved in water Solid Solutions Gas Solid Solution of hydrogen in palladium Liquid Solid Amalgam of mercury with sodium Solid Solid Copper dissolved in gold

7.2. Units for the Expression of Concentration of Solution There are several ways by which we can describe the concentration of the solution quantitatively. Normality: Normality (N) is defined as number of gram equivalent of solute dissolved in one litre (or one cubic decimetre) of solution. Gram equivalent of solute Normality Volume of solution in litre ? 106 ? NSOU ? GE-CH-11

For example, 1.00 g.equiv L<sup>-1</sup> (or 1.00 N) solution of H<sub>2</sub>SO<sub>4</sub> means that 1 gram equivalent (49 g) of H<sub>2</sub>SO<sub>4</sub> is dissolved in 1 litre of solution.

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Molarity: Molarity (M) is defined as number of moles of solute dissolved

in one litre (or one cubic decimetre) of solution. Moles of solute Molarity Volume of solution in litre ? For example, 0.25 mol L<sup>-1</sup> (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre). Molality: Molality (

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m) is defined as the number of moles of the solute per kilogram (kg) of

the solvent and is expressed as: Moles of solute Molality Volume of solvent in kg ? For example, 1.00 mol kg<sup>-1</sup> (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water. Mole fraction: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as: Number of moles of the component Mole fraction of a component Total number of moles of all the components ? For example, in a binary mixture, if

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the number of moles of A and B are n<sub>A</sub> and n<sub>B</sub>

respectively, the mole fraction of A will be  $\frac{n_A}{n_A + n_B}$  and of B will be  $\frac{n_B}{n_A + n_B}$ . For a solution containing i number of components, we have:  $x_1 + x_2 + x_3 + \dots + x_i = 1$ . It can be shown that in a given solution sum of all the mole fractions is unity, i.e.  $x_1 + x_2 + x_3 + \dots + x_i = 1$ . NSOU ? GE-CH-11 ? 107

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures. Parts per million (ppm): When a solute is present in trace quantities, it is convenient to express concentration in parts per million (ppm) and it is defined as:  $\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$ . As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about  $6 \times 10^{-3}$  g of dissolved oxygen (O<sub>2</sub>). Such a small concentration is also expressed as 5.8 g per 10<sup>6</sup> g of sea water or 5.8 ppm. The concentration of pollutants in water or atmosphere is often expressed in terms of  $\mu\text{g mL}^{-1}$  or ppm. 7.3. Ideal Solution The solutions

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which obey Raoult's law over the entire range of concentration are known as ideal solutions.

The ideal solutions have two other important properties. For an ideal solution, enthalpy of mixing is zero ( $\Delta H_{\text{mix}} = 0$ ) and volume of mixing is also zero ( $\Delta V_{\text{mix}} = 0$ ). It means that no heat is absorbed or evolved when the components are mixed and also final volume of the solution is equal to the sum of volume of two components being mixed. In ideal solution,

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the interaction between A-B is same as the interaction between A-A and B-B

which are the constituent. The partial molar volume of a constituent in an ideal solution is equal to the molar volume of the constituent when present in the pure form. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solutions of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category. 7.4. Raoult's law Let us consider a binary solution of two volatile liquids and denote the two components as A and B. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be  $p_{\text{total}}$  and  $p_A$  and  $p_B$  be the partial vapour pressures of the two components A and B respectively. These partial pressures are related

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to the mole fractions  $x_A$  and  $x_B$  of the two components

A and B respectively. The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the

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Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction

present in solution. Thus, for component A

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$p_A = x_A p_A^0$  so,  $p_A = p_A^0 \cdot x_A$  where  $p_A^0$

is the vapour pressure of pure component A at the same temperature. Similarly, for component B  $p_B = p_B^0 \cdot x_B$  where  $p_B^0$  represents the vapour pressure of the pure component B.

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According to Dalton's law of partial pressures, the total pressure ( $p_{\text{total}}$ )

over the solution phase in the container will

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be the sum of the partial pressures of the components of the solution and is given as:  $p_{\text{total}} = p_A + p_B$  Figure 7.1.

The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. NSOU ? GE-CH-11 ? 109

Substituting the values of  $p_A$  and  $p_B$ , we get  $p_{\text{total}} = x_A p_A^0 + x_B p_B^0$

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A plot of  $p_A$  or  $p_B$  versus the mole fractions  $x_A$  and  $x_B$  for a solution gives a linear plot as shown in Fig. 7.1.

These lines (I and II) pass through the points for which  $x_A$  and  $x_B$  are equal to unity. Similarly the plot (line III) of  $p_{\text{total}}$  versus  $x_B$  is also linear (Fig. 7.1). The minimum value of  $p_{\text{total}}$  is  $p_A^0$  and the maximum value is  $p_B^0$ , assuming that component B is less volatile than component A, i.e.,  $p_A^0 < p_B^0$ . 7.5. Non-ideal Solution and Deviation from Raoult's Law Non-ideal solutions are also known as non-ideal liquid mixtures or real solutions. If a solution does not

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obey Raoult's law over the entire range of concentration

and temperature, the solution is said to be non-ideal solution. The vapour pressures of these solutions are higher or lower than the pressure obtained by using Raoult's law. Here the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) and volume of mixing ( $\Delta V_{\text{mix}}$ ) is not equal to zero. In these solutions, the force between A-B is different from A-A and B-B (individual components). Non-ideal solutions are classified into two types: Non-ideal solution showing positive deviation (vapour pressure obtained is higher than calculated using Raoult's law) and non-ideal solution showing negative deviation (vapour pressure obtained is lower than calculated using Raoult's law). Non-ideal solution showing positive deviation: In the solution of component A and B, the interaction between A-B is weaker than A-A and B-B interaction. In this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. Hence the vapour pressure of the solution is higher than the pressure predicted by Raoult. The enthalpy of mixing is positive. For example, the mixture of ethanol and hexane, acetone and carbon disulphide, carbon tetrachloride and benzene, carbon tetrachloride and toluene shows positive deviation. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution of ethanol and acetone shows positive deviation from Raoult's law. Figure 7.2 represents the curve showing positive deviation. 110 ? NSOU ? GE-CH-11 Figure 7.2. The vapour pressures of two component system as a function of composition for a solution that shows

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positive deviation from Raoult's law. Non-ideal solution showing negative deviation:

In the solution of component A and B, the interaction between A-B is stronger than A-A and B-B interaction. Here the vapour pressure of a solution is lower than the pressure predicted by Raoult. The enthalpy of mixing is negative. For example, the mixtures of acetone and water, phenol and aniline, Figure 7.3. The vapour pressures of two component system as a function of composition for a solution that shows negative deviation from Raoult's law. NSOU ? GE-CH-11 ? 111

chloroform and benzene, acetic acid and pyridine shows negative deviation. A mixture of chloroform and acetone shows negative deviation from Raoult's law, because chloroform molecule forms hydrogen bond with acetone molecule which decreases the escaping tendency of molecules for each component. Thus vapour pressure decreases resulting in negative deviation from Raoult's law. Figure 7.3 represents the curve showing negative deviation. 7.6. Vapour Pressure-composition Curves of Ideal and Non-ideal Solutions So far we have seen the variation of total vapour pressure with the mole fraction of the either constituent in the liquid. Now, in order to find the variation of total vapour pressure with the mole fraction of either A or B in the vapour we can plot the vapour pressure composition curve shown in figure 7.4. Curve I shows the variation of total vapour pressure with respect to the mole fraction in the liquid phase. Similarly, curve II shows the variation of the total vapour pressure with respect to the mole fraction in the vapour phase. It is expected that the mole fraction of a more volatile component in an ideal solution will be more in the vapour phase than in the liquid phase. So the vapour Figure 7.4. Liquid and vapour composition curves for an ideal solution. 112 ? NSOU ? GE-CH-11

phase curve (curve II) lies below the liquid phase curve (curve I). The line ab is called a tie line and it gives us the composition of the solution in the liquid and vapour phases in equilibrium at a particular total vapour pressure. The curves I and I1 of Fig. 7.4 are obtained in the case of solutions obeying Raoult's law. In the case of solutions showing positive deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 7.5. Note that there is a maximum point, M, where both the liquid and vapour phases have the same composition. Figure 7.5. Liquid and vapour composition curves for a liquid mixture showing positive deviation. In the case of a solution showing negative deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 7.6. Note that the curves meet at the minimum point M where both the liquid and vapour phases have the same composition. 7.7. Temperature-composition Curves of Ideal and Non- ideal Solutions Let us consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under constant pressure, say, under atmospheric NSOU ? GE-CH-II ? 113 pressure, it will start boiling when

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the total vapour pressure becomes equal to the atmospheric pressure.

If  $p$  represents the atmospheric pressure, then the condition for boiling is  
 $p =$

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$p_A + p_B$  where  $p_A$  and  $p_B$  are the partial pressures of

the two components A and B. Since different compositions of a solution have different vapour pressures, the various solutions will not reach a total vapour pressure equal to the atmospheric pressure at the same temperature. Hence, the solutions of different compositions will boil at different temperatures. In general, solutions of low vapour pressure will boil at temperatures higher than those of solutions for which the vapour pressures are high. It is because solutions of high vapour pressure can have the total pressure equal to the atmospheric pressure at relatively lower temperatures as compared to solutions for which vapour pressures are low. Hence it is possible to draw temperature-composition diagrams which will correspond to the three general types of vapour pressure composition diagrams. For an ideal solution of two miscible liquid A and B the boiling point-composition curve is shown in figure 7.7. Let the vapour pressure of pure A be higher than that of pure B. Consequently at constant pressure, the boiling point of A ( $T_A$ ) will be lower than Figure 7.6. Liquid and vapour composition curves for a liquid mixture showing negative deviation. 114 ? NSOU ? GE-CH-11 that of B ( $T_B$ ). Now as compared to

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the liquid mixture, the vapour is richer in the more volatile component.

So as in the present case A is more volatile than B, hence, the vapour composition at any temperature must lie closer to A than the corresponding liquid composition. In other words, in the composition against temperature plot, the vapour composition curve must lie above the liquid composition curve. From this plot it can be understood that by boiling the solution from a mixture of two miscible liquids pure liquids can be separated. This process is known as fractional distillation. Figure 7.7. Boiling point-composition diagram of an ideal liquid. Boiling point-composition diagram of a liquid mixture showing positive deviation from Raoult's law is shown in Fig. 7.8(I). Note that this system has a minimum point (C) where the liquid and vapour phases have the same composition. Similarly the boiling point-composition diagram of a liquid mixture showing negative deviation from Raoult's law and it is shown in Fig. 7.8(II). For this type of solutions a maximum point D is observed where the liquid and vapour phases have the same composition. The constant boiling mixtures having composition C in type I solutions (Fig. 7.8.(I)) and composition D in type II solutions (Fig. 7.8.(II)) are called azeotropes (i.e., liquids NSOU ? GE-CH-11 ? 115

boiling unchanged). They resemble pure compounds in their boiling behaviour. However, changes in pressure produce changes in the composition as well as the boiling point of the azeotropes. The azeotropes are not chemical compounds but are rather mixtures resulting from the interplay of intermolecular forces in solution. Figure 7.8. (I) Boiling point-composition diagram of a liquid mixture showing positive deviation; (II) Boiling point-composition diagram of a liquid mixture showing negative deviation. 7.8. Partial miscibility of liquids Some liquid pairs do not form solutions in all compositions. Such liquid pairs are said to be partially miscible liquids. However, due to increased solubility with increase or decrease of temperature, these may become completely miscible. We can understand such a system by using the example of a system containing phenol and water. When a very

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small amount of phenol is added to water at room temperature, it

dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve anymore. At this point, two phases, i.e., two liquid layers are formed—one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water-rich layer to phenol-rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking

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equal volumes of phenol and water, two layers are formed— one of saturated solution phenol in water and the other of saturated solution water in

phenol. 116 ?  
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7.9. Critical solution temperature The temperature above (or below) which a pair of partially miscible liquids becomes miscible in all proportions, is called critical solution temperature (CST) or consolute temperature for the pair. As discussed earlier, phenol and water are only partially miscible at ordinary temperature. On shaking these two liquids with each other, two saturated solutions of different compositions, one of phenol in water and the other of water in phenol, are obtained. Such solutions of different compositions co-existing with one another are termed conjugate solutions. Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies on top of the dome. Hence, such liquid systems are said to possess an upper critical solution temperature or upper consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. Outside the curve we have a homogeneous solution of phenol and water and inside the curve we have two conjugate solutions L1 (phenol in water) and L2 (water in phenol) in equilibrium with each other (Figure 7.9). Figure 7.9. Temperature versus solubility plot for phenol-water system. There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities

increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperature. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 7.10. Figure 7.10. Temperature composition diagram for triethylamine-water system. There are a few liquids pairs, e.g., nicotine and water which show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and also below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 7.11. The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid composition at CST.

Substance soluble in only one of the liquids raises the upper CST and lowers the lower CST. 7.10. Principle of steam distillation The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, is made use of in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water. For purification by steam distillation, an impure compound i) must be immiscible in water, ii) should not decompose at the temperature of steam, iii) should have a fairly high vapour pressure at 373 K, iv) should have non-volatile impurities. Figure 7.12. Experimental setup for steam distillation.

For example, chlorobenzene has a boiling point of 405 K. A mixture of water and chlorobenzene distils at a constant temperature of 363.3 K, when the external pressure is  $9.8 \times 10^4$  Pa, by passing steam through it. Let us explain the procedure for purifying an organic liquid using steam distillation. The apparatus used for steam distillation is as shown in Figure 7.12. The impure organic compound is taken in a round-bottomed flask (A) and a small quantity of water is added. The flask must be kept in a slanting position to prevent the impure liquid from splashing up into the condenser. The flask A is then heated gently. Now, steam from container B is bubbled through the contents of the flask A. Vapours of the organic compound mix with steam and escape into the water condenser C. The condensate thus obtained in the flask F is a mixture of water and the organic compound. This mixture can then be separated by means of a separating funnel.

### 7.11. Nernst distribution law and its applications

When two immiscible solvents A and B taken

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in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

Concentration of X in A a constant Concentration of X in B ?

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Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents and gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law or Nernst's Partition law or simply Distribution law or Partition law.

It states that, "

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if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents."

D Concentration of X in A K Concentration of X in B ? 120 ? NSOU ? GE-CH-11

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If  $C_1$  denotes the concentration of the solute in solvent A and  $C_2$  the concentration in solvent B, Nernst's Distribution law can be expressed  $\frac{C_1}{C_2} = K$ . The constant  $K$  (or simply  $K$ ) is called the distribution coefficient or Partition coefficient or Distribution ratio.

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When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, the Distribution Law

is also written

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as,  $\frac{S_1}{S_2} = K$  where  $S_1$  and  $S_2$  are the solubilities of the solute in the two solvents.

Limitations of Distribution law: Nernst distribution law is applicable for the following conditions only

1. Temperature should remain constant
2. Similar molecular species of the solute should remain in the two phases in contact with each other.
3. The solutions should be dilute.
4. The two liquids should be mutually insoluble or only very sparingly soluble (e.g., benzene and water) and their mutual solubility should not be altered by the presence of the solute.

Applications of the Distribution Law: The study of the distribution of a solute between two immiscible solvents is quite useful in a number of ways. A few of these applications are:

1. Association of the solute molecule in one solvent can be studied from the study of distribution. As for example, by studying the distribution of acetic acid and benzoic acid between water and benzene, it is possible to show that acetic acid and benzoic acid exist as dimers in benzene. NSOU ? GE-CH-11 ? 121
2. If a solute dissociates in one of the solvents, then knowing the distribution coefficient, the degree of dissociation of the solute can be calculated at a particular temperature.
3. The distribution law has also been used in the study of many problems e.g., solvent extraction, analysis and determination of equilibrium constants.

7.12. Solvent extraction



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Solvent extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by, ? adding an organic solvent, ? shaking and separating the two layers, and ? finally, distilling off the organic solvent to recover the separated compound. In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the

given volume of the

extracting liquid is used in a number of smaller portions than if the whole of it is used in one portion.

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Let us consider an aqueous solution of volume  $V$ . Let the mass of an organic compound dissolved in it be  $w$ . Let us use volume  $v$  of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water one extraction be  $w_1$ . Then after, the first extraction  
 Concentration of the organic compound in the aqueous layer =  $\frac{w_1}{V}$   
 Mass of the organic compound in the organic layer =  $w - w_1$   
 Concentration of the organic compound in the organic layer =  $\frac{w - w_1}{v}$   
 Distribution coefficient,  $K$ , is given by the following expression:  $K = \frac{w - w_1}{w_1} \frac{V}{v}$

$w - w_1 = \frac{w v}{K V + v}$  NSOU ? GE-CH-11

From this expression we get the amount of the organic compound that remained unextracted after first extraction

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Similarly, after the second extraction, the mass of the organic compound that remains unextracted is,  $w_2 = \frac{w v^2}{K^2 V^2 + 2 K v V + v^2}$ . In general, the mass of the organic compound that remains unextracted after  $n$  extractions is given by,  $w_n = \frac{w v^n}{K^n V^n + n K v V + v^n}$

7.13. Summary In this unit we have learnt about the solutions and different type of solutions. Then we have learnt that completely miscible liquid pairs may be ideal or

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non-ideal. Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from Raoult's law.

We have learnt to draw the vapour pressure-composition and temperature-composition curves for ideal and non-ideal solutions. We have discussed about the partially miscibility of liquids and critical solution temperature. Then we have seen that a pair of immiscible liquids boil at a temperature lower than the boiling points of any of the liquids. This fact is made use of in steam distillation. We have learned about the principle of steam distillation. Finally we have learned about the Nernst distribution law for a system when a solute is added to a pair of immiscible liquids and its applications in solvent extraction.

7.14. Questions

1. Give an example of a solid solution in which the solute is a gas.
2. Define the following terms: (i) Mole fraction (ii) Molality (iii) Molarity.
3. Write down the differences between ideal and non-ideal solution.
4. What is meant by positive and negative deviations from Raoult's law? NSOU ? GE-CH-11 ? 123
5. Draw the phase diagram of phenol-water system and explain the plot.
6. Write down the principle of steam distillation.
7. Describe Nernst distribution law and state its limitations.
8. If the solubility of I<sub>2</sub> in water is 0.345 g/L at 30 °C then what is the solubility of I<sub>2</sub> in CCl<sub>4</sub> at 30 °C? Given that the distribution coefficient for I<sub>2</sub> in CCl<sub>4</sub> and water is 86. (Ans. 29.67 g/L) NSOU ? GE-CH-11



Unit 8 Chemical Kinetics Contents 8.0. Objectives 8.1. Introduction 8.2. The concept of reaction rates 8.3. Factors affecting reaction rates 8.4. Order and molecularity of a reaction 8.5. Derivation of integrated rate equations 8.5.1. Zero order reaction 8.5.2. First order reaction 8.5.3. Second order reaction 8.6. Half-life of a reaction 8.7. General methods for determination of order of a reaction 8.8. Concept of activation energy and its calculation from Arrhenius equation 8.9. Theories of Reaction Rates 8.9.1. Collision theory 8.9.2. Activated complex theory of bimolecular reactions 8.10. Summary 8.11. Questions 8.0. Objectives After studying this unit, we should be able to: ? define rate law, rate constant of reaction, ?

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discuss the dependence of rate of reactions on pressure, temperature and catalyst ?

differentiate between order and molecularity of a reaction, ? state the experimental methods for studying the reaction rates, ? derive integrated rate laws for zero order, first order and second order reactions and use them for calculating rate constants, ? state the methods for determining the order of reaction, ? explain Arrhenius equation and activation energy, ? describe collision theory and activated complex theory. 8.1. Introduction The branch of physical chemistry which deals with the speed or rate at which a reaction occurs is called chemical kinetics. Chemical Kinetics is the study of rate of a reaction under different conditions like different concentrations, pressures, temperatures, catalyst, pH, dielectric constant of the medium, free radical scavengers, neutral salts etc and suggesting a suitable mechanism for the reaction. Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceedings under given condition of temperature, pressure and concentration. The study of chemical kinetics has been highly useful in determining the factors which influence rate of reaction as well as in understanding mechanism of a number of chemical reactions. The experimental data have led to the development of the modern theories of chemical reactivity of molecules. In this Unit, we shall be dealing with rate of reaction and the factors affecting these. Some elementary ideas about the collision theory and activated complex theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate. 8.2. The concept of

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reaction rates The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction  $A \rightarrow B$  The concentration of A decreases and that of B increases with time. The rate of a reaction is defined as the change in concentration of any of reactant or

product

with time. 126 ? NSOU ? GE-CH-11

As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression  $-\frac{dc_A}{dt}$  (1) where  $-dc_A$  is very small decrease in concentration of A in a very small time interval  $dt$ . Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well. Thus  $\frac{dc_B}{dt}$  (2) where  $dc_B$  is very small increase in the concentration of product B in a very small time interval of time  $dt$ . Now it is from (1) and (2)  $-\frac{dc_A}{dt} = \frac{dc_B}{dt}$  (3) So for a reaction  $A + B \rightarrow M + N$  the rate can be expressed  $-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_M}{dt} = \frac{dc_N}{dt}$  (4) Now let us consider a reaction  $aA + bB \rightarrow cC + dD$  In this reaction a moles of A reacts with b moles of B to form c moles of C and d moles of D. The rates of such a reaction can be expressed either in terms

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of decrease in concentration of a reactant per mole or increase in concentration of a product

per mole. NSOU ? GE-CH-11 ? 127

Thus we can write as follows:  $a \frac{dC_A}{dt} = b \frac{dC_B}{dt} = c \frac{dC_C}{dt} = d \frac{dC_D}{dt}$  (5) Rate Law and the Rate Constant: The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products.

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The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called as rate equation or rate expression. The rate of a reaction

decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

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The rate of the reaction  $A \rightarrow \text{Products}$ , is experimentally found to be given by  $\frac{dC_A}{dt} = k C_A^n$  (6) where  $k$  is the rate constant or the

velocity constant of the reaction at the given temperature. This form of rate equation is known as the differential rate equation. If concentration of  $A$  is unity, i.e.,  $C_A = 1$ , then, evidently,  $r = k$ . For a general reaction of the type:

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$aA + bB + cC \rightarrow \text{Products}$  The rate of the reaction is given by the rate law expression  $\frac{dC_A}{dt} = k C_A^m C_B^n C_C^p$

If  $C_A = C_B = C_C = 1$ , then  $k = r$ . Thus,

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the rate constant of a reaction, in general is defined as the rate of the reaction

when the concentration of each reactant is unity. 8.3. Factors affecting reaction rates There are a number of factors which affect the rate of a reaction, the most important of them are: (a) Effect of concentration:

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The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules.

On increasing the concentration of the reactant, the number of collisions will increase and the rate of reaction will increase and on decreasing the concentration the rate will decrease. (b) Effect of nature of reactants: Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred takes a comparatively longer time than the reaction between ionic molecules. We can cite the examples of neutralisation reactions or double displacement reactions which are very fast while the oxidation reduction reactions are slower. (c) Effect of catalyst: A catalyst can increase or decrease

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the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is

slow at ordinary temperature, while it proceeds rapidly in presence of platinum. (d) Effect of surface area of reactant: Surface area of reactants is of importance only for heterogeneous reactions. With the decrease in the particle size, surface area of the reactant for the same mass increases. The smaller particle thus reacts more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than large lump of coal. (e) Effect of temperature: With the exception of few reactions,

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it has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10 °C

C is known as temperature coefficient

of the reaction. The temperatures usually selected for this purpose are 25 °C and 35 °C. Thus  $k_{35} = 2k_{25}$  Rate at 35 °C  
Temperature coefficient  $k_{35} = 2k_{25}$  Rate at 25 °C ? ? The value of temperature coefficient for most of the reactants is close to 2 and in some cases it approaches to 3. 8.4. Order and molecularity of a reaction In the rate equation  $r = k[A]^a[B]^b[C]^c$  ?  
a, b and c indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e.,  $a + b + c$  gives the overall order of a reaction NSOU ? GE-CH-11 ? 129  
whereas a, b and c represent

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the order with respect to the reactants A, B and C respectively. Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions. The number of reacting species (atoms, ions or molecules)

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taking part in an elementary reaction, which must collide simultaneously in order to bring about

a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved as for example, decomposition of ammonium nitrite.  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$  Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed. It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step. The molecularity of any process can only be small positive integers, while order of reaction can have zero as well as fractional values. 130 ? NSOU ? GE-CH-11

8.5. Derivation of integrated rate equations We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate. This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant. The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations for zero, first and second order chemical reactions. 8.5.1.

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Zero order reaction Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$A \rightarrow$

$\frac{dC}{dt} = -kC^0$  (8) As any quantity raised to power zero is unity  $\frac{dC}{dt} = -k$  Let the initial concentration at initial time of the reaction,  $t = 0$  be  $c_0$ . Subsequently at any other time  $t$ , the concentration will be 'c'. On integration we obtain  $\int_{c_0}^c \frac{dc}{k} = -\int_0^t dt$   $\frac{c - c_0}{k} = -t$   $c = -kt + c_0$  (9) This is the integrated rate equation for zero order reaction. If we plot concentration (c)

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against  $t$ , we get a straight line (Fig. 8.1) with slope =  $-k$  and intercept equal to

$c_0$ . NSOU ? GE-CH-11 ? 131

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Further simplifying equation (9), we get the rate constant,  $k$  as

$k = \frac{c_0 - c}{t}$  (10) Photochemical reaction between  $H_2$  and  $Cl_2$  over water (saturated with HCl) surface is an example of zero order reaction. Figure 8.1.

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Variation in the concentration vs time plot for a zero order reaction. 8.5.2.

First order reaction The differential rate expression for the first-order reaction  $A \rightarrow P$  is given by  $\frac{dC}{dt} = -kC$  Bringing concentration terms in one side and the time on the other side, we can write the above equation as  $\frac{1}{C} \frac{dC}{dt} = -k$  Now if the initial concentration at initial time  $t=0$  be  $c_0$ , and at any other time  $t$ , the concentration is  $c$  then, by integration we get  $\int_{c_0}^c \frac{dc}{c} = -\int_0^t k dt$   $\ln \frac{c}{c_0} = -kt$  (11) From equation 11 we can write  $c = c_0 e^{-kt}$  (12) or,  $c = c_0 (2.303 k \log t c)$  (13) This is the expression for the first order rate constant  $k$ . Sometimes equation 12 is expressed in another format. If initial concentration of the reactant is  $a$  and  $x$  moles of it react in time  $t$ ; then the concentration of the reactant left behind at time  $t$  will be  $a-x$ . In such a case the equation 12 can be written as  $a - x = a e^{-kt}$  (14) Figure 8.2. The plot of concentration versus time (a) and  $\ln(\text{concentration})$  versus time (b) for a first-order reaction. NSOU ? GE-CH-11 ? 133

From equation 14 it can be seen that the concentration of reactant in a first order reaction decreases exponentially with time. A plot of  $\ln(\text{concentration})$  versus time will give a straight line with slope =  $-k$ . This is shown in figure 8.2. 8.5.3.

Second order reaction There are two types of second order reactions Case I: When both the reactants are same. This, in effect, means that two molecules of the same reactant are involved in the chemical reaction. The second-order reaction in this case would be represented as  $2A \rightarrow P$  The rate of the reaction can be expressed as  $\frac{dC}{dt} = -k_2 C^2$  Where  $k_2$  is the second order rate constant. Now

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if  $a$  is the initial concentration of  $A$ ,  $x$  is the concentration of

the product formed after time  $t$  and  $(a-x)$  is the concentration of A remaining at time  $t$ , then,  $\frac{dx}{dt} = k(a-x)^2$  (15) By separating the variables and integrating, we get  $\frac{1}{a-x} = \frac{1}{a} + \frac{x}{a(a-x)}$  (16) This is the integrated

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expression for the rate constant of a second order reaction

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in which two molecules of the same reactant are involved in the reaction. The most common example of the above type of the second order reaction is the gaseous decomposition of hydrogen iodide.  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  The rate expression for this reaction is  $\frac{d[\text{HI}]}{dt} = -2k[\text{HI}]^2$  Case II: When the reactants are different Consider a second order reaction  $\text{A} + \text{B} \rightarrow \text{P}$  where the initial concentration of A is  $a \text{ mol dm}^{-3}$  and that of B is  $b \text{ mol dm}^{-3}$ . After time  $t$ ,  $x \text{ mol dm}^{-3}$  of A and  $x \text{ mol dm}^{-3}$  of B react to form  $x \text{ mol dm}^{-3}$  of the product. Thus the reactant concentration at time  $t$  are  $(a-x)$  and  $(b-x)$ , respectively. The differential rate expression for the second order reaction is,  $\frac{dx}{dt} = k(a-x)(b-x)$  (17) where  $k$  is the second order rate constant. Separating the variables, we get  $\frac{dx}{(a-x)(b-x)} = k dt$  (18) Resolving into partial fractions (assuming that  $a \neq b$ ), we can write  $\frac{1}{(a-x)(b-x)} = \frac{1}{a-b} \left( \frac{1}{a-x} - \frac{1}{b-x} \right)$  (19) Using equation 19 in equation 18 and integrating we can write  $\frac{1}{a-b} \ln \frac{a(b-x)}{b(a-x)} = kt$  (20) NSOU ? GE-CH-11 ? 135 By solving this integration we get  $\ln \frac{a(b-x)}{b(a-x)} = (a-b)kt$  (21) Rearranging and solving this equation 21, we get  $\ln \frac{a(b-x)}{b(a-x)} = (a-b)kt$  (22) This is the integrated

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expression for the rate constant of a second order reaction.

Here we have assumed that  $a > b$ . If we had assumed  $b > a$  then the expression becomes as follows  $\frac{1}{a-b} \ln \frac{a(b-x)}{b(a-x)}$  8.6. Half-life of a Reaction The time required for a reaction to reduce

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the concentration of the reactant to the half of its initial concentration is called half life period ( $t_{1/2}$ ). Half life for a zero order reaction:

For a zero order reaction, from the integrated rate law we get  $c = c_0 - kt$  At  $t = t_{1/2}$ ,  $c = \frac{c_0}{2}$  Then,  $0 = c_0 - kt_{1/2}$   $kt_{1/2} = c_0$  (23) So

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for a zero-order reaction, the half-life period depends on the initial concentration of the reactant and the

rate constant. 136 ? NSOU ? GE-CH-11

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Half life for a first order reaction: For the first order

reaction 0 1

$c = 2.303 k \log \frac{c_0}{c} = k t$  At  $t = t_{1/2}$ ,  $c = \frac{c_0}{2}$   $c = 2.303 k \log \frac{c_0}{c_0/2} = k t_{1/2}$   $2.303 \log 2 = k t_{1/2}$   $t_{1/2} = \frac{0.693}{k}$  (24) It can be seen from equation 24,

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that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order reaction can be readily calculated from the rate constant and vice versa.

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Half life for a second order reaction: For the second order reaction,

we can write from equation 16  $\frac{1}{a-x} = \frac{1}{a} + \frac{k t}{a(a-x)}$  At  $x = a/2$ ,  $t = t_{1/2}$   $\frac{1}{a-a/2} = \frac{1}{a} + \frac{k t_{1/2}}{a(a-a/2)}$   $\frac{2}{a} = \frac{1}{a} + \frac{k t_{1/2}}{a(a/2)}$   $\frac{1}{a} = \frac{k t_{1/2}}{a/2}$   $t_{1/2} = \frac{2}{k a}$  (25) So from equation 25, we can find that  $t_{1/2}$

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of a second order reaction is inversely proportional to the initial concentration

of the reactant

and thus it does not remain constant as the reaction proceeds. Half life for  $n$ th order reaction: It can be shown that for a  $n$ th order reaction of  $nA \rightarrow$  Products The half life time can be expressed by the following equation  $t_{1/2} = \frac{1}{k a^{n-1} (n-1)}$  (26)

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Where  $a_0$  is the initial concentration of the reactant A and

$k_n$  is the  $n$ th-order rate constant. From the equation 26 we can see that  $t_{1/2} = \frac{1}{k_n a_0^{n-1} (n-1)}$  (27) 8.7. General methods for determination of

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order of a reaction The order of a reaction is

never known before hand, though most of the reactions are of the first or second order. In order to write the rate law, we must know the order of reaction with respect to each reactant. The following methods are commonly used for determining the order of a reaction i) Method of Initial Rate: The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,  $A + B \rightarrow$  Products 138 ? NSOU ? GE-CH-11

Let the rate of reaction be represented as,  $r = k [A]^m [B]^n$  where the reaction is  $m$ th order in A and  $n$ th order in B. The rate constant for the reaction is  $k$ . We have to obtain the initial rates from at least two experiments in which the initial concentrations of A ( $a_1$  and  $a_2$ ) are different while the initial concentration of B ( $b_1$ ) is constant. Rate in Experiment I =  $r_1 = k a_1^m b_1^n$  Rate in Experiment II =  $r_2 = k a_2^m b_1^n$  From the ratio  $\frac{r_1}{r_2} = \left(\frac{a_1}{a_2}\right)^m$ , we can calculate order  $m$ , since  $a_1$  and  $a_2$  are known. Similarly, the rate for one more experiment in which the initial concentration of A is  $a_2$  and the initial concentration of B is  $b_2$ . So, rate in Experiment III =  $r_3 = k a_2^m b_2^n$  Rate in experiment II =  $r_2 = k a_2^m b_1^n$  Rate in experiment III =  $r_3 = k a_2^m b_2^n$  Taking logarithms we can write  $\log \frac{r_3}{r_2} = n \log \frac{b_2}{b_1}$  (28) Similarly, the rate for one more experiment in which the initial concentration of A is  $a_1$  and the initial concentration of B is  $b_2$ . So, rate in Experiment IV =  $r_4 = k a_1^m b_2^n$  Rate in experiment II =  $r_2 = k a_2^m b_1^n$  Rate in experiment IV =  $r_4 = k a_1^m b_2^n$  Taking logarithms we can write  $\log \frac{r_4}{r_2} = m \log \frac{a_1}{a_2} + n \log \frac{b_2}{b_1}$  (29) Since  $r_2, r_3, b_1$  and  $b_2$  are known,  $n$  can be calculated. The overall reaction order =  $m + n$ . NSOU ? GE-CH-11 ? 139

ii) Using Integrated Rate Expression: We can determine the order of reaction a) by substitution of experimental data into integrated rate law equations; i.e., in equation 10, 13 and 16. b) by graphical method using plots such as  $[A]$  against  $t$ ,  $\log[A]$  against  $t$  and  $1/[A]$  against  $t$ . The order of the reaction is one, two or zero depending on which of the equations gives rise to a constant value for  $k$  or which of the plots gives a straight line. iii) Half-Life Method: The half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order. In general, half-life period ( $t_{1/2}$ ) is proportional to  $(1/a_0)^{n-1}$  where  $a_0$  is the initial concentration of the reactant and  $n$  is the order of the reaction. If the half-life periods are  $(t_{1/2})_1$  and  $(t_{1/2})_2$  corresponding to the initial concentrations  $a_1$  and  $a_2$  of a reactant, then  $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$  or,  $\ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \ln \frac{a_2}{a_1}$  (30) 140 ? NSOU ? GE-CH-11

iv) Isolation Method: In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. This procedure is called van't Hoff's isolation method. 8.8. Concept of activation energy and its calculation from Arrhenius Equation We have seen about the temperature dependence of rate of a reaction in section 8.3.

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The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

Arrhenius proposed the following empirical relationship between the rate constant,  $k$ , and temperature,  $T$ .

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$k = A e^{-E_a/RT}$  (31) where  $A$  is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction.  $R$  is gas constant and  $E_a$  is activation energy measured in joules/mole (

J mol<sup>-1</sup>).

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It can be understood clearly using the following simple reaction



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According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

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The energy required to form this intermediate, called activated complex (C), is known as activation energy ( $E_a$ ). Fig. 8.3 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products. Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

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Figure 8.3. Diagram showing plot of potential energy vs. reaction coordinate.

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All the molecules in the reacting species do not have the same kinetic energy.

For the formation of product the reactant molecules must possess sufficient energy.

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Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than

$E_a$ . Thus, with increase of the reaction temperature the rate of the reaction increases.

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In the Arrhenius equation (31) the factor  $e^{-E_a/RT}$  corresponds to the fraction of molecules that have kinetic energy greater than

$E_a$ . Taking natural logarithm of both sides of equation 31, we get  $\ln k = \ln A - \frac{E_a}{RT}$  (32) From equation 32, it is evident that a plot of  $\ln k$  versus  $1/T$  (figure 8.4) gives a straight line with slope =  $-E_a/R$  and intercept =  $\ln A$ . By differentiating equation 32 with respect to temperature, we can write  $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$  (33) Integrating equation 33 between temperature  $T_1$  and  $T_2$  when the corresponding rate constants are  $k_1$  and  $k_2$ , respectively and assuming that  $E_a$  is constant over this temperature range, we obtain  $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$  (34) 142 ? NSOU ? GE-CH-11 Figure 8.4. Plot of  $\ln k$  vs  $1/T$ . This is the integrated Arrhenius equation. From this equation 34 by knowing the rate constants at two different temperatures, the energy of activation  $E_a$  can be readily determined. 8.9. Theories of reaction rates There are two important theories of reaction rates. These are the collision theory developed by Arrhenius and van't Hoff and the modern activated complex theory, or also called the transition state theory developed by Eyring, Polanyi and Evans. 8.9.1.



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Collision theory This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase,

we will restrict our discussion to bimolecular reactions in the gaseous phase. From the kinetic theory of gases (discussed in unit 4), the number of bimolecular collisions per second per cm<sup>3</sup> among molecules of one species is given by  $\frac{1}{2} Z_{AA} = \frac{1}{2} N_A^2 \sigma_{AA} \bar{v}_{AA} \left( \frac{2\pi}{kT} \right)^{-3/2}$  (35) NSOU ? GE-CH-11 ? 143

For a reaction involving two different gases A and B, the rate of bimolecular collisions between unlike molecules is given by  $\frac{1}{2} Z_{AB}$

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$Z_{AB} = \frac{1}{2} N_A N_B \sigma_{AB} \bar{v}_{AB} \left( \frac{2\pi}{kT} \right)^{-3/2}$  (36) where  $n_A$  and  $n_B$  are numbers of A and B molecules, respectively,

$\sigma_{AB}$  is the average collision diameter defined as  $(\sigma_A + \sigma_B)/2$  and  $\mu$  is the reduced mass defined as  $\mu = (m_A m_B)/(m_A + m_B)$ . The collision number  $Z_{AB}$  is given, in terms of molar masses  $M_A$  and  $M_B$  of the two gases, by the expression  $Z_{AB} = \frac{1}{2} N_A N_B \sigma_{AB} \bar{v}_{AB} \left( \frac{2\pi}{kT} \right)^{-3/2} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2}$  (37) Let us calculate  $Z_{AB}$  for the reaction between H<sub>2</sub> and I<sub>2</sub> at 700 K and 1 atm pressure, the quantities of the two gases being 1 mole each. Accordingly,  $n_{H_2} = 2.5 \times 10^{25}$  molecules cm<sup>-3</sup>,  $r_{H_2} = 2.2 \text{ \AA}$ ,  $r_{I_2} = 4.6 \text{ \AA}$  so that  $\sigma_{AB} = 3.4 \text{ \AA}$ . Hence, according to Eq. 37,  $Z_{AB} = \frac{1}{2} \times 2.5 \times 10^{25} \times 2.5 \times 10^{25} \times 3.4 \times 10^{-8} \times \left( \frac{2\pi}{8.314 \times 700} \right)^{-3/2} \left( \frac{2 \times 2 \times 254}{2 + 254} \right)^{1/2} = 10.38 \times 1.16 \times 10^{-15} \times 8.58 \times 10^5 \times 10^{29}$  collisions s<sup>-1</sup> cm<sup>-3</sup> Since there are approximately  $10^{29}$  collisions per second for  $10^{19}$  molecules of each species, each molecule makes about  $10^{10}$  collisions s<sup>-1</sup> with the molecules of other species. If each collision were lead to a chemical reaction, then the whole reaction would have been completed in about  $10^{-10}$  s. However this is not in agreement with the experimental value. So each collision does not result in chemical reaction. In order for a reaction to occur, the energy of collision must equal or exceed the threshold energy. The effective energy is, of course, not the total kinetic energy of the colliding molecules but is, instead, the kinetic energy corresponding to the component at the moment of the relative velocity of the two molecules along the line of their centres at the moment of collision. It is this energy with which the two molecules are pressed together. 144 ? NSOU ? GE-CH-11

The detailed analysis of the dynamics of bimolecular collisions leads to the result that the number of collisions S<sup>-1</sup> cm<sup>-3</sup> between molecules A and B, when the relative kinetic energy  $E$  along the line of centres is greater than the threshold energy is given by  $E_{RT} Z_{AB} \exp(-E/E_{RT})$  (38) Assuming that  $Z_{AB} \exp(-E/E_{RT})$  gives the rate of relative collisions between A and B,

we can write  $\frac{dN_A}{dt} = -Z_{AB} \exp(-E/E_{RT})$  So,  $\frac{dN_A}{dt} = -\frac{1}{2} N_A N_B \frac{E_{RT}}{M_A M_B} \frac{1}{kT} \frac{dN}{dt} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT})$  (39) Now if the concentrations of the reactants are expressed in mol dm<sup>-3</sup>, then  $\frac{d[A]}{dt} = -\frac{1}{2} N_A N_B \frac{E_{RT}}{M_A M_B} \frac{1}{kT} \frac{dN}{dt} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT})$  (40) Here  $N_A$  is Avogadro's number. Hence, the rate law expression  $-\frac{d[A]}{dt} = k_2 [A][B]$  Can be written as  $\frac{1}{2} N_A^2 \frac{E_{RT}}{M_A M_B} \frac{1}{kT} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT}) = k_2$  (41) Hence,  $k_2 = \frac{1}{2} N_A^2 \frac{E_{RT}}{M_A M_B} \frac{1}{kT} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT})$  (42) Using equation 39 for,

we have  $k_2 = \frac{1}{2} N_A^2 \frac{E_{RT}}{M_A M_B} \frac{1}{kT} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT})$  (43) NSOU ? GE-CH-11 ? 145

Comparing equation 43 with the Arrhenius equation (Eq 31)  $k = A \exp(-E_a/RT)$ , we find that the Arrhenius pre-exponential factor is given by  $\frac{1}{2} N_A^2 \frac{E_{RT}}{M_A M_B} \left( \frac{M_A M_B}{M_A + M_B} \right)^{1/2} \exp(-E/E_{RT})$  (44) The activation energy  $E_a$ , in the Arrhenius equation is thus identified with the relative kinetic energy  $E$  along the line of centres of the two colliding molecules which is required to cause a reaction between them. Now let us calculate  $A$  and  $k_2$  for the H<sub>2</sub>-I<sub>2</sub> reaction at 700 K, considered in the beginning of this section.  $E_a$  has been found to be 167.4 kJ mol<sup>-1</sup>. Substituting the various values in equation 44,  $A$  comes out to be  $= 6.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Hence, from Arrhenius equation (Eq 31),  $k_2 = 6.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \cdot \exp(-167400 \text{ J mol}^{-1} / 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 700\text{K}) = 0.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  which is comparable with the experimental value of  $0.064 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , considering the uncertainty in the values of the activation energy

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and average collision diameter. The collision theory is applicable to simple gaseous reactions. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate.

The discrepancy arises due to the facts that the colliding reactant molecules are treated as hard spheres without any

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internal energy. Again the spherical model ignores the dependence of the effectiveness of the collision on the relative orientation of the colliding molecules. Also the activation energy was treated as though it were related entirely

on translational

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motion. For this reasons the collision theory is applicable to reactions between very simple gaseous molecules. The collision theory can be generalized by introducing

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so-called steric factor,  $p$ , into the equation for the bimolecular rate constant in order to take account

of the orientational requirement. Accordingly the equation becomes  $k_2 = p A e^{-E_a/RT}$  (45) 8.9.2. Activated complex theory of bimolecular reactions As a result of the development of the quantum mechanics, another theoretical approach to chemical reaction rates has been developed which gives a deeper understanding of the 146 ? NSOU ? GE-CH-11 reaction process. It is known as the absolute reaction rate theory or the transition state theory or more commonly as activated complex theory. According to the activated complex theory, the bimolecular reaction between two molecules  $A_2$  and  $B_2$  progresses through the formation of the so-called activated complex which then decomposes to yield the product  $AB$ . It must be remembered that the activated complex is not merely an intermediate in the process of breaking or forming of chemical bonds. It is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants (Figure 8.5). The difference between the energy of the activated complex and the energy of the reactants is the activation energy,  $E_a$ . Figure 8.5. Energy versus reaction coordinate in activated complex theory in the case of an exothermic and endothermic reaction. Let us consider a simple bimolecular reaction # 2  $K \# A B (AB)$  Products ? ???? ?? ? (46) where  $(AB) \#$  is the activated complex and  $K \#$  is the equilibrium constant between the reactants and activated complex. From classical mechanics, the energy of vibration of the activated complex  $(AB) \#$  is given by  $RT/N A$  (or  $k_B T$  where  $k_B$  is the Boltzmann constant) whereas from quantum mechanics, it is given by  $h\nu$  so that  $h\nu = RT/N A$  or  $\nu = RT/N A h = k_B T/h$ . The vibrational frequency  $\nu$  is the rate at which the activated complex molecules move across the energy barrier. Thus, the rate constant  $k_2$  can be identified with  $\nu$ . NSOU ? GE-CH-11 ? 147

The reaction rate is given by  $k \frac{d[A][B]}{dt} = k \frac{d[A][B]}{dt} \frac{[AB]}{[AB]}$  (47) where the factor  $k$ , called the transmission coefficient, is a measure of the probability that a molecule, once it passes over the barrier, will keep on going ahead and not return. The value of  $k$  is taken to be unity; it is thus omitted from the rate expression. The concentration of the activated complex, can be obtained by writing the equilibrium expression  $K = \frac{[AB]}{[A][B]}$  (48) Hence  $K = \frac{[AB]}{[A][B]}$  (48) Substituting the value in equation 47, we get  $k = \frac{d[A][B]}{dt} K$  (49) Thus the rate constant  $k$  may be expressed as  $k = \frac{d[A][B]}{dt} K$  (50) The equilibrium constant  $K$  can be expressed in terms of  $(\Delta G^\ddagger)$ , called the standard Gibbs free energy of activation. Since for the activated complex, we can write  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$  (51) Here,  $(\Delta H^\ddagger)$  is the standard enthalpy of activation and  $(\Delta S^\ddagger)$  is the standard entropy of activation So we can write,  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$  (52) 148 ? NSOU ? GE-CH-11

Now substituting in equation 50, we get  $k = \frac{d[A][B]}{dt} \frac{e^{-\Delta G^\ddagger/RT}}{e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/RT}}$  This is the well known Eyring equation. The application of the activated complex theory to reactions in solution is quite complicated because of the participation of the solvent molecules in the activated complex. Fortunately, the Eyring equation is applicable for reactions in the solutions phase also. Taking logs of both sides of equation 53 and differentiating with respect to T we get  $2.303 \frac{d \ln k}{dT} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$  (54) Also, from the Arrhenius equation we get,  $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$  (55) By comparing equation 54 and 55, we obtain  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$  (56) Again, by comparing equation 53 and 45, we have  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT} + \frac{p}{RT}$  (57) If  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$ , we can equate the exponential factors in equation 57  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$  (58) For a first order gaseous reaction,  $p = 1$  and  $A = 10^{10} \text{ s}^{-1}$ . At room temperature the value of  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$  . NSOU ? GE-CH-11 ? 149 Hence,  $\frac{E_a}{RT^2} = \frac{\Delta H^\ddagger}{RT^2} + \frac{\Delta S^\ddagger}{RT}$  (59) So if  $p > 1$  (as in the case of complex molecules)  $(\Delta S^\ddagger)$  is lower than this value. Qualitatively, a negative value of entropy of activation corresponds to an increase in molecular order in the activated complex relative to the reactant molecules. A large negative value of  $(\Delta S^\ddagger)$  corresponds to a highly ordered activated complex and this implies a small value of the steric factor. Finally it may be remarked that for reactions involving simple molecules, the collision theory and the activated complex theory give identical results. 8.10. Summary In this unit, we started with the definitions of the terms such as, rate of reaction, rate law, order and molecularity of reaction. We derived the integrated forms of rate expressions for first order, second order and zeroth order reactions. We have discussed about the half life of the different order reactions. We explained the methods of determination of order of reaction. Finally the concepts of activation energy, Arrhenius equation, collision theory and the activated complex theory were discussed. 8.11. Questions 1. Rate of reaction depends upon which factors? 2. What are the differences between order and molecularity of a reaction? 3. What do you mean by a zero order reaction? Give example. 4. Show that half life of a first order reaction does not depend on the initial concentration of the reactants. 5. Describe any method for determination of order of reaction. 6. How the rate of a reaction depends upon temperature? 7. What is activation energy of a reaction? 150 ? NSOU ? GE-CH-11 8. Why the rate of a reaction increases in the presence of a catalyst? 9. The half life of a first order reaction is 15 min. What is the rate of the reaction? How much time it will take to complete the 80 % of the reaction? (Ans. 0.0462 min<sup>-1</sup>, 34.84 min) 10.

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The rate of a reaction is  $3.46 \times 10^{-5} \text{ min}^{-1}$  and  $4.87 \times 10^{-5} \text{ min}^{-1}$  at 298 K and 338 K

respectively. Calculate the activation energy of the reaction. Given the value of  $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . (Ans. 24.756 kcal/mol) 8.12 Further Readings 1. Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, 3rd ed., 1983. 2. Physical Chemistry, P.C. Rakshit. Sarat Book House, 5th ed., 1988. 3. Principles of Physical Chemistry, Puri, Sharma and Pathania, Vishal Publishing Co., 46th ed., 2012. 4. General Chemistry- Principles and Modern Applications, Petrucci, Herring, Madura and Bissonnette, Pearson Canada Inc., 11th ed, 2017. 5. Physical Chemistry through Problems, S. K. Dogra and S. Dogra, Wiley Eastern Ltd., 1984. 6. Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., 4th ed., 1985. NSOU ? GE-CH-11 ? 151 Notes 152 ? NSOU ? GE-CH-11

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<b>1/224</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>65% MATCHING TEXT</b>	19 WORDS
<p>All rights reserved. No part of this Study material be reproduced in any form without permission in writing from</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>2/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>81% MATCHING TEXT</b>	17 WORDS
<p>After reading this unit, we will be able to: ? define the commonly used terms in thermodynamics</p> <p>After reading this lesson will be able to: • define the commonly used terms in thermodynamics; •</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>3/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>92% MATCHING TEXT</b>	22 WORDS
<p>System is the part of the physical universe which is under study, while the rest of the universe is surroundings. The system</p> <p>System is the part of the physical universe which is under study, while the rest of the universe is surrounding. • system</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>4/224</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>100% MATCHING TEXT</b>	14 WORDS
<p>open system is a system which can exchange both energy and matter with surroundings.</p> <p>Open system is a system which can exchange both energy and matter with surroundings.</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>5/224</b>	<b>SUBMITTED TEXT</b>	76 WORDS	<b>100% MATCHING TEXT</b>	76 WORDS
<p>When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, <math>C_6H_{12}O_6</math> by the process of photosynthesis requires the absorption of light energy from the sun. Thus,</p>		<p>When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, <math>C_6H_{12}O_6</math> by the process of photosynthesis requires the absorption of light energy from the sun. Thus,</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>6/224</b>	<b>SUBMITTED TEXT</b>	84 WORDS	<b>100% MATCHING TEXT</b>	84 WORDS
<p>surroundings. 1.2.2 State of a system We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system 1.2.3</p>		<p>Surroundings -230- 11.1.2 State of a System We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system (</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>7/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>76% MATCHING TEXT</b>	27 WORDS
<p>In this lesson we would come across some frequently used terms. Let us understand the meaning of these terms first. 8 ? NSOU ? GE-CH-11 1.2.1 System and surrounding</p>		<p>In this lesson you would come across some frequently used terms. Let us understand the meaning of these terms first. 11.1.1 System and Surrounding</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>8/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>93% MATCHING TEXT</b>	23 WORDS
<p>Properties of a system The measurable properties of a system are called state variables. They may be further divided into two main types –</p>		<p>Properties of a System As stated earlier, the measurable properties of a system are called state variables. They may be further divided into two main types.</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				

<b>9/224</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>100% MATCHING TEXT</b>	25 WORDS
<p>The method of bringing about a change in state is called process. Processes could be of different types. The different types of processes are explained below.</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>The method of bringing about a change in state is called process. Processes could be of different types. The different types of processes are explained below. (</p>		
<b>10/224</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>100% MATCHING TEXT</b>	25 WORDS
<p>In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature.</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature. (</p>		
<b>11/224</b>	<b>SUBMITTED TEXT</b>	35 WORDS	<b>97% MATCHING TEXT</b>	35 WORDS
<p>Isothermal process: When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>isothermal process as When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system. (</p>		

12/224

**SUBMITTED TEXT**

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You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows: Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant. Mathematically the first law of thermodynamics is stated as:  $\Delta U = q + w$  where  $\Delta U$  = change in internal energy,  $q$  = heat absorbed by the system, and  $w$  = work done on the system. 1.2.8 Internal energy (U) Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei. The internal energy may be defined as the sum of the energies of NSOU ? GE-CH-11 ? 11 all the atoms, molecules or ions contained in the system. It is a state variable. It is not possible to measure the absolute values of internal energy. However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is  $U_1$  and that in the final state is  $U_2$ , then change in internal energy  $\Delta U$  is independent of the path taken from the initial to the final state. We can write this change as:  $\Delta U = U_2 - U_1$  The internal energy of the system can be changed in two ways: (i) either by allowing heat to flow into the system or out of the system; and (ii) by work done on the system or by the system. 1.2.9

You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows : Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant. Mathematically the first law of thermodynamics is stated as :  $\Delta U = q + w$  (11.1) where  $\Delta U$  = change in internal energy,  $q$  = heat absorbed by the system, and  $w$  = work done on the system. These terms are explained as : 11.4.1 Internal Energy (U) Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei. The internal energy may be defined as the sum of the energies of all the atoms, molecules or ions contained in the system. It is a state variable. It is not possible to measure the absolute values of internal energy. -235- However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is  $U_1$  and that in the final state is  $U_2$ , then change in internal energy  $\Delta U$  is independent of the path taken from the initial to the final state. We can write this change as :  $\Delta U = U_2 - U_1$  The internal energy of the system can be changed in two ways : i) either by allowing heat to flow into the system or out of the system; and ii) by work done on the system or by the system 11.4.2

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**SUBMITTED TEXT**

33 WORDS

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Enthalpy (H) For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by  $H = U + pV$

Enthalpy (H) For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by  $H = U + pV$  (9.5)

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<b>14/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>76% MATCHING TEXT</b>	13 WORDS
<p>heat required to raise the temperature of one unit mass of the substance.</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>heat required to raise the temperature of one mole of the substance (</p>		
<b>15/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>55% MATCHING TEXT</b>	20 WORDS
<p>The Zeroth law of thermodynamics is states that, if two thermodynamic systems, A and B are in thermal equilibrium with</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>the zeroth law of thermodynamics is: If two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with</p>		
<b>16/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>91% MATCHING TEXT</b>	18 WORDS
<p>Where, U is the internal energy, p is the pressure and V is the volume of the system.</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>where E is the internal energy, P is the pressure and V is the volume of the system.</p>		
<b>17/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>83% MATCHING TEXT</b>	27 WORDS
<p>q (at constant pressure) We denote q at constant pressure by q p hence <math>\Delta H = q p</math> So, by measuring heat lost or gained at constant pressure</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>q (at constant pressure) We denote q at constant pressure by q p hence <math>\Delta H = q p</math> (11.8) Equation 11.8 shows that by measuring heat lost or gained at constant pressure,</p>		
<b>18/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>100% MATCHING TEXT</b>	17 WORDS
<p>Let as denote total enthalpy of reactants as H reactants and total enthalpy of 12 ?</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>Let as denote total enthalpy of reactants as H reactants and total enthalpy of</p>		
<b>19/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>100% MATCHING TEXT</b>	12 WORDS
<p>products as H products . The difference between these enthalpies, <math>\Delta</math></p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>products as H products . The difference between these enthalpies, <math>\Delta</math></p>		

<b>20/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>100% MATCHING TEXT</b>	27 WORDS
<p>H, is the enthalpy of the reaction <math>\Delta_r H = H_{\text{products}} - H_{\text{reactants}}</math> When <math>H_{\text{products}}</math> is greater than <math>H_{\text{reactants}}</math> then <math>\Delta</math></p>		<p>H, is the enthalpy of the reaction <math>\Delta_r H = H_{\text{products}} - H_{\text{reactants}}</math> When <math>H_{\text{products}}</math> is greater than <math>H_{\text{reactants}}</math> then <math>\Delta</math></p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>21/224</b>	<b>SUBMITTED TEXT</b>	92 WORDS	<b>96% MATCHING TEXT</b>	92 WORDS
<p>H is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example, <math>H_2(g) + I_2(g) \rightarrow 2HI(g)</math>; <math>\Delta_r H = 52.5 \text{ kJ}</math> When <math>H_{\text{products}}</math> is less than <math>H_{\text{reactants}}</math> then <math>\Delta_r H</math> is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example, <math>CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)</math>; <math>\Delta_r H = -890.4 \text{ kJ}</math> Enthalpy of a reaction changes with pressure and temperature. 1.3.2</p>		<p>H is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example, <math>H_2(g) + I_2(g) \rightarrow 2HI(g)</math>; <math>\Delta_r H = 52.5 \text{ kJ}</math> When <math>H_{\text{products}}</math> is greater than <math>H_{\text{reactants}}</math> then <math>\Delta H</math> is negative and heat is evolved in the reaction, and the reaction will be exothermic, For example, <math>CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)</math>; <math>\Delta_r H = -890.4 \text{ kJ}</math> Enthalpy of a reaction changes with pressure and temperature.</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>22/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>Thermochemical equations You are familiar with equations for chemical reactions</p>		<p>Thermochemical Equations You are familiar with equations for chemical reactions.</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>23/224</b>	<b>SUBMITTED TEXT</b>	98 WORDS	<b>97% MATCHING TEXT</b>	98 WORDS
<p>we write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below: (i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) alongside the chemical formulae respectively. For example, to represent burning of methane in oxygen, we write <math>CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + \text{heat}</math></p>		<p>we shall write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below: (i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) along side the chemical formulae respectively. For example, to represent burning of methane in oxygen, we write <math>CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + \text{heat}</math></p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				

<b>24/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>100% MATCHING TEXT</b>	16 WORDS
<p>In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol</p>		
<b>25/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>The amount of heat evolved or absorbed is written after the equation followed by semicolon.</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>The amount of heat evolved or absorbed is written after the equation followed by semicolon.</p>		
<b>26/224</b>	<b>SUBMITTED TEXT</b>	63 WORDS	<b>90% MATCHING TEXT</b>	63 WORDS
<p>is negative for exothermic reactions and it is positive for endothermic reactions. For example: An exothermic reaction is written as <math>\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})</math>; <math>\Delta_r H = -891 \text{ kJ}</math> Whereas an endothermic reaction is written as <math>\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})</math>;</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>is negative for exothermic reactions and it is positive for endothermic reactions. For example : An exothermic reaction is written as <math>\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})</math>; <math>\Delta H = -891 \text{ kJ}</math> Whereas an endothermic reaction is written as <math>\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})</math>;</p>		
<b>27/224</b>	<b>SUBMITTED TEXT</b>	57 WORDS	<b>77% MATCHING TEXT</b>	57 WORDS
<p>Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the <math>\Delta_r H</math> values given correspond to these quantities of substances. (iv) In case, if the coefficients are multiplied or divided by a factor,</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the <math>\Delta H</math> values given correspond to these quantities of substances. (v) In case the coefficients are multiplied or divided by a factor,</p>		
<b>28/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>value must also be multiplied or divided by the same factor. In such cases, the</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>value must also be multiplied or divided by the same factor. In such cases, the</p>		

<b>29/224</b>	<b>SUBMITTED TEXT</b>	55 WORDS	<b>88% MATCHING TEXT</b>	55 WORDS
<p>value will depend upon the coefficients. For example, in equation <math>\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})</math>; <math>\Delta_r H = -242</math> kJ If coefficients are multiplied by 2, we would write the equation <math>2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})</math>;</p>		<p>value will depend upon the coefficients. For example, in equation. <math>\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})</math>; <math>\Delta H = -242</math> kJ If coefficients are multiplied by 2, we would write the equation <math>2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})</math>;</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>30/224</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>88% MATCHING TEXT</b>	14 WORDS
<p>When a chemical equation is reversed, the value of <math>\Delta_r H</math> is</p>		<p>When a chemical equation is reversed, the sign of <math>\Delta_r H</math> is</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>31/224</b>	<b>SUBMITTED TEXT</b>	37 WORDS	<b>73% MATCHING TEXT</b>	37 WORDS
<p><math>\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})</math>; <math>\Delta_r H = -91.8</math> kJ <math>2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})</math>; <math>\Delta_r H = +91.8</math> kJ 1.3.3</p>		<p><math>\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g})</math>; <math>\Delta_r H = 502</math> kJ/mol <math>\text{OH}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H = 472</math> kJ/</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>32/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>69% MATCHING TEXT</b>	29 WORDS
<p>standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. It is denoted by <math>\Delta_r H</math>.</p>		<p>standard enthalpy of reaction. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is denoted by <math>\Delta_r H</math>.</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>33/224</b>	<b>SUBMITTED TEXT</b>	8 WORDS	<b>100% MATCHING TEXT</b>	8 WORDS
<p>Hess's law of constant heat summation Hess's law</p>		<p>Hess's Law of constant heat summation : Hess's law</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>34/224</b>	<b>SUBMITTED TEXT</b>	39 WORDS	<b>92% MATCHING TEXT</b>	39 WORDS
<p>graphite) + <math>\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})</math>; <math>\Delta_r H_1 = -393.5</math> kJ C (diamond) + <math>\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})</math>; <math>\Delta_r H_2 = -395.4</math> kJ</p>		<p>graphite) + <math>\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})</math>; <math>\Delta_r H_3 = -283.0</math> kJ C (graphite) + <math>\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})</math>; <math>\Delta_r H_2 = [(-393.5) - (-283.0)] = -110.5</math> kJ/</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

35/224	SUBMITTED TEXT	145 WORDS	97% MATCHING TEXT	145 WORDS
	<p>The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by <math>\Delta_f H^\circ</math>. When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by <math>\Delta_f H^\circ</math>. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero. For example: <math>C(\text{Graphite}) + O_2(g) \rightarrow CO_2(g)</math>; <math>\Delta_f H^\circ = -393.5 \text{ kJ}</math> This means that carbon dioxide is formed from its elements in their most stable states, carbon in the form of graphite at room temperature and gaseous <math>O_2</math> and <math>CO_2</math> being at 1 bar. 1.5. Enthalpies of</p>		<p>The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by <math>\Delta_f H^\circ</math>. When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by <math>\Delta_f H^\circ</math>. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero. For example : <math>C(\text{Graphite}) + O_2(g) \rightarrow CO_2(g)</math>; <math>\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1}</math> This means that carbon dioxide is formed from its elements in their most stable states. Carbon in the form of graphite and at room temperature and gaseous <math>O_2</math> and <math>CO_2</math> being at 1 bar. -239- 11.5.2 Enthalpy of</p>	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			

36/224	SUBMITTED TEXT	18 WORDS	83% MATCHING TEXT	18 WORDS
	<p>In a chemical reaction, we have seen that energy is either absorbed or evolved. The origin of this</p>		<p>In a chemical reaction, have seen that energy is either absorbed or evolved. Do you know the origin of this</p>	
	<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>			

37/224	SUBMITTED TEXT	184 WORDS	94% MATCHING TEXT	184 WORDS
	<p>energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only. At high temperature, hydrogen molecules dissociate into atoms as <math>\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 435 \text{ kJ/mol}</math> The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the <math>\text{H}_2</math> molecules. For a diatomic molecule like <math>\text{H}_2(\text{g})</math>, we define bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms. Now, let us consider a polyatomic molecule like <math>\text{CH}_4(\text{g})</math>. The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in <math>\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 431.8 \text{ kJ/mol}</math> <math>\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 471.1 \text{ kJ/mol}</math></p>		<p>energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only. At high temperature, hydrogen molecules dissociate into atoms as <math>\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H = 435 \text{ kJ/mol}</math> The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the <math>\text{H}_2</math> molecules. For a diatomic molecule like <math>\text{H}_2(\text{g})</math>, we define bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms. Now, let us consider a polyatomic molecule like <math>\text{H}_2\text{O}(\text{g})</math>. The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in <math>\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g})</math>; <math>\Delta_r H^\circ = 502 \text{ kJ/mol}</math> <math>\text{OH}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 472 \text{ kJ/mol}</math></p>	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			
38/224	SUBMITTED TEXT	27 WORDS	68% MATCHING TEXT	27 WORDS
	<p><math>\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 421.7 \text{ kJ/mol}</math> <math>\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 338.8 \text{ kJ/mol}</math></p>		<p><math>\text{g}) \rightarrow \text{g})</math>; <math>\Delta_r H^\circ = -394 \text{ kJ/mol}</math> (1) <math>\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(1)</math>; <math>\Delta_r H^\circ = -286 \text{ kJ/mol}</math> (2)</p>	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			
39/224	SUBMITTED TEXT	18 WORDS	76% MATCHING TEXT	18 WORDS
	<p><math>\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 1663.4 \text{ kJ/mol}</math> In this reaction</p>		<p><math>\text{g}) \rightarrow \text{H}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H = 435 \text{ kJ/mol}</math> The heat absorbed in this reaction</p>	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			
40/224	SUBMITTED TEXT	19 WORDS	87% MATCHING TEXT	19 WORDS
	<p><math>\text{H}_6(\text{g}) \rightarrow 2\text{C}(\text{g}) + 6\text{H}(\text{g})</math>; <math>\Delta_r H^\circ = 2842.4 \text{ kJ/mol}</math> The</p>		<p><math>\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g}) + \text{H}(\text{g})</math>; <math>\Delta_r H = 435 \text{ kJ/mol}</math> The</p>	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			

<b>41/224</b>	<b>SUBMITTED TEXT</b>	50 WORDS	<b>97% MATCHING TEXT</b>	50 WORDS
<p>bond enthalpy data can be used to calculate <math>\Delta_r H</math> for a chemical reaction occurring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products. <math>\Delta_r H = \Sigma \text{B.E. (reactants)} - \Sigma \text{B.E. (products)}</math>.</p>		<p>bond enthalpy data can be used to calculate <math>\Delta_r H</math> for a chemical reaction occurring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products. <math>\Delta_r H = \Sigma \text{B.E. (reactants)} - \Sigma \text{B.E. (products)}</math> (11.10)</p>		
<b>W</b>	<a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a>			
<b>42/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>63% MATCHING TEXT</b>	29 WORDS
<p>Integrating the equation between temperature <math>T_1</math> and <math>T_2</math>, <math>\int_{T_1}^{T_2} \frac{dT}{T} = \int_{C_1}^{C_2} \frac{dT}{T} = \ln \frac{C_2}{C_1}</math></p>		<p>Integrating the equation between temperature <math>T_1</math> and <math>T_2</math>, we have <math>\int_{T_1}^{T_2} \frac{dT}{T} = \int_{C_1}^{C_2} \frac{dT}{T} = \ln \frac{C_2}{C_1}</math></p>		
<b>W</b>	<a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a>			
<b>43/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>80% MATCHING TEXT</b>	23 WORDS
<p>The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This</p>		<p>the entropy of a pure perfectly crystalline substance approaches zero as the temperature approaches absolute zero. This is known as the Third law of thermodynamics. This</p>		
<b>W</b>	<a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a>			
<b>44/224</b>	<b>SUBMITTED TEXT</b>	41 WORDS	<b>72% MATCHING TEXT</b>	41 WORDS
<p><math>C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = -393.5 \text{ kJ}</math>  <math>CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = -283.5 \text{ kJ}</math></p>		<p><math>C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = -393.5 \text{ kJ/mol.}</math>  <math>[CO(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)]; \Delta_r H^\circ = -283.0 \text{ kJ}</math></p>		
<b>W</b>	<a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a>			
<b>45/224</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>71% MATCHING TEXT</b>	19 WORDS
<p>Le Chatelier's principal 2.7.1. Effect of change of concentration 2.7.2. Effect of change of pressure 2.7.3. Effect of change of temperature 2.7.4.</p>		<p>LE CHATELIER'S PRINCIPLE EFFECT OF A CHANGE IN CONCENTRATION EFFECT OF A CHANGE IN PRESSURE EFFECT OF CHANGE OF TEMPERATURE</p>		
<b>W</b>	<a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a>			



<b>46/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>100% MATCHING TEXT</b>	16 WORDS
<p>This stage of the system is the dynamic equilibrium and the rates of the forward and</p> <p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>		<p>This stage of the system is the dynamic equilibrium and the rates of the forward and</p>		
<b>47/224</b>	<b>SUBMITTED TEXT</b>	26 WORDS	<b>100% MATCHING TEXT</b>	26 WORDS
<p>reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture.</p> <p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>		<p>reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture.</p>		
<b>48/224</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>95% MATCHING TEXT</b>	14 WORDS
<p>a reaction when the reactants and products are in their standard states (25</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>a reaction, when the reactants and the products are in their standard states.</p>		
<b>49/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>60% MATCHING TEXT</b>	20 WORDS
<p>the rate of the back reaction becomes equal to the rate of the forward reaction. The composition of the reaction</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>the rate of the reverse reaction (c) equal to the rate of the reverse reaction (d) unrelated to the rate of the reverse reaction</p>		
<b>50/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>39% MATCHING TEXT</b>	29 WORDS
<p>where, <math>\Delta G</math> is the change in free energy of the reaction, <math>\Delta H</math> is the change in enthalpy of the reaction and <math>\Delta S</math> is the change in entropy of the</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>51/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>61% MATCHING TEXT</b>	30 WORDS
<p>The law of mass action may be stated as follows: The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>the law of mass action which states: The rate at which a substance reacts is proportional to its active mass (molar concentration) the overall rate of the reaction is</p>		

<b>52/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>88% MATCHING TEXT</b>	17 WORDS
<p>the rate of forward reaction is equal to the rate of the reverse reaction, that is, a</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>the rate of the forward reaction is equal to the rate of the reverse reaction (b) is a</p>		
<b>53/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>66% MATCHING TEXT</b>	18 WORDS
<p>A and <math>\mu_B</math> are the chemical potentials of the species A and B, respectively.</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>54/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>88% MATCHING TEXT</b>	27 WORDS
<p>isotherm. It may be used to calculate the change in free energy of a reaction in the standard condition (<math>\Delta G^0</math>) from the equilibrium constant and vice-versa. 2.5.</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (<math>\Delta G^\circ</math>) from the equilibrium constant and vice-versa.</p>		
<b>55/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>a b a b a b A B A B A B</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>A B A B A B A B A B A B</p>		
<b>56/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>a b a b a b A B A B A B</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>A B A B A B A B A B A B</p>		
<b>57/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>96% MATCHING TEXT</b>	23 WORDS
<p>We can write, <math>p_A = c_A RT</math>, <math>p_B = c_B RT</math>,</p> <p><b>W</b> <a href="https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>		<p>we can write <math>P_A = C_A RT</math> and <math>P_B = C_B RT</math></p>		

<b>58/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>76% MATCHING TEXT</b>	13 WORDS
<p>the number of moles of products equals to the number of moles of</p> <p><b>SA</b> 1534974732_540__Solucionario_de_Química,_10a_ed.pdf (D40945983)</p>				
<b>59/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>70% MATCHING TEXT</b>	15 WORDS
<p>the equilibrium would shift in such a way so as to oppose the effect of</p> <p>the equilibrium shifts itself in such a way so as to neutralize the effect of</p> <p><b>W</b> <a href="http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf">http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf</a></p>				
<b>60/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>87% MATCHING TEXT</b>	12 WORDS
<p>in such a way so as to reduce the effect of the</p> <p>in such a way so as to neutralize the effect of the</p> <p><b>W</b> <a href="http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf">http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf</a></p>				
<b>61/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>88% MATCHING TEXT</b>	12 WORDS
<p>the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction.</p> <p>The synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction.</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>62/224</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>87% MATCHING TEXT</b>	19 WORDS
<p>the synthesis of ammonia: <math>N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)</math> If the</p> <p>the synthesis of ammonia <math>N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)</math> the</p> <p><b>W</b> <a href="http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf">http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf</a></p>				
<b>63/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>61% MATCHING TEXT</b>	16 WORDS
<p>the temperature of the system is increased at equilibrium then according to Le Chatelier's principle, the</p> <p>the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>64/224</b>	<b>SUBMITTED TEXT</b>	31 WORDS	<b>94% MATCHING TEXT</b>	31 WORDS
<p>the reaction <math>2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})</math> is <math>1.9 \times 10^{-3} \text{ atm}^{-1}</math>. Calculate the value of <math>K_c</math> at</p>		<p>the reaction <math>2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})</math> is <math>1.9 \times 10^{-3} \text{ atm}^{-1}</math>. Calculate the value of <math>K_c</math> at</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>65/224</b>	<b>SUBMITTED TEXT</b>	40 WORDS	<b>100% MATCHING TEXT</b>	40 WORDS
<p>At equilibrium, the concentrations of <math>\text{N}_2 = 3.0 \times 10^{-3} \text{ M}</math>, <math>\text{O}_2 = 4.2 \times 10^{-3} \text{ M}</math> and <math>\text{NO} = 2.8 \times 10^{-3} \text{ M}</math> in a sealed vessel at 800</p>		<p>At equilibrium, the concentrations of <math>\text{N}_2 = 3.0 \times 10^{-3} \text{ M}</math>, <math>\text{O}_2 = 4.2 \times 10^{-3} \text{ M}</math> and <math>\text{NO} = 2.8 \times 10^{-3} \text{ M}</math> in a sealed vessel at</p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				
<b>66/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>100% MATCHING TEXT</b>	22 WORDS
<p>K. What will be <math>K_c</math> for the reaction <math>\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})</math> (</p>		<p>K. What will be <math>K_c</math> for the reaction <math>\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})</math></p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				
<b>67/224</b>	<b>SUBMITTED TEXT</b>	87 WORDS	<b>95% MATCHING TEXT</b>	87 WORDS
<p>There are numerous equilibria that involve ions only. In the following sections we will study the equilibrium involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (NaCl) is added to water it conducts electricity. Also, the conductance of electricity increases with increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not</p>		<p>There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not</p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				

<b>68/224</b>	<b>SUBMITTED TEXT</b>	98 WORDS	<b>98% MATCHING TEXT</b>	98 WORDS
<p>are, referred to as non electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is</p>		<p>are thus, referred to as non- electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is 2021-22 213</p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				
<b>69/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>97% MATCHING TEXT</b>	18 WORDS
<p>established between ions and unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium. 3.2.</p>		<p>established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium.</p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				
<b>70/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>90% MATCHING TEXT</b>	29 WORDS
<p>The degree of ionisation may be defined as the fraction of total amount of a weak electrolyte that exists in the ionized form. It is denoted by a Greek letter 'α'.</p>		<p>The degree of ionisation may be defined as the fraction of total amount of a weak acid or a base that exists in the ionized form. It is denoted by a Greek letter 'α'.</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>71/224</b>	<b>SUBMITTED TEXT</b>	33 WORDS	<b>80% MATCHING TEXT</b>	33 WORDS
<p><math>K_c</math> or, <math>c \text{ ? ? ? ?}</math> (3) So if we know the value of the dissociation constant of the weak electrolyte and the concentration of the weak electrolyte we can find its degree of dissociation or</p>		<p><math>K_c \alpha = K_c a</math> (14.34) So if we know the value of the dissociation constant of the acid and the concentration of the weak acids we can find its degree of dissociation or</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>72/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>47% MATCHING TEXT</b>	22 WORDS
<p>degree of ionization: The degree of ionization of a weak electrolyte depends on the following factors: 1. Nature of electrolytes: The degree of</p>		<p>DEGREE OF DISSOCIATION The degree of dissociation of an electrolyte in solution depends upon the following factors : (1) Nature of Solute The nature of</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>73/224</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>86% MATCHING TEXT</b>	21 WORDS
<p>degree of ionization of weak electrolyte by the addition of strong electrolyte having common ion is called common ion effect. 3.4. Ionization of</p>		<p>degree of dissociation of a weak electrolyte by the addition of strong electrolyte having common ion is called common ion effect. Example: the ionization of</p>		
<p><b>W</b> <a href="http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf">http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf</a></p>				
<b>74/224</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>47% MATCHING TEXT</b>	25 WORDS
<p>calculate the degree of dissociation of a weak acid. 38 ? NSOU ? GE-CH-11 Now the concentration of H + ion in the solution</p>		<p>Calculate the degree of dissociation of acetic acid its 0.05 M Calculate the concentration of acetate ion in the solution</p>		
<p><b>W</b> <a href="https://www.ncert.nic.in/textbook/pdf/kech107.pdf">https://www.ncert.nic.in/textbook/pdf/kech107.pdf</a></p>				
<b>75/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>83% MATCHING TEXT</b>	13 WORDS
<p>Applying law of chemical equilibrium, its dissociation constant K, is given by ? ? 2</p>				
<p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>76/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>63% MATCHING TEXT</b>	27 WORDS
<p>of the molar concentration of H + and OH - ions. The value of K w at 298 K (25 0 C) is</p>		<p>of the solute and relative of H + and OH - ions. However, the value of K w depends on temperature. At 25°C it is <math>1.0 \times 10^{-14}</math>.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>77/224</b>	<b>SUBMITTED TEXT</b>	56 WORDS	<b>100% MATCHING TEXT</b>	56 WORDS
<p>It is quite inconvenient to express these concentrations by using powers of 10. In 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called pH scale) for expressing the concentrations of H + ions. He defined pH as the negative logarithm of the molar concentration of hydrogen ions. That is, <math>\text{pH} = -\log_{10} [\text{H}^+]</math> (19)</p>		<p>It is quite inconvenient to express these concentrations by using powers of 10. in 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called pH scale) for expressing the concentrations of H + ions. He defined pH as the negative logarithm of the molar concentration of hydrogen ions. That is, <math>\text{pH} = -\log_{10} [\text{H}^+]</math> (14.43)</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>78/224</b>	<b>SUBMITTED TEXT</b>	44 WORDS	<b>93% MATCHING TEXT</b>	44 WORDS
<p>In the previous unit we have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.</p>		<p>In the previous lesson you have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>79/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>71% MATCHING TEXT</b>	17 WORDS
<p>H CH COO K CH COOH ? ? ? ? ? ? ? ? (22) or, ? ? 3 a 3 CH COOH H K CH COO ? ? ? ? ? ? ? ? ? ? (23)</p>		<p>H O ][CH COO ] K [CH COOH] a + - = rearranging, we get 3 3 3 [CH COOH] [H O ] K [CH COO ] + - = x</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>80/224</b>	<b>SUBMITTED TEXT</b>	31 WORDS	<b>100% MATCHING TEXT</b>	31 WORDS
<p>The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a</p>		<p>The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>81/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>100% MATCHING TEXT</b>	20 WORDS
<p>reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts. (i) Salt of strong acid</p>		<p>reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts. Salt of strong acid +</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				



<b>82/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>100% MATCHING TEXT</b>	20 WORDS
<p>dissociation of a weak acid such as acetic acid, CH<sub>3</sub>COOH ? H<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup></p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>83/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>89% MATCHING TEXT</b>	16 WORDS
<p>weak base (e.g. HCl + NH<sub>4</sub>OH) NH<sub>4</sub>Cl (iii) Salt of weak acid</p> <p>weak base ( e.g. HCl + NH<sub>4</sub>OH) NH<sub>4</sub>Cl Salt of weak acid +</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>84/224</b>	<b>SUBMITTED TEXT</b>	72 WORDS	<b>80% MATCHING TEXT</b>	72 WORDS
<p>Salt of weak acid and weak base (e.g. CH<sub>3</sub>COOH + NH<sub>4</sub>OH) CH<sub>3</sub>COONH<sub>4</sub> Let us consider the acid base behaviour of the different type of salts. (i) Salt of strong acid and strong base: The cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore the salts of this category do not show any acid-base behaviour and are neutral. (ii) Salt of strong acid</p> <p>Salt of weak acid + weak base ( eg. CH<sub>3</sub>COOH + NH<sub>4</sub>OH) CH<sub>3</sub>COONH<sub>4</sub> Let us learn about the acid - base behaviour of the different types of salts. Salt of strong acid + strong base : The cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore the salts of this category do not show any acid- base behaviour and are neutral. Salt of strong acid +</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>85/224</b>	<b>SUBMITTED TEXT</b>	44 WORDS	<b>96% MATCHING TEXT</b>	44 WORDS
<p>weak base: the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid. For example, NH<sub>4</sub>Cl dissociates as: NH<sub>4</sub>Cl (aq) → NH<sub>4</sub><sup>+</sup> (aq) Cl<sup>-</sup> (aq) The anion</p> <p>weak base: the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid . For example, NH<sub>4</sub>Cl dissociates as : 4 4 NH<sub>4</sub>Cl(aq) NH<sub>4</sub><sup>+</sup> (aq) Cl<sup>-</sup> (aq) + - → + As mentioned above, the anion</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>86/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>95% MATCHING TEXT</b>	30 WORDS
<p>does not get hydrolysed but the cation get hydrolysed as per the following equation: NH<sub>4</sub><sup>+</sup> + (aq) + H<sub>2</sub>O (l) NH<sub>4</sub>OH + H<sup>+</sup> (aq)</p> <p>does not get hydrolysed but the cation does get hydrolysed as -318- per the following equation. NH<sub>4</sub><sup>+</sup> (aq) + H<sub>2</sub>O (l) → NH<sub>4</sub>OH (aq) + H<sup>+</sup> (aq)</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>87/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
	the salt of a weak base and a strong acid		the salt of a weak base and a strong acid,	
	<b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a>			
<b>88/224</b>	<b>SUBMITTED TEXT</b>	90 WORDS	<b>99% MATCHING TEXT</b>	90 WORDS
	Salt of weak acid and strong base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. For example, CH <sub>3</sub> COONa dissociates as: CH <sub>3</sub> COONa (aq) → Na <sup>+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq) in this case the cation does not get hydrolysed but the anion get hydrolysed as per the following equation. CH <sub>3</sub> COO <sup>-</sup> (aq) + H <sub>2</sub> O (l) ? CH <sub>3</sub> COOH (aq) + OH <sup>-</sup> (aq)		Salt of weak acid and strong base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. for example, CH <sub>3</sub> COONa dissociates as : CH <sub>3</sub> COONa(aq) Na <sup>+</sup> (aq) CH <sub>3</sub> COO <sup>-</sup> (aq) + - → + in this case the cation does not get hydrolysed but the anion does get hydrolysed as per the following equation. - - CH <sub>3</sub> COO <sup>-</sup> (aq) + H <sub>2</sub> O(l) CH <sub>3</sub> COOH (aq) + OH <sup>-</sup> (aq)	
	<b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a>			
<b>89/224</b>	<b>SUBMITTED TEXT</b>	73 WORDS	<b>100% MATCHING TEXT</b>	73 WORDS
	Salt of weak acid and weak base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. For example, ammonium acetate, CH <sub>3</sub> COONH <sub>4</sub> dissociates as: CH <sub>3</sub> COONH <sub>4</sub> (aq) → NH <sub>4</sub> <sup>+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq) In this case both the cation as well as the anion would undergo hydrolysis		Salt of weak acid and weak base : The salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. for example, ammonium acetate, CH <sub>3</sub> COONH <sub>4</sub> dissociates as : CH <sub>3</sub> COONH <sub>4</sub> (aq) NH <sub>4</sub> <sup>+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq) In this case both the cation as well as the anion would undergo hydrolysis	
	<b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a>			
<b>90/224</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>85% MATCHING TEXT</b>	42 WORDS
	NH <sub>4</sub> <sup>+</sup> (aq) + H <sub>2</sub> O (l) ? NH <sub>4</sub> OH + H <sup>+</sup> (aq) CH <sub>3</sub> COO <sup>-</sup> (aq) + H <sub>2</sub> O (l) ? CH <sub>3</sub> COOH (aq) + OH <sup>-</sup> (aq)		NH <sub>4</sub> <sup>+</sup> (aq) + H <sub>2</sub> O(l) = NH <sub>3</sub> (aq) + H <sub>3</sub> O <sup>+</sup> (aq) : K CH <sub>3</sub> COO <sup>-</sup> (aq) + H <sub>2</sub> O(l) = CH <sub>3</sub> COOH(aq) + OH <sup>-</sup> (aq) :	
	<b>W</b> <a href="https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a>			
<b>91/224</b>	<b>SUBMITTED TEXT</b>	5 WORDS	<b>83% MATCHING TEXT</b>	5 WORDS
	w h a b K K K K ? (32) w a b K h K K ? ? (33)		w h a b K K K K = x (b) w a h b K K K	
	<b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a>			

92/224	SUBMITTED TEXT	16 WORDS	68% MATCHING TEXT	16 WORDS
	we can see that the pH of the solution is independent of the concentration of the		We can see that the pH of the solution depends on the relative concentrations of the	
	<p><b>W</b> <a href="https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>			

93/224	SUBMITTED TEXT	210 WORDS	99% MATCHING TEXT	210 WORDS
	that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids / bases and a salt of common ion are important in a yet another way. These act as buffer solutions. Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base. In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemoglobin in our blood and activity of the enzymes in our cells depends very strongly on the pH of our body fluids. pH of the blood is very close to 7.4 and pH of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in pH by the presence of buffers. There are two kinds of commonly used buffer-solutions i) A weak acid and a soluble ionic salt of the weak acid		that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids/ bases and a salt of common ion are important in a yet another way. These act as buffer solutions. Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base. In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemoglobin in our blood and activity of the enzymes in our cells depends very strongly on the pH of our body fluids. pH of the blood is very close to 7.4 and pH of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in pH by the presence of buffers. There are two kinds of commonly used buffer - solutions i. A weak acid and a soluble ionic salt of the weak acid	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			

94/224	SUBMITTED TEXT	19 WORDS	87% MATCHING TEXT	19 WORDS
	e.g. acetic acid and sodium acetate. ii) A weak base and a soluble ionic salt of the weak base		e.g. acetic acid and sodium acetate ; $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ and, ii. A weak base and a soluble ionic salt of the weak base	
	<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>			

<b>95/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>the pH of the solution will depend on the extent of the hydrolysis of the</p> <p><b>SA</b> 1534974732_540__Solucionario_de_Química,_10a_ed.pdf (D40945983)</p>				
<b>96/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>100% MATCHING TEXT</b>	18 WORDS
<p>Let us consider a buffer solution containing acetic acid, CH<sub>3</sub>COOH and sodium acetate CH<sub>3</sub>COONa to understand</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>97/224</b>	<b>SUBMITTED TEXT</b>	106 WORDS	<b>87% MATCHING TEXT</b>	106 WORDS
<p>components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation. CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) ⇌ CH<sub>3</sub>COO<sup>-</sup> (aq) + H<sup>+</sup> (aq) CH<sub>3</sub>COONa (aq) → Na<sup>+</sup> (aq) + CH<sub>3</sub>COO<sup>-</sup> (aq) If we add a strong acid such as HCl to this solution, it produces H<sup>+</sup>. These added H<sup>+</sup> (acid) react with an equivalent amount of the base reserve [CH<sub>3</sub>COO<sup>-</sup>] to generate undissociated acetic acid. The reaction being CH<sub>3</sub>COO<sup>-</sup> (aq) +</p> <p>components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation. + - 3 2 3 3 + - 3 3 CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) ⇌ H<sup>+</sup> (aq) + CH<sub>3</sub>COO<sup>-</sup> (aq) Na<sup>+</sup> (aq) + CH<sub>3</sub>COO<sup>-</sup> (aq) → ZZX If we add a strong acid such as HCl to this solution, it produces H<sup>+</sup>. These added H<sup>+</sup> (acid) react with an equivalent amount of the base reserve [CH<sub>3</sub>COO<sup>-</sup>] to generate undissociated acetic acid. The reaction being 3 3 3 2 CH<sub>3</sub>COO (aq)</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>98/224</b>	<b>SUBMITTED TEXT</b>	98 WORDS	<b>90% MATCHING TEXT</b>	98 WORDS
<p>H<sup>+</sup> (aq) → CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being CH<sub>3</sub>COOH (aq) + HCl (aq) CH<sub>3</sub>COOH (aq) + NaCl (aq) Similarly, when small amount of a strong base like NaOH is added, it generates OH<sup>-</sup> ions. These additional OH<sup>-</sup> neutralize some of the H<sup>+</sup> ions present in the solution.</p> <p>H<sup>+</sup> (aq) + CH<sub>3</sub>COO<sup>-</sup> (aq) → CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being HCl (aq) + CH<sub>3</sub>COONa (aq) → CH<sub>3</sub>COOH (aq) + NaCl (aq) Similarly, when small amounts of a strong base like NaOH is added, it generates OH<sup>-</sup> ions. These additional OH<sup>-</sup> neutralize some of the H<sup>+</sup> ions present in the solution,</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

99/224	SUBMITTED TEXT	27 WORDS	100% MATCHING TEXT	27 WORDS
	<p>Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of CH<sub>3</sub>COOH to re-establish the equilibrium.</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of CH<sub>3</sub>COOH to re-establish the equilibrium.</p>	

100/224	SUBMITTED TEXT	156 WORDS	87% MATCHING TEXT	156 WORDS
	<p>The net result is the neutralization of OH<sup>-</sup> by CH<sub>3</sub>COOH. In other words we can say that the added OH<sup>-</sup> ions (base) react with the acid reserve to produce CH<sub>3</sub>COO<sup>-</sup> ions. OH<sup>-</sup> (aq) + CH<sub>3</sub>COOH (aq) → CH<sub>3</sub>COO<sup>-</sup> (aq) + H<sub>2</sub>O (l) The effective reaction is the reaction of the added base with acid reserve. NaOH (aq) + CH<sub>3</sub>COOH (aq) → CH<sub>3</sub>COONa (aq) + H<sub>2</sub>O (l) The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve. So we can observe that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the hydronium ions and thereby the pH does not change significantly. Now the pH of a buffer solution</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>The net result is the neutralization of OH<sup>-</sup> by CH<sub>3</sub>COOH. In other words we can say that the added OH<sup>-</sup> ions (base) react with the acid reserve to produce CH<sub>3</sub>COO<sup>-</sup> ions OH<sup>-</sup> (aq) + CH<sub>3</sub>COOH (aq) CH<sub>3</sub>COONa (l) + H<sub>2</sub>O (l) The effective reaction being the reaction of the added base with acid reserve. NaOH (aq) + CH<sub>3</sub>COOH (aq) → CH<sub>3</sub>COONa (aq) + H<sub>2</sub>O (l) The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve. You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the hydronium ions and thereby the pH does not changes significantly. Let us derive a mathematical expression for the pH of a buffer solution. 14.5.2</p>	

101/224	SUBMITTED TEXT	60 WORDS	76% MATCHING TEXT	60 WORDS
	<p>Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) CH<sub>3</sub>COO<sup>-</sup> (aq) + H<sub>3</sub>O<sup>+</sup> (aq) NSOU ? GE-CH-11 ? 49 which is characterized by the acid dissociation constant, ? ? 3 3</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is + - 3 2 3 3 CH<sub>3</sub>COOH(aq) + H<sub>2</sub>O (aq) + CH<sub>3</sub>COO<sup>-</sup> (aq) ZZ which is characterized by the acid dissociation constant, 3 3 3 [</p>	

<b>102/224</b>	<b>SUBMITTED TEXT</b>	57 WORDS	<b>85% MATCHING TEXT</b>	57 WORDS
	<p>H O CH COO K CH COOH ? ? ? ? ? ? ? ? ? ? Rearranging, we get ? ? 3 3 3 a CH COOH H O K CH COO ? ? ? ? ? ? ? ? ? ? The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [Salt]. Thus the above equation may be re written as 3</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>H O ][CH COO ] K [CH COOH] a + - = rearranging, we get 3 3 3 [ CH COOH] [H O ] K [CH COO ] + - = x a The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [Salt]. In the light of this the above equation may be re written as 3 [</p>	
<b>103/224</b>	<b>SUBMITTED TEXT</b>	33 WORDS	<b>86% MATCHING TEXT</b>	33 WORDS
	<p>pK log [Acid] ? ? (35) This equation is known as Henderson's equation. A similar expression can be derived for a basic buffer (e.g., ammonium hydroxide and ammonium chloride). The expression is b [Salt] pOH pK log [Base] ? ? (36) 50 ?</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>		<p>pK log [Salt] [Acid] = - = + a a p This equation is known as Henderson-Hasselbalch equation. A similar expression can be derived for a basic buffer ( e.g., ammonium hydroxide and ammonium chloride) . The expression is [ Salt] pOH pK log [Base] = +</p>	
<b>104/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>52% MATCHING TEXT</b>	23 WORDS
	<p>the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation</p> <p><b>W</b> <a href="https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>		<p>the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.</p>	
<b>105/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>100% MATCHING TEXT</b>	30 WORDS
	<p>K<sub>sp</sub> = [A<sup>y+</sup>] x [B<sup>x-</sup>] y = [xS] x [yS] y = x x . y y . (S) x+y (39)</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>K<sub>sp</sub> = [A<sup>y+</sup>] x [B<sup>x-</sup>] y = (xs) x (ys) y = x x y y s x+y</p>	

<b>106/224</b>	<b>SUBMITTED TEXT</b>	50 WORDS	<b>97% MATCHING TEXT</b>	50 WORDS
<p>What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt? We may reason out that according to Le Chatelier's principle, the common-ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us</p>		<p>What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt ? You may reason out that according to Le Chatelier's principle, the common- ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>107/224</b>	<b>SUBMITTED TEXT</b>	191 WORDS	<b>97% MATCHING TEXT</b>	191 WORDS
<p>Application of solubility product in qualitative analysis: The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon selective precipitation of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the <math>K_{sp}</math> of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of <math>H_2S</math>. The dissociation of <math>H_2S</math> can be written as <math>H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)</math> Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions. We know that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the <math>S^{2-}</math> ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out. 3.11.</p>		<p>Application of Solubility Product in Qualitative Analysis The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon selective precipitation of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the <math>K_{sp}</math> of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of <math>H_2S</math>. The dissociation of <math>H_2S</math> can be written as <math>+ 2- 2 H S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)</math> Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions. You are aware, that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the <math>S^{2-}</math> ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out.</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				

<b>108/224</b>	<b>SUBMITTED TEXT</b>	59 WORDS	<b>100% MATCHING TEXT</b>	59 WORDS
<p>the presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called Henderson'</p>		<p>The presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called Henderson</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				



<b>109/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>100% MATCHING TEXT</b>	30 WORDS
<p>the product of the concentration of the ions in the solubility equilibrium is a constant called solubility product (<math>K_{sp}</math>) and is proportional to the solubility of the sparingly soluble</p>		<p>The product of the concentration of the ions in the solubility equilibrium is a constant called solubility product (<math>K_{sp}</math>) and is proportional to the solubility of the sparingly soluble</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>110/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>94% MATCHING TEXT</b>	24 WORDS
<p>the presence common ion decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis. 3.12.</p>		<p>The presence common ions decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis.</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>111/224</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>87% MATCHING TEXT</b>	14 WORDS
<p>the actual volume of molecules is negligible when compared to the total volume of the gas.</p>		<p>The actual volume of the molecules is negligible compared to the total volume of the gas.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>112/224</b>	<b>SUBMITTED TEXT</b>	31 WORDS	<b>85% MATCHING TEXT</b>	31 WORDS
<p>of the vessel. v. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>113/224</b>	<b>SUBMITTED TEXT</b>	35 WORDS	<b>96% MATCHING TEXT</b>	35 WORDS
<p>The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained. vii. The average kinetic energy of gas molecules is directly proportional to absolute temperature.</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

<b>114/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>80% MATCHING TEXT</b>	15 WORDS
<p>m is the mass of the each gas molecule, N is the total number of</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>		<p>m is the mass of a gas molecule. N is the total number of</p>		
<b>115/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>mc 2 2 c 2RT dN M 4 e c dc N 2 RT ? ? ? ? ? ? ? ? ? ? (3)</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>MC c RT dN M e C dc N RT ( ) =</p>		
<b>116/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>100% MATCHING TEXT</b>	16 WORDS
<p>This means that the average kinetic energy of molecules is the same at a given temperature. 4.3.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>117/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>79% MATCHING TEXT</b>	17 WORDS
<p>the number of molecules with which a single molecule will collide per unit time is given by 2 1</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>		<p>the number of molecules, n, with which a single molecule will collide per second, is given by</p>		
<b>118/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>94% MATCHING TEXT</b>	24 WORDS
<p>Collision diameter: The kinetic theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>119/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>the mean distance travelled by a gas molecule between two successive collisions.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

<b>120/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>58% MATCHING TEXT</b>	17 WORDS
<p>the volume of the gas particles depends on the number of moles of gas in the container,</p>		<p>the volume, <math>V</math> of the gas (2) its pressure, <math>P</math> (3) its temperature, <math>T</math> (4) the number of moles, <math>n</math>, of gas in the container</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>121/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>96% MATCHING TEXT</b>	22 WORDS
<p>Figure 4.6. Compressibility factor <math>Z</math>, plotted against pressure for <math>H_2</math>, <math>N_2</math> and <math>CO_2</math> at constant temperature.</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>122/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>90% MATCHING TEXT</b>	20 WORDS
<p>Critical volume, <math>V_C</math> is the volume occupied by one mole of the gas at critical temperature and critical pressure.</p>		<p>critical volume, <math>V_c</math>, is the volume occupied by a mole of the gas at the critical temperature and critical pressure.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>123/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>87% MATCHING TEXT</b>	12 WORDS
<p>temperatures. The isotherm of carbon dioxide determined by him at different temperatures</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>124/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>Increase in temperature increases the kinetic energy of the molecules</p>		<p>increase in temperature increases the kinetic energy of the molecules</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>125/224</b>	<b>SUBMITTED TEXT</b>	56 WORDS	<b>30% MATCHING TEXT</b>	56 WORDS
<p>and <math>n_2</math> are the number of drops formed by the same volume <math>V</math> of the two liquids, then; <math>v_l</math>, the volume of a single drop of first liquid (i.e., liquid one) = <math>V/n_1</math>. Thus, weight of the single drop of the first liquid = <math>w_1 = V/n_1 \cdot d_1</math>.</p>		<p>and <math>n_2</math> be the number of drops produced by the same volume <math>V</math> of the two liquids. Thus, The volume of one drop of liquid 1 = <math>V/n_1</math> The mass of one drop of liquid 1 = <math>(V/n_1)d_1</math> where <math>d_1</math> is the density of liquid 1. Similarly, The mass of one drop of liquid 2 = <math>(V/n_2)d_2</math></p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>126/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>93% MATCHING TEXT</b>	22 WORDS
<p>These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, liquids tend to</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>127/224</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>62% MATCHING TEXT</b>	22 WORDS
<p>drop of the second liquid = <math>w_2 = V/n_2 \cdot d_2</math> .g, where <math>d_2</math> is the density of drop of liquid 1 = <math>(V/n_1)d_1</math> where <math>d_1</math> is the density of</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>128/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>55% MATCHING TEXT</b>	20 WORDS
<p>of Crystallography 6.7.1. Law of constancy of interfacial angles 6.7.2. Law of symmetry 6.7.3. Law of rational indices 6.8. Miller indices 6.9. X-Ray diffraction</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>129/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>94% MATCHING TEXT</b>	18 WORDS
<p>if thermal energy is much greater than the forces of attraction then we have matter in gaseous state.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>130/224</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>100% MATCHING TEXT</b>	42 WORDS
<p>The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them.</p> <p>The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them.</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>131/224</b>	<b>SUBMITTED TEXT</b>	71 WORDS	<b>98% MATCHING TEXT</b>	71 WORDS
<p>In the liquid state the forces of attraction are greater than the thermal energy. We have also studied that molecules in liquid state too have kinetic energy, they cannot move very far away because of the larger forces of attraction amongst them. Because of this property, liquids have definite volume, but they do not have definite shape. Liquids also resemble gases in their ability to flow. Gaseous and liquid states are, therefore, both classified as fluids.</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>132/224</b>	<b>SUBMITTED TEXT</b>	50 WORDS	<b>94% MATCHING TEXT</b>	50 WORDS
<p>A true solid possesses the following characteristics (a) A sharp melting point (b) A characteristic heat of fusion (c) General incompressibility (d) A definite three-dimensional arrangement Hence solids are characterised by high density and low compressibility compared to those of the gas phase. In solids, atoms, ions and molecules are held together by relatively 86 ?</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>133/224</b>	<b>SUBMITTED TEXT</b>	37 WORDS	<b>100% MATCHING TEXT</b>	37 WORDS
<p>strong chemical forces- ionic bond, covalent bond, or by intermolecular Van der Waal's forces. They do not translate although they vibrate to some extent on their fixed positions. This explains why solids are rigid and have definite shape. 6.2.</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>134/224</b>	<b>SUBMITTED TEXT</b>	33 WORDS	<b>100% MATCHING TEXT</b>	33 WORDS
<p>A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the crystal lattice.</p>				
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>135/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>100% MATCHING TEXT</b>	13 WORDS
<p>Solids can generally be classified into two broad categories: (i) Crystalline solids (ii) Amorphous solids</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>136/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>82% MATCHING TEXT</b>	16 WORDS
<p>glass. In their disordered structure, amorphous solids are regarded as super-cooled liquids with high viscosity. The</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>137/224</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>100% MATCHING TEXT</b>	42 WORDS
<p>Anisotropy and isotropy: Amorphous substances differ from crystalline solids and resemble liquids in another important aspect. Their properties such as electrical conductivity, thermal conductivity mechanical strength and refractive index are same in all directions. Amorphous substances are said to isotropic. Liquids and gases are also isotropic.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>138/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>89% MATCHING TEXT</b>	15 WORDS
<p>Figure 6.2. Anisotropy in crystals is due to different arrangement of particles along different directions.</p> <p>Figure 12.2 Anisotropy in crystals is due to different arrangements of particles in different directions. 449</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>139/224</b>	<b>SUBMITTED TEXT</b>	52 WORDS	<b>100% MATCHING TEXT</b>	52 WORDS
<p>Crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. For example the velocity of light through a crystal varies with the direction in which it is measured. Thus, a ray of light enter such a crystal may split up into two components each following different velocity.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

<b>140/224</b>	<b>SUBMITTED TEXT</b>	94 WORDS	<b>98% MATCHING TEXT</b>	94 WORDS
<p>This phenomenon is known as double refraction. This can be shown in fig 6.2 in which simple two-dimensional arrangement of only two different kinds of atoms is depicted if the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case; each row is made up of one type of atoms only. In amorphous solids, atoms or molecules</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>141/224</b>	<b>SUBMITTED TEXT</b>	54 WORDS	<b>67% MATCHING TEXT</b>	54 WORDS
<p>Centre of Symmetry It is a found at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distance on either side. It may be pointed out that a crystal may have number of planes or axis of symmetry but it has only one centre of symmetry.</p> <p>Centre of Symmetry It is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side. It is noteworthy that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>142/224</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>100% MATCHING TEXT</b>	20 WORDS
<p>and in a disorderly manner and, therefore all directions are identical and all properties are alike in all directions. 88 ?</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>143/224</b>	<b>SUBMITTED TEXT</b>	74 WORDS	<b>100% MATCHING TEXT</b>	74 WORDS
<p>a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry. Axis of symmetry An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of <math>360^\circ</math>. Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				



<b>144/224</b>	<b>SUBMITTED TEXT</b>	37 WORDS	<b>78% MATCHING TEXT</b>	37 WORDS
<p>all crystals of the same substance possess the same elements of symmetry. Symmetry in crystals may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>145/224</b>	<b>SUBMITTED TEXT</b>	59 WORDS	<b>90% MATCHING TEXT</b>	59 WORDS
<p>as follows: (i) Write the intercepts as multiples of a, b, c say la, mb, nc (ii) Take the reciprocals of l, m and n (iii) Clear fraction to get whole numbers h,k,l. (iv) Miller indices to the plane are (h,k,l). Example: calculate the Miller indices of crystal planes which cut through the crystal axes at (i) 2a, 3b, c and (ii) 6a, 3b, 3c</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>146/224</b>	<b>SUBMITTED TEXT</b>	80 WORDS	<b>97% MATCHING TEXT</b>	80 WORDS
<p>Bragg's pointed that the scattering of x-rays by crystal could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However the reflection of x- rays can take place only at certain angles which are dependent on wavelength of the x- rays and the distance between the planes of the crystal. The fundamental equation which gives a simple relation between the wavelength of x-rays, the interplaner distance in the crystal and the angle of reflection is known as Bragg's equation.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>147/224</b>	<b>SUBMITTED TEXT</b>	49 WORDS	<b>92% MATCHING TEXT</b>	49 WORDS
<p>Each sodium ion is surrounding by six chloride ions and each chloride ions is surrounded by six sodium ions. The maximum intensity of reflection occurs at the glancing angle of 5.9 0 , 8.4 0 and 5.2 0 for 100, 110 and 111 planes, respectively for first order reflection.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

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**SUBMITTED TEXT**

13 WORDS

**100% MATCHING TEXT**

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the KCl crystal, the maximum reflection of x-rays, corresponding to first order reflections

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**149/224**

**SUBMITTED TEXT**

26 WORDS

**89% MATCHING TEXT**

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are observed to occur at the glancing angles of  $5.38^\circ$ ,  $7.61^\circ$  and  $9.38^\circ$  for (100), (110) and (111) faces, respectively

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**150/224**

**SUBMITTED TEXT**

160 WORDS

**96% MATCHING TEXT**

160 WORDS

a simple cubic lattice structure. The explanation for this apparent anomaly is very simple and can be explained on the basis that the x-rays scattering power for an atom or ion is governed by the number of electrons or atomic number. The atomic numbers of potassium ( $K=19$ ) and chlorine ( $Cl=17$ ) are not very different and the x-rays are unable to detect any difference between the two kinds of atoms. If we imagine all the atoms to be identical, it is evident that face-centred arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face-centred, but the face-centred characteristics are marked by the fact that the two types of atoms composing the substance have nearly the same atomic numbers and atomic weights ( $K=39$ ,  $Cl=35.5$ ). But in the case of sodium chloride the atomic numbers differ considerably ( $Na=11$ ,  $Cl=17$ ), and so their scattering powers are different and hence the true structure as two interpenetrating face-centred lattices become apparent.

**SA** UGCHE-103-English-234.pdf (D146862396)

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**SUBMITTED TEXT**

19 WORDS

**63% MATCHING TEXT**

19 WORDS

will be able to ? describe the formation of different types of solutions; ? express concentration of solution in different

will be able to: • identify the components of different types of solution; • express the concentration of solutions in different

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<b>152/224</b>	<b>SUBMITTED TEXT</b>	44 WORDS	<b>100% MATCHING TEXT</b>	44 WORDS
<p>structure. In its crystal lattice, each Cs + ion is surrounded by 8 Cl - ions and its coordination number is 8. The value of distance between Cs + ion and Cl - ion as determined by Bragg's spectrometer is 3.510Å (figure 6.11).</p>				
<p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>153/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>83% MATCHING TEXT</b>	13 WORDS
<p>Molarity: Molarity (M) is defined as number of moles of solute dissolved</p>				
<p>Molarity: Molarity is defined as the number of moles of solute dissolved</p>				
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>154/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>80% MATCHING TEXT</b>	15 WORDS
<p>m) is defined as the number of moles of the solute per kilogram (kg) of</p>				
<p>m) is defined as the number of moles of solute per kilogram of</p>				
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>155/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>71% MATCHING TEXT</b>	15 WORDS
<p>the number of moles of A and B are <math>n_A</math> and <math>n_B</math></p>				
<p>the number of the moles of A and B respectively. <math>n_A n_A + n_B -190-</math></p>				
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>156/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>On the basis of physical state of solute and solvent</p>				
<p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>157/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>71% MATCHING TEXT</b>	13 WORDS
<p>the interaction between A-B is same as the interaction between A-A and B-B</p>				
<p>the intermolecular interactions between A and B molecules also be exactly the same as the interactions between A-A and B-B</p>				
<p><b>W</b> <a href="https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				

<b>158/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>which obey Raoult's law over the entire range of concentration are known as ideal solutions.</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>159/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>84% MATCHING TEXT</b>	27 WORDS
<p>Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction</p> <p>Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each liquid in the solution is directly proportional to its mole fraction.</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>160/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>76% MATCHING TEXT</b>	16 WORDS
<p><math>p_A = x_A p_A^0</math> where <math>p_A</math></p> <p><math>P_A \propto X_A</math> or <math>P_A = P_A^0 X_A</math> Similarly, <math>P_B</math></p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				
<b>161/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>100% MATCHING TEXT</b>	16 WORDS
<p>to the mole fractions <math>x_A</math> and <math>x_B</math> of the two components</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>162/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>47% MATCHING TEXT</b>	27 WORDS
<p>be the sum of the partial pressures of the components of the solution and is given as: <math>p_{\text{total}} = p_A + p_B</math> Figure 7.1.</p> <p>be the sum of partial pressures of the components; assuming that the component liquids are A and B, <math>p_T = p_A^0 + p_B^0</math> Figure 2.51</p> <p><b>W</b> <a href="https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>163/224</b>	<b>SUBMITTED TEXT</b>	70 WORDS	<b>29% MATCHING TEXT</b>	70 WORDS
<p><math>p_A = x_A p_A^0 + x_B p_B^0 = (1 - x_B) p_A^0 + x_B p_B^0 = p_A^0 - x_B (p_B^0 - p_A^0)</math> A plot of <math>p_A</math> or <math>p_B</math> versus the mole fractions <math>x_A</math> and <math>x_B</math> for a solution gives a linear plot as shown in Fig. 7.1.</p> <p><math>P_A = P_A^0 X_A</math> Similarly, <math>P_B = P_B^0 X_B</math> where <math>P_A^0</math> and <math>P_B^0</math> represent the vapour pressures of pure A and B respectively. If the values of <math>P_A</math> and <math>P_B</math> are plotted against the values of <math>X_A</math> and <math>X_B</math> for a solution, two straight lines are obtained as shown in Fig. 9.2</p> <p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				

<b>164/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>95% MATCHING TEXT</b>	12 WORDS
<p>According to Dalton's law of partial pressures, the total pressure (p</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>165/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>obey Raoult's law over the entire range of concentration</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>166/224</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>80% MATCHING TEXT</b>	19 WORDS
<p><math>p_A + p_B</math> where <math>p_A</math> and <math>p_B</math> are the partial pressures of <math>P_A(g)</math> where <math>P_A</math> and <math>P_B</math> are the partial pressures of</p> <p><b>W</b> <a href="https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>167/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>87% MATCHING TEXT</b>	10 WORDS
<p>positive deviation from Raoult's law. Non-ideal solution showing negative deviation:</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>168/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>87% MATCHING TEXT</b>	12 WORDS
<p>the liquid mixture, the vapour is richer in the more volatile component.      the liquid As the vapour is richer in the more volatile component</p> <p><b>W</b> <a href="https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>169/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>the total vapour pressure becomes equal to the atmospheric pressure.</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				

<b>170/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>74% MATCHING TEXT</b>	24 WORDS
<p>equal volumes of phenol and water, two layers are formed– one of saturated solution phenol in water and the other of saturated solution water in</p>		<p>equal volumes of ether and water are shaken two layers are formed, one of a saturated solution of ether in water and the other of a saturated solution of water in</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>171/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>87% MATCHING TEXT</b>	12 WORDS
<p>small amount of phenol is added to water at room temperature, it</p>		<p>small amount of phenol is added to water at room temperature, it</p>		
<p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>172/224</b>	<b>SUBMITTED TEXT</b>	61 WORDS	<b>96% MATCHING TEXT</b>	61 WORDS
<p>in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.</p>		<p>in a beaker, they form separate layers. When a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from solvent B to A. Finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced (18.1).</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>173/224</b>	<b>SUBMITTED TEXT</b>	43 WORDS	<b>96% MATCHING TEXT</b>	43 WORDS
<p>Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents and gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law or Nernst's Partition law or simply Distribution law or Partition law.</p>		<p>Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law (or Nernst's Partition law) or simply Distribution law or Partition law.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>174/224</b>	<b>SUBMITTED TEXT</b>	26 WORDS	<b>100% MATCHING TEXT</b>	26 WORDS
<p>if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents."</p>		<p>If a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>175/224</b>	<b>SUBMITTED TEXT</b>	44 WORDS	<b>98% MATCHING TEXT</b>	44 WORDS
<p>If <math>C_1</math> denotes the concentration of the solute in solvent A and <math>C_2</math> the concentration in solvent B, Nernst's Distribution law can be expressed as <math>\frac{C_1}{C_2} = \frac{K_D}{K}</math>. The constant <math>K_D</math> (or simply <math>K</math>) is called the distribution coefficient or Partition coefficient or Distribution ratio.</p>		<p>If <math>C_1</math> denotes the concentration of the solute in solvent A and <math>C_2</math> the concentration in solvent B, Nernst's Distribution law can be expressed as <math>\frac{C_1}{C_2} = \frac{K_D}{K}</math>. The constant <math>K_D</math> (or simply <math>K</math>) is called the Distribution coefficient or Partition coefficient or Distribution ratio.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>176/224</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>94% MATCHING TEXT</b>	27 WORDS
<p>When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, the Distribution Law</p>		<p>When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>177/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>100% MATCHING TEXT</b>	24 WORDS
<p>as, <math>\frac{C_1}{C_2} = \frac{S_1}{S_2}</math> where <math>S_1</math> and <math>S_2</math> are the solubilities of the solute in the two solvents.</p>		<p>as <math>\frac{C_1}{C_2} = \frac{S_1}{S_2}</math> where <math>S_1</math> and <math>S_2</math> are the solubilities of the solute in the two solvents.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>178/224</b>	<b>SUBMITTED TEXT</b>	96 WORDS	<b>90% MATCHING TEXT</b>	96 WORDS
<p>Solvent extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by, adding an organic solvent, shaking and separating the two layers, and finally, distilling off the organic solvent to recover the separated compound. In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the</p>				
<p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				

<b>179/224</b>	<b>SUBMITTED TEXT</b>	96 WORDS	<b>96% MATCHING TEXT</b>	96 WORDS
<p>Let us consider an aqueous solution of volume <math>V</math>. Let the mass of an organic compound dissolved in it be <math>w</math>. Let us use volume <math>v</math> of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water one extraction be <math>w_1</math>. Then after, the first extraction Concentration of the organic compound in the aqueous layer = <math>\frac{w_1}{V}</math> Mass of the organic compound in the organic layer = <math>w - w_1</math> Concentration of the organic compound in the organic layer = <math>\frac{w - w_1}{v}</math> ? Distribution coefficient, <math>K</math>, is given by the following expression: <math>K = \frac{w - w_1}{w_1} \cdot \frac{V}{v}</math> ? ? 1 1 1 1</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>180/224</b>	<b>SUBMITTED TEXT</b>	40 WORDS	<b>84% MATCHING TEXT</b>	40 WORDS
<p><math>KV</math> (<math>w - w_1</math>) <math>w_1</math> <math>v</math> <math>KV</math> ? ? Similarly, after the second extraction, the mass of the organic compound that remains unextracted is, <math>w_2 = \frac{w_1}{K + \frac{V}{v}}</math> ? ? ? ? ? ? ? ? In general, the mass of the organic compound that remains unextracted after <math>n</math> extractions is given by, <math>w_n = \frac{w}{1 + \frac{V}{v}(K - 1)^n}</math> ?</p> <p><b>SA</b> Chemistry Textbook Vol. 3 (2018)_pdf.pdf (D128729992)</p>				
<b>181/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>50% MATCHING TEXT</b>	16 WORDS
<p>non-ideal. Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from Raoult's law.</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>182/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>87% MATCHING TEXT</b>	13 WORDS
<p>discuss the dependence of rate of reactions on pressure, temperature and catalyst ?</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				



<b>183/224</b>	<b>SUBMITTED TEXT</b>	49 WORDS	<b>82% MATCHING TEXT</b>	49 WORDS
<p>reaction rates The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction <math>A \rightarrow B</math> The concentration of A decreases and that of B increases with time. The rate of a reaction is defined as the change in concentration of any of reactant or</p>		<p>REACTION RATE The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction <math>A \longrightarrow B</math> The concentration of the reactant A decreases and that of B increases time The rate of reactions is defined as the change in concentration of any of reactant or</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>184/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>71% MATCHING TEXT</b>	16 WORDS
<p>of decrease in concentration of a reactant per mole or increase in concentration of a product</p>		<p>of decrease in concentration of a reactant(s), or the rate of increase in concentration of a product,</p>		
<p><b>W</b> <a href="https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>185/224</b>	<b>SUBMITTED TEXT</b>	32 WORDS	<b>90% MATCHING TEXT</b>	32 WORDS
<p>The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called as rate equation or rate expression. The rate of a reaction</p>				
<p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>186/224</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>50% MATCHING TEXT</b>	21 WORDS
<p><math>aA + bB + cC \rightarrow \text{Products}</math> The rate of the reaction is given by the rate law expression <math>a \frac{dC_A}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \frac{dC_C}{dt}</math></p>		<p><math>aA + bB + cC + dD</math> and the rate law of the reaction is given by; <math>\text{Rate} = k [A][B]^2</math> (a)</p>		
<p><b>W</b> <a href="https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdf/files/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>187/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>39% MATCHING TEXT</b>	24 WORDS
<p>The rate of the reaction <math>A \rightarrow \text{Products}</math>, is experimentally found to be given by <math>-\frac{dC_A}{dt} = k C_A^2</math> (6) where k is the rate constant or the</p>				
<p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				

<b>188/224</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>60% MATCHING TEXT</b>	19 WORDS
<p>The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules.</p>		<p>the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules.</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>189/224</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>58% MATCHING TEXT</b>	18 WORDS
<p>the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is</p>		<p>the speed of a reaction. For example, the reaction between hydrogen and oxygen to give water is</p>		
<p><b>W</b> <a href="https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf">https://apopenschool.ap.gov.in/INTERTEXTBOOKS/313_Chemistry_E.M_Vol_I.pdf</a></p>				
<b>190/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>73% MATCHING TEXT</b>	29 WORDS
<p>it has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10 0</p>		<p>It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. the ratio of rate constants of a reaction at two different temperatures differing by 10</p>		
<p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>191/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>71% MATCHING TEXT</b>	16 WORDS
<p>the rate constant of a reaction, in general is defined as the rate of the reaction</p>				
<p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>192/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>96% MATCHING TEXT</b>	15 WORDS
<p>taking part in an elementary reaction, which must collide simultaneously in order to bring about</p>		<p>taking part in an elementary reaction step, which must collide simultaneously in order to bring about</p>		
<p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				

<b>193/224</b>	<b>SUBMITTED TEXT</b>	62 WORDS	<b>81% MATCHING TEXT</b>	62 WORDS
<p>the order with respect to the reactants A, B and C respectively. Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>194/224</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>100% MATCHING TEXT</b>	24 WORDS
<p>Zero order reaction Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>195/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>100% MATCHING TEXT</b>	17 WORDS
<p>against t, we get a straight line (Fig. 8.1) with slope = <math>-k</math> and intercept equal to</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>196/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>Further simplifying equation (9), we get the rate constant, k as 0</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>197/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>100% MATCHING TEXT</b>	13 WORDS
<p>Variation in the concentration vs time plot for a zero order reaction. 8.5.2.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

<b>198/224</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>76% MATCHING TEXT</b>	13 WORDS
<p>if a is the initial concentration of A, x is the concentration of</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>199/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>82% MATCHING TEXT</b>	30 WORDS
<p>a x) a ? ? ? 2 1 1 1 1 x k t (a x) a t a(a x) ? (16) This is the integrated</p> <p>a x a = + 1 1 - - k t a x a = Thus 1 . ( - ) x k t a a x = This is the integrated</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>200/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>expression for the rate constant of a second order reaction</p> <p>expression for the rate constant of a second order reaction,</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>201/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>expression for the rate constant of a second order reaction.</p> <p>expression for the rate constant of a second order reaction,</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>202/224</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>90% MATCHING TEXT</b>	11 WORDS
<p>Half life for a first order reaction: For the first order</p> <p>half-life (for a first order reaction) For example, consider the first order</p> <p><b>W</b> <a href="https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf">https://nie.lk/pdffiles/other/eGr13OM%20Physical%20Chemistry-Part%202.pdf</a></p>				
<b>203/224</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>46% MATCHING TEXT</b>	25 WORDS
<p>the concentration of the reactant to the half of its initial concentration is called half life period ( t 1/2 ). Half life for a zero order reaction:</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				

<b>204/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>60% MATCHING TEXT</b>	17 WORDS
<p>for a zero-order reaction, the half-life period depends on the initial concentration of the reactant and the</p> <p><b>SA</b> 1534974732_540__Solucionario_de_Química,_10a_ed.pdf (D40945983)</p>				
<b>205/224</b>	<b>SUBMITTED TEXT</b>	37 WORDS	<b>89% MATCHING TEXT</b>	37 WORDS
<p>that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half- life of a first order reaction can be readily calculated from the rate constant and vice versa.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>206/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>95% MATCHING TEXT</b>	12 WORDS
<p>Half life for a second order reaction: For the second order reaction,</p> <p>Half-life for a Second order Reaction For the simple second order reaction 2</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>207/224</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>100% MATCHING TEXT</b>	14 WORDS
<p>Where a 0 is the initial concentration of the reactant A and</p> <p>where [A] 0 is the initial concentration of the reactant A and [</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				
<b>208/224</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>95% MATCHING TEXT</b>	12 WORDS
<p>of a second order reaction is inversely proportional to the initial concentration</p> <p><b>SA</b> 1534974732_540__Solucionario_de_Química,_10a_ed.pdf (D40945983)</p>				
<b>209/224</b>	<b>SUBMITTED TEXT</b>	9 WORDS	<b>100% MATCHING TEXT</b>	9 WORDS
<p>order of a reaction The order of a reaction is</p> <p>ORDER OF A REACTION The order of a reaction is</p> <p><b>W</b> <a href="https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf">https://chemistlibrary.files.wordpress.com/2015/02/essential-of-physical-chemistry.pdf</a></p>				

<b>210/224</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>100%</b>	<b>MATCHING TEXT</b>	17 WORDS
<p>The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>					
<b>211/224</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>100%</b>	<b>MATCHING TEXT</b>	42 WORDS
<p><math>k = A e^{-E_a / RT}</math> (31) where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and <math>E_a</math> is activation energy measured in joules/mole (</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>					
<b>212/224</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100%</b>	<b>MATCHING TEXT</b>	10 WORDS
<p>It can be understood clearly using the following simple reaction</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>					
<b>213/224</b>	<b>SUBMITTED TEXT</b>	41 WORDS	<b>98%</b>	<b>MATCHING TEXT</b>	41 WORDS
<p>According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>					

<b>214/224</b>	<b>SUBMITTED TEXT</b>	62 WORDS	<b>100% MATCHING TEXT</b>	62 WORDS
<p>The energy required to form this intermediate, called activated complex (C), is known as activation energy (E<sub>a</sub>). Fig. 8.3 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products. Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>215/224</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>All the molecules in the reacting species do not have the same kinetic energy.</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>216/224</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>100% MATCHING TEXT</b>	16 WORDS
<p>Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>217/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>100% MATCHING TEXT</b>	23 WORDS
<p>In the Arrhenius equation (31) the factor <math>e^{-E_a/RT}</math> corresponds to the fraction of molecules that have kinetic energy greater than</p> <p><b>SA</b> UGCHE-103-English-234.pdf (D146862396)</p>				
<b>218/224</b>	<b>SUBMITTED TEXT</b>	28 WORDS	<b>60% MATCHING TEXT</b>	28 WORDS
<p><math>A B \text{ av } 8 kT Z 2n n \text{ ? ? ? ? ? ? ? ? ? ?}</math> (36) where <math>n_A</math> and <math>n_B</math> are numbers of A and B molecules, respectively, <math>A B n \times n n = +</math> Where <math>n_A</math> and <math>n_B</math> are the number of the moles of A B respectively.</p> <p><b>W</b> <a href="https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf">https://nios.ac.in/media/documents/SrSec313NEW/313_E_book1.pdf</a></p>				

<b>219/224</b>	<b>SUBMITTED TEXT</b>	52 WORDS	<b>92% MATCHING TEXT</b>	52 WORDS
<p>Collision theory This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase,</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>220/224</b>	<b>SUBMITTED TEXT</b>	30 WORDS	<b>85% MATCHING TEXT</b>	30 WORDS
<p>and average collision diameter. The collision theory is applicable to simple gaseous reactions. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate.</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>221/224</b>	<b>SUBMITTED TEXT</b>	33 WORDS	<b>85% MATCHING TEXT</b>	33 WORDS
<p>internal energy. Again the spherical model ignores the dependence of the effectiveness of the collision on the relative orientation of the colliding molecules. Also the activation energy was treated as though it were related entirely</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>222/224</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>89% MATCHING TEXT</b>	23 WORDS
<p>motion. For this reasons the collision theory is applicable to reactions between very simple gaseous molecules. The collision theory can be generalized by introducing</p> <p><b>SA</b> MCHE 13 - Physical Chemistry.doc (D112801935)</p>				
<b>223/224</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>70% MATCHING TEXT</b>	29 WORDS
<p>The rate of a reaction is <math>3.46 \times 10^{-5} \text{ min}^{-1}</math> and <math>4.87 \times 10^{-5} \text{ min}^{-1}</math> at 298 K and 338 K</p> <p>The rate constant values of a certain reaction is <math>7.2 \times 10^{-10}</math> and <math>3.9 \times 10^{-7}</math> at 600K and 800K.</p> <p><b>W</b> <a href="http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf">http://pue.kar.nic.in/PUE/PDF_files/recogn/ipu_qb/34_ch7.pdf</a></p>				



**224/224**

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so-called steric factor,  $p$ , into the equation for the  
bimolecular rate constant in order to take account






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## Document Information

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PREFACE In the curricular structure introduced by this University for students of Post- Graduate degree programme, the opportunity to pursue Post-Graduate course in a subject introduced by this University is equally available to all learners. Instead of being guided by any presumption about ability level, it would perhaps stand to reason if receptivity of a learner is judged in the course of the learning process. That would be entirely in keeping with the objectives of open education which does not believe in artificial differentiation. I

am happy to note that university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade 'A'.

Keeping this in view, study materials of the Post-Graduate level in different subjects are being prepared on the basis of a well laid-out syllabus. The course structure combines the best elements in the approved syllabi of Central and State Universities in respective subjects. It has been so designed as to be upgradable with the addition of new information as well as results of fresh thinking and analysis. The accepted methodology of distance education has been followed in the preparation of these study materials. Co-operation in every form of experienced scholars is indispensable for a work of this kind. We, therefore, owe an enormous debt of gratitude to everyone whose tireless efforts went into the writing, editing, and devising of a proper layout of the materials. Practically speaking, their role amounts to an involvement in 'invisible teaching'. For, whoever makes use of these study materials would virtually derive the benefit of learning under their collective care without each being seen by the other. The more a learner would seriously pursue these study materials the easier it will be for him or her to reach out to larger horizons of a subject. Care has also been taken to make the language lucid and presentation attractive so that they may be rated as quality self-learning materials. If anything remains still obscure or difficult to follow, arrangements are there to come to terms with them through the counselling sessions regularly available at the network of study centres set up by the University. Needless to add, a great deal of these efforts are still experimental— in fact, pioneering in certain areas. Naturally, there is every possibility of some lapse or deficiency here and there. However, these do admit of rectification and further improvement in due course. On the whole, therefore, these study materials are expected to evoke wider appreciation the more they receive serious attention of all concerned.

Professor (Dr.) Subha Sankar Sarkar Vice-Chancellor

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Unit 1 □□□□□ Chemical Bonding-1 Structure Ionic Bond 1.0 Objectives 1.1 Introduction 1.2 Lattice Energy 1.3 Born-Landé equation Importance of Kapustinskii equation for lattice energy 1.4 Born Haber Cycle 1.5 Polarising Power and Polarizability of ions 1.5.1 Fajan's Rules 1.6 Radius Ratio Rules 1.7 Solvation Energy and Solubility Energetics of dissolution process 1.8 Packing in Crystals, packing efficiency 1.9 Structure of ionic solids (i) Rock salt, (ii) Zinc blende, (iii) Wurtzite, (iv) Fluorite, (v) Anti fluorite, (vi) Perovskite, (vii) Layer lattice 1.10 Qualitative idea of stoichiometric and nonstoichiometric Crystal Defects 1.11 Summary 1.12 Self Assessment

Questions 1.13 Further Reading 1.0 Objectives After reading this unit you will be able to know the followings : \* Definition of ionic bonding, lattice energy. \* Details of Born-Landé equation and Born Haber Cycle. 7 NSOU I CC-CH-07 8 \* About Fajan's Rules and Radius Ratio Rules. \* Relation between solvation energy and solubility. \* Ionic Structure of some ionic solids. \* About stoichiometric and non stoichiometric crystal defects. 1.1 Introduction When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a chemical bond. There are different types of chemical bonds like— \* Ionic or electrovalent bond \* Covalent bond \* Coordinate covalent bond. In ionic bond formation the positively charged ions are held together by electrostatic attractions. The bond so formed is called an electrovalent or an ionic bond. The compounds formed by the ionic bond are called ionic compounds, like NaCl, KCl, etc. 1.2 Lattice Energy Ionic Bond: Ionic bond results from the electrostatic attraction between two ions of opposite charge. The binding energy of an ionic crystal, formed by a number of ionic units, is the standard molar enthalpy change for the formation of the crystal (solid) from the constituent ions in gaseous state.  $M(g) + X(g) \rightarrow MX(s) + U$ , U = Lattice energy. This standard enthalpy change for the process is actually lattice energy, that is the energy released when the constituent gaseous ions come together from infinite separation to form a solid crystal. 1.3

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Born Landé Equation The theoretical treatment of the ionic lattice energy was

first introduced by Born and Landé. It follows as :



NSOU I CC-CH-07 13  $\Delta H_f$  = Heat of formation of the crystal.  $\Delta H_s$  = Heat of sublimation enthalpy of sublimation or enthalpy of atomisation of the metal.  $\Delta H_D$  = Heat of dissociation of  $X_2$ . (here Cl 2)  $\Delta H_{IE}$  = Ionisation Energy of M (here Na)  $\Delta H_{EA}$  = Electron affinity energy of X. (here Cl According to Hess's Law, the following is necessary for the cycle.  $\Delta H_f = \Delta H_s + \frac{1}{2} \Delta H_D + \Delta H_{IE} + \Delta H_{EA} + u_0$   $\therefore U_0 = \Delta H_f - (\Delta H_s + \frac{1}{2} \Delta H_D + \Delta H_{IE} + \Delta H_{EA})$  .....(vi) The Born-Haber Cycle may be utilised to understand the stability of many ionic solids. i) The formation of both  $Mg^{2+}$  and  $O^{2-}$  ions require very large amount of energy. Yet  $MgO$  is a stable ionic compound because its lattice energy is very high. It is a consequence of high charge on both the ions. ii) Electron affinity of the anion may be well calculated from Born Haber Cycle when the lattice energy is previously known from Born-Landé equation. iii) The proton affinity energy. (Proton affinity = negative of proton affinity energy i.e  $PA = -\Delta H_{PA}$ . For  $NH_3(g)$  e.g.  $PA = 886 \text{ KJmol}^{-1}$ ) i.e., the energy released when a proton(s) is added to a gaseous species, such as  $NH_3(g) + H^+(g) = NH_4^+(g)$   $\Delta H_{PA} = -886 \text{ KJ mol}^{-1}$  It can be shown that the proton affinity of water is greater than that of phosphine. So phosphonium compounds are readily decomposed by water./ iv) From the ionization enthalpy values of  $O_2$  ( $1170 \text{ KJmol}^{-1}$ ) and  $Xe$  ( $1169 \text{ KJmol}^{-1}$ ), it was speculated that like  $O_2 +$  species present in  $O_2 + PtF_6^-$ ,  $Xe +$  ion may be prepared. This led to the idea that  $Xe + PtF_6^-$  might have a lattice energy sufficient for its formation from  $Xe$  and  $PtF_6^-$ .)  
Stabilization of high oxidation state of metals: Metals form many fluorides with higher oxidation state than usual. Iodides combine with metal in a relatively lower oxidation state. This can be explained by the higher lattice energies of the fluorides than the iodides.

NSOU I CC-CH-07 14 1.5 Polarising Power and Polarizability of ions The ionic bonds and covalent bonds assumed to be totally distinct is actually an idealization. Most of the compounds are neither hundred percent ionic or hundred percent covalent. The formation of bonds intermediate in nature may occur through a process of ion deformation or polarization. When ions approach each other, the attraction of the positive field of the cation for the orbital electrons of the anion, coupled with the simultaneous repulsion of the nuclei, results in the distortion or polarisation of the anion. Fig 3. Polarisation effects (a) idealised ionpair with no polarisation (b) mutually polarised ion pair (c) polarisation sufficient to form covalent bond. The cation will be similarly polarised by the anion, but because of the smaller size, the effect is less pronounced. As the cations are generally smaller in size, the charge density is high on the cation. Thus the polarising power of the cation is directly proportional to the charge on the cation and inversely proportional to the size of the same. The term ionic potential ( $\phi$ ) is a measure of the polarising power of the cation: Ionic potential ( $\phi$ ) = charge on the cation / radius of the cation For large value of  $\phi$ , polarisation is greater, i.e. the bond becomes more covalent in nature. Ionic polarisation is governed by a number of factors which are summarized in the following rules called Fajan's rules (1924):  
1.5.1 Fajan's Rule i) For small cation with high polarising power, effect of positive charge on polarising the anion will be large. ii) Large anions have a high polarisability, since their outermost electrons are shielded from the positive nuclear field by a number of completely occupied orbitals and

NSOU I CC-CH-07 15 readily polarised by a suitable cation. iii) For effective polarisation there should be a high charge on the cation or the anion or on both. iv) The cation should not possess an inert gas or 18 electron configuration. Inert gas electronic structure have most effective shielding of the nuclear charge. The ionic bond will be favoured when— a) The electronic structure of the ion is stable. b) The charge on the ion is small. c) A small atom forms the anion and large atom forms the cation. The covalent bond will be favoured when— a) The charges on the ions are high. b) Size of the cation is small and size of the anion is large. c) Cations have non-inert gas or pseudo inert gas configuration. The increase in covalent character is reflected in the decreasing melting point of the compounds as illustrated in the table. Table 3 :  
Variation of melting points with size and charge of the ions. Compound M.P. (°C) Compound MP(°C) Compound MP(°C)  $LiF$  870  $BeCl_2$  405  $AlF_3$  1291  $LiCl$  613  $MgCl_2$  712  $AlCl_3$  180  $LiBr$  547  $CaF_2$  1392  $AlBr_3$  975  $LiI$  446  $CaBr_2$  730  $SnF_4$  705  $NaF$  988  $CaI_2$  575  $SnCl_4$  -33  $NaCl$  800  $CaCl_2$  772  $SnCl_2$  246  $NaBr$  755  $SrCl_2$  872  $PbCl_2$  501  $NaI$  651  $BaCl_2$  966  $PbCl_4$  -15 However other factors like packing also contributes to the melting point. Basic Character of metal oxides also decrease with increase in  $\phi$ , reflected in the series

NSOU I CC-CH-07 16 Na<sub>2</sub>O &lt; Li<sub>2</sub>O &lt; MgO &lt; BeO. With increase of  $\rho$ . Covalency in metal-oxygen bond increases and O<sup>2-</sup> ion is not released in water to form OH<sup>-</sup> ion. 1.6 Radius ratio rule The formation of a close-packed crystal lattice of ions of different spherical size is reflected from the ratio of the radius of cation and anion. Radius ratio ( $\rho$ ) = smaller ion / larger ion. The 'r' terms refer to radii of different ions. In a tetrahedral lattice, the size of cation exactly fitting the tetrahedral hole formed by the anions of radius r is equal to 0.225 r. Therefore a tetrahedral hole created by ions of radius r cannot accommodate any ion with radius greater than 0.225 r. The size of the hole formed by closest packed anions may be calculated from the geometric structure, keeping in mind that in the preferred geometry, oppositely charged ions will remain in contact with each other. For an octahedral lattice, simple geometry allows to fix the diagonal of the square as  $2r_c + 2r_a$ . The angle formed by the diagonal in the corner is 45°, so  $2r_c \cos 45^\circ = 2r_a \sin 45^\circ$  or,  $0.707 r_c = 0.707 r_a$  or,  $r_c = 0.707 r_a$  or,  $r_c/r_a = 0.707$ . This is the limiting ratio, since a cation will be stable in an octahedral hole only when it is large enough to keep the anion from touching, i.e.,  $r_c/r_a \geq 0.414$ . Smaller cations will preferentially fit into tetrahedral hole. By a similar geometrical calculation, the lower limit of  $r_c/r_a$  for a tetrahedral lattice may be determined to be 0.225. The radius ratio ranging from 0.225 to 0.414, tetrahedral structure is preferred. Above 0.414, octahedral coordination is favoured. Similarly it is possible to calculate the ratio when a cation accommodates eight anions (0.732) or twelve anions (1.000). The use of radius ratio to govern the structure and preferred coordination number is shown below: For beryllium sulphide, in which  $r_{Be^{2+}} = 59 \text{ pm}$  and  $r_{S^{2-}} = 170 \text{ pm}$ ,  $r_c/r_a = 0.35$ . It is expected that the coordination number of Be<sup>2+</sup> be 4, as the ion fits into the tetrahedral holes of the close-packed lattice. It is found experimentally that BeS adopts a wurtzite structure (Tetrahedral). In the same way it can be predicted that sodium ions will

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prefer octahedral holes in a closest packed lattice of chloride ions. a

NaCl  $r_c/r_a = 116 \text{ pm}/167 \text{ pm} = 0.69$ ,  $r_c/r_a \geq 0.414$  forming NaCl structure having six coordinated sodium ions. NSOU I CC-CH-07 18 Applications of radius ratio rule: (i) Prediction of crystal geometry : It is possible to predict the geometrical structure and coordination number in a particular ionic crystal of the AX type by considering the limiting radius ratio. The predictions are correct when compared with experimental observations.  $r_c/r_a$  determines coordination number of cation and the coordination of anion should be same in AX type crystal to maintain stoichiometry. For AX<sub>2</sub> type crystal as SrF<sub>2</sub>,  $r_{Sr^{2+}} = 132 \text{ pm}$  and  $r_{F^-} = 119 \text{ pm}$ ,  $r_c/r_a = 1.11$ . So both can have coordination number of 8. But from stoichiometry, coordination number of Sr<sup>2+</sup> must be twice that of F<sup>-</sup>. So coordination number (C.N.) of Sr<sup>2+</sup> is 8 and F<sup>-</sup> is 4 in SrF<sub>2</sub> as in fluorite structure. In K<sub>2</sub>O,  $r_{K^+} = 152 \text{ pm}$  and  $r_{O^{2-}} = 126 \text{ pm}$ ,  $r_c/r_a = 1.21$ . Both can have C.N. 8, but from stoichiometry, C.N. of O<sup>2-</sup> = 8 and C.N. of K<sup>+</sup> = 4 with antifluorite structure. For AX<sub>2</sub> type of crystals, the C.N. of A is predicted from limiting radius ratio rule and C.N. of X is determined by stoichiometry and C.N. of A. (See Table 4) (ii) Prediction of thermal stability of some ionic compounds : The anions will be much larger than cation for small values of  $r_c/r_a$  ( $< 0.2$ ). There will be anion-anion repulsion and bad cation-anion contact which destabilises the system. Examples of such crystals are with small cations as Li<sup>+</sup>, Be<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> and large polyatomic anions as SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, ClO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup> etc. or large monoatomic anions as Br<sup>-</sup>, I<sup>-</sup>. These systems are thermally unstable because of inefficient crystal packing and decompose to form small anions which gives an efficient packing. For example:  $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2$ ;  $\text{LiBF}_4 \rightarrow \text{LiF} + \text{BF}_3$ ;  $\text{BeSO}_4 \rightarrow \text{BeO} + \text{SO}_3$ ;  $2\text{Na}_2\text{O}_2 \rightarrow \text{Na}_2\text{O} + 3/2\text{O}_2$  For a particular large anion, the thermal stability falls with decrease of  $r_c/r_a$ . So alkali metal salts of Li<sup>+</sup>, and alkaline earth metal salts of Be<sup>2+</sup> of this type are least thermally stable can also be explained by polarising power of cations. (iii) Prediction for tendency of metal ions to form hydrated salts: For salts with low  $r_c/r_a$ , there is unfavourable crystal packing (anion-anion repulsion etc.) and the cations have a tendency to get surrounded by water molecules i.e. gets hydrated, to increase the effective size of the cation. For example:



NSOU I CC-CH-07 19  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  (or,  $\text{Li}^+ + \text{hyd ClO}_4^-$ ) where  $r_+/r_- = 0.44$  (or  $0.44 < r_+/r_- < 0.732$ ) hyd  $\text{LiClO}_4$  r r r r Alkali metal ions with larger size do not have strong tendency to form hydrated salts. (can also be explained by solvating power of cations). (iv) Prediction of solubility: Salts with small  $r_+/r_-$  ratio are more soluble in water. In efficient packing in crystals reduces lattice energy. Therefore solubility order of alkali metal perchlorates follow the order  $\text{LiClO}_4 > \text{NaClO}_4 > \text{KClO}_4 > \text{RbClO}_4 > \text{CsClO}_4$ . v) Instability in the systems present near the limiting radius ion: The ratio  $r_+/r_-$  should be in the range 0.414 to 0.732 for octahedral coordination of cation. As the limiting value is reached anion-anion repulsion increases and so there is a decrease in lattice energy. For NaCl type structure,  $\text{LiF}$  ( $0.44 < r_+/r_- < 0.732$ ) and  $\text{NaI}$  ( $0.44 < r_+/r_- < 0.732$ ) have values close to 0.414 and are relatively unstable. This is shown by lowering of melting point and increase of solubility. Limitations of Radius ratio rules The radius ratio rule was worked out based on some approximations, they are: i) The ions are considered as non-compressible hard spheres. Such approximation is not supported by quantum mechanical treatment of atoms. Many polyvalent ions as  $\text{CN}^-$ ,  $\text{NO}_2^-$  etc. (except tetrahedral or octahedral moieties) are not spherical in shape. ii) The electron clouds of adjacent ions is not affected from idealised spherical shapes but true only for 100% ionic compounds. Actual situation is very often different from idealised situation. iii) It is assumed that the stability of a system is not influenced by Madelung constant (which is not considered in formulating radius ratio rule. This is not true. iv) It is assumed that crystal geometry does not affect ionic radii and the radius of an ion is an inherent property of the ion, independent of the type of crystal in which it exists. The fact is not supported by theoretical treatment (Born equation) and experimental results. It has been found that  $r_4 : r_6 : r_8 = 0.95 : 1.00 : 1.03$  where  $r_n$  is the radius of a particular ion in a geometry where C.N. around the ion is n.

NSOU I CC-CH-07 20 v) The heavier lithium halides obey the rule only marginally. For  $\text{LiCl}$ ,  $\text{LiBr}$  and  $\text{LiI}$  the radius ratio lies around 0.3, that is tetrahedral lattice is suggested. Similarly for  $\text{KF}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ ,  $\text{CsF}$  radius ratio above 0.73 corresponds to coordination number 8 or above. However, all the above salts adopt 6:6 coordination. Table 4 : Radius ratio and structural type

Radius ratio	Geometry	Coordination no.	Example
$0.155 - 0.225$	Linear	2	$\text{HF}_2^-$
$0.225 - 0.414$	Tetrahedral	4	$\text{ZnS}$ , $\text{NiAs}$
$0.414 - 0.732$	Octahedral	6	$\text{NaCl}$ , $\text{TiO}_2$
$0.732 - 1.0$	Cubic	8	$\text{CaF}_2$ , $\text{UO}_2$

Example: Calculate the minimum value of  $r_+/r_-$  required for coordination number four:  $\text{OA} = \text{OB} = \text{OC} = r_+ + r_-$ ,  $\text{AB} = \text{BC} = 2r_-$  BOM is a right angled triangle where  $\text{BM} = \text{MC} = r_-$ ,  $\text{OM}$  bisects the angle  $\angle \text{BOC} = 109.5^\circ$ ,  $\angle \text{BOM} = 54.75^\circ$ . In the Triangle BOM,  $\sin 54.75^\circ = \text{BM}/\text{BO} = r_- / (r_+ + r_-)$ . This gives  $r_+/r_- = 0.225$ .

1.7 Solvation Energy and Solubility Energetics of dissolution process To dissolve an electrolyte in a suitable solvent, the primary requirement is to overcome the lattice energy of the ionic crystal. The energy is compensated from the solvation energy of the ions. In the solution, the ions get solvated and the energy evolved during solvation must be greater than the lattice energy of the crystal. Solvent sol sol sol  $\text{MX} \rightarrow \text{M}^+ + \text{X}^-$  energy (E)  $+\text{solvent} \rightarrow \text{M}^+(\text{solvent}) + \text{X}^-(\text{solvent})$  The solvation process occurs by the electrostatic interaction between the solute ion and the solvent molecules (ion-dipole interaction). When the solvent is polar, the negative end of the solvent molecule is coordinated to the cation. In case of water like solvents, the ions are separated by the solvent molecules of high dielectric constant ( $\epsilon$ )  $2 \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$   $81.7 = \epsilon$ .

NSOU I CC-CH-07 21 The process of dissolution of an ionic compound in water may be depicted by a Born-Haber cycle: Two factors will contribute to the magnitude of solvation: (i) inherent ability of the solvent to coordinate strongly to the ions involved. (ii) type of ions involved, particularly the size. The forces in the lattice are stronger (ion-ion) than those holding the solvent molecule to the ion (ion-dipole). But there are several of the latter interaction for each ion. As a result, the enthalpy of solvation is roughly of the same order of magnitude as the lattice energy. Therefore the total enthalpy of the solution can be either +ve or -ve, depending upon the specific salt. When the enthalpy of the solution is -ve and the entropy of solution is +ve, the free energy of solution is favourable as the enthalpy and entropy of solution reinforce each other. When enthalpy of solution for ionic compound is +ve, the temperature drops on dissolution in water. If the enthalpy is sufficiently positive, favourable entropy may not be able to overcome it and the compound will be insoluble in water, e.g.,  $\text{KClO}_4$ . From Born-Landé equation, Lattice energy is inversely proportional to the sum of radii of the ions.  $U_f = \frac{1}{4\pi\epsilon_0} \frac{z_+ z_- e^2}{r_+ + r_-} \left( 1 - \frac{r_+ r_-}{r_+ + r_-} \right)$  But enthalpy of hydration depends on individual ion,  $\text{hyd} \text{M}^+ + \text{M}^+(\text{aq})$   $\Delta H_{\text{hyd}} = -\frac{z_+^2 e^2}{4\pi\epsilon_0 r_+} \left( 1 - \frac{r_+}{r_+ + r_-} \right)$   $\Delta H_{\text{hyd}} = -\frac{z_-^2 e^2}{4\pi\epsilon_0 r_-} \left( 1 - \frac{r_-}{r_+ + r_-} \right)$  It is clear that two functions will respond differently to the variation in  $r_+$  and  $r_-$ . Lattice Energy is favoured when ions are smaller in size. In contrast, the hydration enthalpy is the sum of the enthalpies of two individual ions. If one of them is very large ( $r_- > r_+$  or  $r_+ > r_-$ ) the total may be stabilized. Therefore lattice energy will be favoured more when  $r_+ + r_-$  compared to  $\Delta H_{\text{hyd}}$ . So ionic compounds with comparable sizes of



NSOU I CC-CH-07 22 cation and anion have high lattice energy compared to hydration energy and so their solubility is disfavoured. In contrast, ionic solids with dissimilar sized ions have comparatively lower lattice energy and are favourable for dissolution. Though the larger ion may have lower hydration energy, the smaller counter ion have higher hydration energy which overcomes the lattice energy to favour dissolution. This fact is related to crystal packing efficiency. For dissimilar sized ions in the lattice, packing is inefficient and there is a repulsion among the larger sized ions of same charge to destabilise the crystal. The effect may be seen from the solubility of alkali halides in solution: LiF is the least soluble of the Lithium halides, as well as the least soluble alkali fluoride. CsI is the least soluble cesium halide and the least soluble alkali iodide, LiF and CsI have comparable sized ions, so least soluble. CsF is the highest soluble alkali halide. There is a very practical consequence of the relation of solubility to size. It is often possible to prepare a large complex ion with a metal and several ligands which is stable in solution but it is difficult to isolate the large complex ion. Only when a large counter ion is introduced, the precipitation is possible. In qualitative idea:  $\Delta H_{\text{solution}} = \Delta H_{\text{solute-solvent}} - \Delta H_{\text{solute-solute}} - \Delta H_{\text{solvent-solvent}}$  Where the various energies result from ion-ion, ion-dipole, ion-induced dipole, dipole-dipole and London forces.  $\Delta H_{\text{solution}} > 0$  and  $\Delta S_{\text{solu}}$  favours solubility.

1.8 Packing in crystals, packing efficiency The structural type of a crystal is well understood from the unit lattice which on infinite repetition produces the total structure of the crystal. A closed packed structure is attained with minimum unfilled space. Ionic crystals are close-packed assembly of oppositely charged ions of different sizes. The simplest type of structure is cubic lattice. Substituting the lattice points, for simplicity, by eight equal sized spheres gives the arrangement shown in the figure 5(a). In the extended lattice, each corner-sphere will be shared by eight cubes, four in the same layer and four above. So total contribution of the lattice points per unit cell is  $8 \times \frac{1}{8} = 1$ . Hence the effective volume occupied within the cube is equal to the volume of one sphere. If the radius of each sphere is  $r$ , the cube will have sides  $a$ , equal to  $2r$  and volume  $(2r)^3$

NSOU I CC-CH-07 23 =  $\frac{4}{3}\pi r^3$ . The fraction occupancy of the cube obtained from the volume of one sphere  $\frac{4}{3}\pi r^3$  i.e.  $\frac{4}{3}\pi r^3 / 8r^3$  comes out to be 0.524 (or, 52.4 percent packing efficiency). The lattice of a body centered cube (figure 5b) contains an additional point at the centre, which is exclusively belongs inside the cube. The sphere filling model shows that each cube effectively contains  $8 \times \frac{1}{8} + 1$  or two spheres. The fraction of volume of the cube occupied by the spheres taking length of body diagonal  $(\sqrt{3}a = 4r)$  is calculated to be 0.680 i.e. 68 percent packing efficiency or packing efficiently = 68. The face centred cubic lattice (figure 5c) has in addition to eight corner points, one point at the centre of each face. The sphere occupying the faces are shared between two adjacent cubes. So the unit cell contains  $8 \times \frac{1}{8} + 6 \times \frac{1}{2}$ , a total of 4 spheres. The size correlation between the cube edge ( $a$ ) and the radius of the sphere,  $r$ ; is shown in the figure 5. The face diagonal is  $2a$  equals to  $4r$ . The fraction of space occupied by the spheres is 0.740. i.e., 74 percent. (percent packing efficiency=74). Simple Body-centered Face-centered

	(a)	(b)	(c)
Fig. 5 : Cubic Lattice			
Table 5 : Properties of various cubic close packing of uniform sphere			
Cube	a	a	a
a) Volume of unit cell	$a^3$	$a^3$	$a^3$
b) Lattice point per cell	1	2	4
c) Distance of nearest neighbour touching each other	$a$	$\frac{\sqrt{3}}{2}a$	$\frac{a}{\sqrt{2}}$
d) Number of spheres per unit cell	1	2	4
e) Fraction of volume occupied.	0.521	0.680	0.740
f) Coordination number	6	8	12

NSOU I CC-CH-07 24 c) Distance of nearest neighbour touching each other d) Number of spheres per unit cell 1 2 4 e) Fraction of volume occupied. 0.521 0.680 0.740 f) Coordination number 6 8 12

1.9 Structure of ionic solids Structure of some simple ionic crystal consistent with the previous study is given below with examples. Assumptions: i) Ions are essentially spherical. ii) Ions are not polarised. iii) The cation is usually smaller in size. Formula of type AB like zinc blende (ZnS) is close-packed face centred cubic lattice (fcc) consisting of sulphide ions occupying the lattice points of fcc lattice and the zinc ions occupying half the tetrahedral holes. Again as spheres give rise to 2n tetrahedral holes, any structure involving all the tetrahedral holes occupied should become AB<sub>2</sub> type. Where B ions occupy all the tetrahedral holes provided by close packing of A ions in lattice points of a fcc lattice. This situation is found in fluorite structure (CaF<sub>2</sub>). The fluoride ions occupy the tetrahedral holes in an fcc array of calcium ions. The position of cations and anions are interchanged in compounds of forms A<sub>2</sub>B e.g., Na<sub>2</sub>O, Where the sodium ions occupy all the tetrahedral holes in a close-packed fcc array of oxide ions. This structure is termed as antifluorite structure. Examples of fluorite structure: CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>, BaCl<sub>2</sub>, MO<sub>2</sub> (M=Zr, Hf, Ce, Th, Np, Pu). Examples of antifluorite structure: Li<sub>2</sub>O, Na<sub>2</sub>O etc. The sodium chloride structure (6 : 6 coordination) In rock salt or NaCl structure, the chloride ions form a face centred cubic lattice.

NSOU I CC-CH-07 25 Similarly sodium ion also form an fcc lattice. The entire structure is formed by two interpenetrating fcc lattices of  $\text{Na}^+$  and  $\text{Cl}^-$ . The structure can also be interpreted in terms of cubic close packing (ccp i.e. fcc) of  $\text{Cl}^-$  ions in which each of octahedral holes is occupied by  $\text{Na}^+$  ions, and there is one octahedral hole per  $\text{Cl}^-$  ion. Hence in the crystal all the octahedral holes are occupied by  $\text{Na}^+$  ions. Fig. 6 NaCl structure The unit cell has effectively 4  $\text{Na}^+$  and 4  $\text{Cl}^-$  ions.  $\text{Na}^+ = 1$  (centre) +  $1/4 \times 12$  (edge-centre) = 4  $\text{Cl}^- = 1/8 \times 8$  (corner) +  $1/2 \times 6$  (face-centre) = 4 each  $\text{Na}^+$  is surrounded by 6  $\text{Cl}^-$  ion as nearest neighbour and vice versa. The structure is not a closest-packed one since the ions along the diagonals of a cubic face do not touch each other. Zinc blende or Sphalerite Structure (4 : 4 coordination number) : In zinc blende structure 4 zinc ions and 4 sulphide ions are present per unit cell to give a cubic structure. (Discussed previously). The fcc lattice, of  $\text{S}^{2-}$  have one octahedral hole and two tetrahedral (Td) holes per  $\text{S}^{2-}$  ion. Only half of the 8 alternate. Td holes are occupied. Examples are  $\text{ZnX}$ ,  $\text{CdX}$ ,  $\text{HgX}$  (X=S, Se, Te)  $\text{CuX}$  (X=Cl, Br, I)  $\text{BeS}$ . Wurtzite structure (4 : 4 coordination) : Zinc sulphide also crystallises in a different way when the unit cell is hexagonal, or it may be defined as half tetrahedron. Here the  $\text{S}^{2-}$  ions are in hcp array and  $\text{Zn}^{+2}$  ions occupy half of Td holes. Each ion is tetrahedrally surrounded by the opposite ions. Examples are  $\text{MgTe}$ ,  $\text{CdS}$ ,  $\text{AlN}$ ,  $\text{BeO}$  etc. Larger circle O =  $\text{Na}^+$  Smaller circle o =  $\text{Cl}^-$

NSOU I CC-CH-07 26 Figure 7 (a) Zinc blende cubic (b) Wurtzite Hexagonal Fluorite structure (8 : 4 coordination) : The structure can be seen as interpenetrating simple cubic (sc) and face centred cubic (fcc) lattices of ions. The coordination numbers are 8 for cation. Eight fluoride ions form a cube about each calcium ion. Coordination number is for the anion. Four calcium ions are tetrahedrally arranged about each  $\text{F}^-$  ion. The  $\text{Ca}^{2+}$  ions are at the lattice points of fcc lattice and all 8 Td holes are occupied by  $\text{F}^-$  ions. There are 4  $\text{Ca}^{+2}$  ions per unit cell in which the 8 Td holes possess 8  $\text{F}^-$  ions. Fig. 8 : Fluorite Structure Antefluorite: If the numbers and positions of the cations and anions are reversed as in the structure of fluorite, the antefluorite structure is generated adopted by the oxides and the sulphides of Li, Na, K and Rb. Perovskite: The mixed metal oxides with the structure of the mineral perovskite ( $\text{CaTiO}_3$ ). The  $\text{O}^{2-}$  and  $\text{Ca}^{2+}$  ions both form ccp array in which the Oh holes formed by  $\text{O}^{2-}$  ions are occupied by smaller cations ( $\text{Ti}^{+4}$ ). General representation of perovskite structure are  $\text{A} \text{II} \text{B} \text{IV} \text{O}_3$  (A=Ca, Sr, Ba; B=Ti, Zr, Ge, Sn)  $\text{A} \text{IV} \text{B} \text{IV} \text{O}_3$  (A=La; B=Al, Cr, Mn, Ti),  $\text{A} \text{I} \text{B} \text{V} \text{O}_3$  (A=Na, K; B=Nb, Ta). Mixed

NSOU I CC-CH-07 27 fluorides as  $\text{KZnF}_3$ ,  $\text{K}_2\text{NiF}_4$ ,  $\text{ANiF}_4$ ,  $\text{AIBIIICl}_3$  (A=Cs; B=Ca, Cd, Hg),  $\text{AII BIVS}_3$  (A=Sr, Ba; B=Ti) also have perovskite structure. Nowadays they are of special interest. They have high temperature super conducting property such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ , at high temperature  $100 \pm 20\text{K}$ , greater than the boiling point of nitrogen (77K) but much lower than normal temperature of earth. The super conductor has perovskite like structure. There are systematic oxygen vacancies in the unit cell compared to a simple perovskite unit cell. These occur between the adjacent copper atoms in the chain along z axis. The vacancies are on the yttrium atom-plane. Layer lattice structure (Two dimensional lattices): Ionic compounds with significant covalent character having properties between typical ionic and covalent compound, may adopt chain structures sheet structures etc. These compounds crystallize in structures that are hard to recognize. In the structure of simple cadmium iodide the cadmium ions occupy octahedral holes in a hexagonal closed packed structure of iodide ions with half of octahedral holes occupied by Cd but in a definite layered structure that can only be described in terms of co-valent bonding and infinite layer of molecules. A schematic relationship in terms of size and polarisability is shown: Increasing polarisation due to electronic configuration and cation electronegativity increasing polarisation  $\text{CaF}_2$  due to small cation and  $\text{TiO}_2$   $\text{CdCl}_2$  large anion  $\text{SiO}_2$   $\text{CdI}_2$ ,  $\text{HgCl}_2$  Transition metal halides. layered structure is seen in most of the transition metal halides which adopts  $\text{CdCl}_2$  or  $\text{CdI}_2$  structure.  $\text{CdI}_2$  like structure:  $\text{TiCl}_2$ ,  $\text{VCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{FeBr}_2$ ,  $\text{CoCl}_2$ ,  $\text{PbI}_2$ ,  $\text{CaI}_2$ ,  $\text{TlI}_2$  etc.  $\text{CdCl}_2$  like structure:  $\text{MgCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{NiBr}_2$ ,  $\text{ZnBr}_2$ ,  $\text{NiI}_2$ ,  $\text{ZnI}_2$  etc. &lt; &lt;

NSOU I CC-CH-07 28 1.10 Qualitative idea about stoichiometric and nonstoichiometric method crystal defects: In a crystal there occurs infinite repetition of the unit cells where the number of cations and anions are same. But there may occur some imbalances of the constituents somewhere in the crystal. Such condition is termed as lattice defect. When one or two lattice sites are missing it is called point defect. When one line is missing it is called line defect and when one plane is missing, it is called plane defect. Point defects in crystals can be of two types: (i) stoichiometric defects and (ii) non-stoichiometric defects. Stoichiometric defect also can be of two types namely Schottky and Frenkel defects. In stoichiometric defects, the ratio of the number of constituent positive and negative ions in the crystal do not change as indicated by chemical formula. Schottky defect: Schottky defect arises from a missing cation which is accompanied by a vacancy of nearby anion site. That is a cation-anion pair is absent. Thus the electrical neutrality and the stoichiometry of the crystal is preserved, creating a pair of holes or void space. Crystals of NaCl, KCl, KBr, CaCl<sub>2</sub> etc. exhibits Schottky defect. In NaCl crystal, missing of a Na<sup>+</sup> ion is accompanied by a missing Cl<sup>-</sup> ion, while in CaCl<sub>2</sub> crystal missing of one Ca<sup>2+</sup> ion is accompanied by two missing Cl<sup>-</sup> ions. At 130°C NaCl shows 10<sup>6</sup> Schottky pair per cm<sup>3</sup>. The number of ions per cm<sup>3</sup> is about 10<sup>22</sup>. So there are about one Schottky defect per 10<sup>16</sup> ions. Frenkel defect: In Frenkel defect an ion gets missing from its normal site and occupies an interstitial void. Usually smaller sized cations tend to occupy interstitial sites rather than the anions. Electrical neutrality and stoichiometry of the compound is not lost. Small cations in combination with large anions, or crystals with a rather open structure exhibit this defect. Example: AgCl, AgBr, AgI, ZnS, CaF<sub>2</sub>. Both Schottky and Frenkel defect may occur in a same compound like AgBr. In Schottky defect the dielectric constant of the crystalline substance is not changed significantly. But in Frenkel defect proximity of like charges (usually cation) increases the dielectric constant.

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A +

B - B -

**74%**

**MATCHING BLOCK 2/128**

**W**

A + A + B - B - A + B - A + B - A + A + B - A + B - A + B - A + B - B - A + A + B - B - A + B - A + B - A + A + B - A + B - A + B -

B - Frenkel defect Fig. 9 Stoichiometric defects. Non stoichiometric defects or Berthollide defect: In the compounds showing this type of defect, the ratio of positive and negative ion differ from that indicated in their representative chemical formula. The balance of -ve or +ve charge is maintained by extra electrons or positive ions as necessary. Nonstoichiometric defect is of the main types: i) Metal excess and ii) Metal deficient. In some cases incorporation of impurity may also show a third type. Metal excess: Metal excess defect may occur in two ways— i) An anion may be missing from its lattice site, an electron is present there to maintain the electroneutrality. Sodium chloride treated with sodium vapour forms this type of yellow nonstoichiometric variety. ii) An extra metal atom may be present in an interstitial position. An electron in some other interstitial position balance the charge. Zinc Oxide exhibits this type of metal excess defect. When heated, ZnO lattice loses oxygen resulting Z<sub>1+x</sub>O. The additional Zn ions cause lattice defect, with trapped electrons. These electrons can be excited by absorption of visible light and shows an yellow colour when hot. Anion vacancies are created on heating the alkalimetal halides. The excess metal ions on the surface the crystal diffuse inwards and ionize by crystal energy. The metal ion occupies a normal cation site where as the electron occupies an anion site Resulting compound becomes Na<sub>1+x</sub>Cl where x > 1. The electron trapped in anion vacancies give rise to different colours. LiCl-pink, KCl-violet, KBr-blue green, NaCl-orange. These

NSOU I CC-CH-07 30 electrons in halide ion vacancies are known as colour centres or F-centres (from German Farbenzentrum). F-centres can be generated by exposing the crystal to an X-ray beam. Metal deficient defect : This can occur in two ways: i) A positive ion is absent from its lattice site, oxidation of another cation maintains the charge balance. ii) An extra negative ion occupies an interstitial position, charge being balanced as above. There are no known examples, as large anions are difficult to fit into Interstitial positions. This type of defect require variable valency of the cation. FeS, FeO, NiO are examples of this type (Represented as  $Fe_{1-x}S$ ,  $Fe_{1-x}O$ ,  $Ni_{1-x}O$  etc.) When NiO (pale green) is heated to 1500K with excess oxygen, the colour turns black and the oxide becomes semiconductor. The second possibility of metal deficiency by gaining an extra anion is not possible since the anions being large, it is difficult to occupy an interstitial position by an anion as already stated above. Nonstoichiometric defect may also occur through substitution, when a foreign cation of comparable size replaces a cation in the lattice. A  $Cd^{2+}$  ion of comparable size to  $Ag^+$  can replace two  $Ag^+$  ion from a crystal of AgCl. When a little  $Li_2O$  is dissolved in NiO, some  $Li^+$  ion replaces  $Ni^{2+}$ . More  $Ni^{3+}$  is produced in the lattice to balance the charge of univalent  $Li^+$  ion. This enhances the electrical conductance of the doped NiO making it a p-type semiconductor. 1.11 Summary In this chapter the structure, energetics and properties of ionic crystals have been discussed. Crystal Lattice: The pattern in space formed by the identical repetition of basic unit of the ionic crystalline compound. Unit Cell: It is the smallest part of the crystal which produce, by infinite repetition in three dimensional space: There are seven main types of unit cells—cubic, tetragonal, orthorhombic, monoclinic,

NSOU I CC-CH-07 31 hexagonal, triclinic and rhombohedral. Cubic unit are of three types: simple cube, body centre cube and face centre cube. The rock-salt structure, Zinc-Blende structure and CsCl structure are the most common ionic structures. Radius Ratio: Radius ratio  $r^+/r^-$  helps to determine the coordination number and structure of a crystal.

**84%**

**MATCHING BLOCK 4/128**

**SA**

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Lattice Energy: It is the amount of energy required for complete separation of

the constituent ions of the lattice to infinity for one mole of the crystal. Madelung Constant: It is the measure of the net electrostatic interaction of all ions in a given lattice. Polarisation: Ionic compounds in some cases may have covalent character. This is caused by the electrostatic attraction of the charge clouds of the anion by the cations of small size. Ionic Potential ( $\phi$ ): It is a measure of polarising power of the cation. Ionic Potential ( $\phi$ ) = Charge of the ion / radius of the ion. Fajan's Rules: The effect of polarization is summarised in Fajans rules. Lattice Defect: The imperfection in the internal distribution of ions in a crystal is defined as lattice defect. The two main types of defect are i) Schottky defect ii) Frenkel defect. 1.12 Self Assessment Questions Unit I Chemical bonding-I (Ionic bonds) 1. Sub unit: Lattice Energy Q1. Establish Born-Landé equation for the formation of crystals having NaCl structure, explaining the various terms involved in it. Q2. Calculate the lattice energy for CsI crystal for which the equilibrium inter ionic distance is  $3.95 \text{ \AA}$ . Madelung constant = 1.763 and Born exponent = 12.

NSOU I CC-CH-07 32 Q3. Define lattice energy. Establish Born-Haber cycle for the formation of sodium chloride starting from metallic sodium and gaseous chlorine. State the usefulness of Born-Haber Cycle. Q4. State the importance of Kapustinskii equation. Find the value of K in Kapustinskii equation. [Hint:  $K = 0.874 e^2 N_A / 4\pi\epsilon_0$ ]. Q5. On the basis of change in the value of lattice enthalpy, comment on the products of the reaction between group I metals and dioxygen. Sub unit 2: Polarization Q1. What are polarising power and polarisability of ions? Explain with examples. Q2. State Fajan's rules and state its usefulness. Q3. Define ionic potential. Q4. Explain: i)  $HgCl_2$  is colourless while  $HgI_2$  is red. ii)  $PbCl_2$  is colourless while  $PbI_2$  is yellow. iii) M.P. of  $LiCl$  is greater than that of  $LiI$ . iv)  $AgI$  is much less soluble than  $AgCl$ . Q5. State the effect of outer electronic configuration on the covalent character of ionic compounds. Q6. Why is the melting point of  $CuCl$  ( $422^\circ C$ ) much lower than  $KCl$  ( $776^\circ C$ ). Q7. What is meant by partial ionic character of a covalent bond? What are its consequences? Sub unit 3: Radius ratio rule Q1. State the role of radius ratio in the packing of ionic solids. What are its limitations? Q2. Calculate the radius ratio for Tetrahedral, Octahedral and Cubic crystal structures. Q3. Calculate the minimum value of  $r^+/r^-$  required for attaining coordination no. eight. Q4. Why does KCl adopt the rock salt structure in spite of a radius ratio greater than 0.732?

NSOU I CC-CH-07 33 Sub unit 4: Solvation energy Q1. Explain the solubility trends :— a)  $MgSO_4$  &lt;  $CaSO_4$  &lt;  $BaSO_4$  b)  $MgOH$  >  $Ca(OH)_2$  >  $Ba(OH)_2$  [large cation large anion and small cation small anion favours precipitation.] Q2.  $CsF$  is more soluble than  $CsI$  whereas  $LiF$  less soluble than  $LiI$  explain. Q3. State the role of solvation energy in the dissolution process. What is the role of solvent molecules in the dissolution process? Q4. Establish a Born-Haber cycle for the process of dissolution of an ionic compound (MX). What are the factors on which the magnitude of solvation depends? Sub unit 5 & 6: Packing of crystals and structure Q1. Name the different types of crystal lattice for common ionic compounds. Q2. Depict the rock salt, wurtzite and zinc-blends structure of crystal lattice. Q3. The radius of  $NH_4^+$  ion (148 pm) suggests a CsCl structure for  $NH_4F$  but  $NH_4F$  adopts the wurtzite structure: Explain. [Strong H-bonding forms 4 : 4 coordinate] Sub unit 7: Crystal Defects. Q1. Name different types of crystal defects found in ionic solids. Explain with diagram. Q2. What are semiconductors? Q3. Define Schottky and Frenkel defects with examples. Q4. When Ge is doped with Ga, it becomes a p-type semiconductor: Explain. Q5. Discuss the kind of defect observed in the crystal structure of ZnO when heated., What is the consequence of heating? 1.13 Further Reading 1. General and Inorganic Chemistry, Pt I, 3rd ed. 2011, R.P. Sarker, New Central Book Agency, P. L.

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NSOU I CC-CH-07 35 Unit 2 □□□□ Chemical Bonding-II Structure Covalent Bond 2.0 Objectives 2.1 Introduction on Chemical bonding-II (Covalent bond) 2.2 Lewis Structures 2.3 Formal Charge 2.4 Qualitative idea of Valence Bond Theory (VBT) 2.5 Directional properties of Covalent Bond 2.6 Concept of equivalent and non-equivalent hybridisation and shapes of simple molecules and ions (examples from main groups) 2.7 Stereochemically non-rigid molecules-Berry's pseudo rotation 2.8 Resonance of Inorganic molecules 2.9 Dipole moments of Inorganic molecules and ions 2.10 VSEPR Theory, Bent's rule and their Applications 2.11 Molecular Orbital Theory (Elementary pictorial approach) 2.12 Bond Order 2.13 Molecular Orbitals of Heteronuclear diatomic Molecules 2.14 Electron Sea model and Band Theory 2.15 Classification of Inorganic solids and their Conduction Properties According to Band Theory 2.16 Hydrogen bonding 2.17 Vander Waal's Forces 2.18 Summary 2.19 Self Assessment Questions 2.20 Further Reading 2.0 Objectives After reading the chapter you will be able to know about— \* Lewis structures of many compounds. \* Idea about formal charge and calculation 35

NSOU I CC-CH-07 36 \* Qualitative idea of V.B.T \* Properties of covalent bond, hybridisation and shapes of simple molecules. \* Resonance of Inorganic molecules \* Idea about V.S.EPR theory. MO theory \* Concept on Band theory, hydrogen bonding and Vander Waal's forces. 2.1 Covalent bond Apart from the ion formation, atoms combine with each other by sharing electrons to get an inert electronic structure (2 for hydrogen, 8 for other elements.). From Pauli exclusion principle it is obvious that 2 electrons should have to be spin paired when they occupy the same region in space (orbital) between the two nuclei (Lewis-Langmuir concept). The bond formed by sharing electrons of two atoms is called the covalent bond, expressed by a—(line) between the atoms. Octet rule: For most of the atoms bonded by covalent linkage, the sum of shared and unshared (lone pair) pair of electron must be eight (two for hydrogen or rule of duplet). 2.2 Lewis structure The most common expression of writing the structure was first placed by G.N.Lewis. It is termed as Lewis dot structure.  $H \cdot \cdot H$  ( $H-H$ ) —  $H : H$   $C : H$   $H : H$   $\cdot \cdot \cdot$   $:Cl : Cl :$  ( $Cl-Cl$ )  $\cdot \cdot \cdot \cdot \cdot$  —  $J J J J$   $H : F :$  ( $H-F$ )  $\cdot \cdot \cdot$  —  $J J H |$  ( $H-C-H$ )  $| H H O H$  ( $H_2O$ )  $O H \cdot \cdot \cdot \cdot \cdot$  —  $J J$  ,  $H N H : H \cdot \cdot \cdot$   $J J H - N - H | H ? ? ? ? ?$

NSOU I CC-CH-07 37 There are exceptions to the Octet rule where combining atoms have less than eight (i.e. incomplete octet) or more than eight (expansion of octet) electrons in the covalently bonded molecules. For elements having fewer than four valence electrons, the octet will not usually be fulfilled. e.g.,  $:Cl : Cl :$   $B : Cl :$   $\cdot \cdot \cdot \cdot \cdot$   $J J J J J$  ,  $H \cdot \cdot$   $Be \cdot \cdot$   $H \cdot \cdot$   $Li \cdot \cdot$   $CH_3 Cl | Cl - B - Cl H - Be - H Li - CH_3$  The central atom does not attain the octet, but the other attain octet or duplet. These compounds are referred to as electron deficient compounds. For elements with available d-orbitals, the valence shells can be expanded beyond an octet.  $:F : : P : : F : F : F : : : : : : : : : : F : S :$

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The central atoms have 10, 12 and 14 electrons respectively. The molecules will seek the lowest overall energy. Maximum number of bonds and strongest possible bonds will be formed, and the arrangement of atoms in the molecule will be such so as to minimise the repulsion between the bonds, electron pairs and the nuclei. The actual structures of the molecules are not reflected in the Lewis dot structures. The molecules are represented in a planar form. 2.3 Formal Charge The formal charge of an atom in a Lewis dot structure of a molecule is the hypothetical charge on the atom when equal sharing of bonding electrons (constituent atoms are considered to be of same electronegativity occur and the non bonding electrons (lone pair) remain completely on the respective atoms.

NSOU l CC-CH-07 38 The formal charge is calculated as follows: a) Half of the electrons in all bonds to the atom under consideration =  $n/2$  b) Both electrons of lone pair to the atom =  $n l$  c) The no. of valence electrons of the free atom =  $n u$  Then Formal charge =  $n u - (n l + n b/2)$  For boron atom in  $BF_3$  :  $n u = 3, n b = 6, n l = 0$ . Formal charge =  $3 - (0 + 6/2) = 0$

In  $COCl_2$ , for carbon atom,  $n u = 4, n b = 8, n l = 0$ .  $\therefore$  Formal charge =  $(4 - (0 + 8/2)) = 0$

In  $CO_3^{2-}$ , for single bonded 'O' atom,  $n u = 6, n b = 2, n l = 6$ . Formal charge on single bonded 'O' =  $(6 - (6 + 2/2)) = -1$

For double bonded 'O' in  $CO_3^{2-}$ ,  $n u = 6, n b = 4, n l = 4$ . Formal charge =  $(6 - (4 + 4/2)) = 0$

Fig. 1 Lewis structures of some molecules 2.4 Qualitative idea of Valence Bond Theory (VBT) The basic idea of valence bond theory is the formation of the bond through spin pairing of valence electrons between the constituent atoms. The combining species approach each other from infinity and at equilibrium distance the potential energy drops to a minimum. The VBT was proposed by Heitler and London and extended by Pauling and Slater. The simplest electron pair bond is represented in the dihydrogen molecule,  $H_2$ .

NSOU l CC-CH-07 39 calculate the energy of a system of two hydrogen atoms, say H A and H B at various inter nuclear separation  $R_{AB}$ , Schrödinger equation ( $H\psi = E\psi$ ) may be applied. Now the energy (E) may be compared for different inter nuclear separation from the molecular potential energy curve. (Fig.2) E o R pm a b c d e Fig 2. Theoretical energy curves for hydrogen molecule a = experimental curve b, c, d = compared with the experimental curve, shows successive approximation in the wave function. e = the repulsive interaction of two electrons of like spin.

Now,  $\psi_A$  and  $\psi_B$  are the two wave functions of H-atom A and atom B. When they are sufficiently isolated that they do not interact, then the wave for the system of two atoms,  $\psi = \psi_A(1)\psi_B(2)$ , electron (1) is under the control of atom A and electron (2) is under the control of atom B. Now a second term may be introduced when the two electrons interchange their position. Then  $\psi = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$

Again, both the electrons may come under the influence of hydrogen atom A or under the atom B, then

$\psi = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) + \lambda\psi_A(1)\psi_A(2) + \lambda\psi_B(1)\psi_B(2)$ .

The first two terms represents the covalent bond and the last two terms represent the ionic contribution of valence bond theory. Thus  $\psi = \psi_{\text{covalent}} + \lambda\psi_{\text{ionic}}$  where  $\lambda$  is a mixing coefficient. It is less probable that finding both the electrons on the

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SA

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$\psi = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) + \lambda\psi_A(1)\psi_A(2) + \lambda\psi_B(1)\psi_B(2)$ .

The first two terms represents the covalent bond and the last two terms represent the ionic contribution of valence bond theory. Thus  $\psi = \psi_{\text{covalent}} + \lambda\psi_{\text{ionic}}$  where  $\lambda$  is a mixing coefficient. It is less probable that finding both the electrons on the



NSOU | CC-CH-07 40 same atom as they tend to repel each other. So  $\lambda > 1$ . The two bonding electrons are of opposite spin. If they are of parallel spin, no bonding occurs, but there is repulsion (curve 1 c, fig.2). This is a result of Pauli exclusion principle and therefore VBT is also referred to as electron pair theory.

2.5 Directional Properties of Covalent Bond From the Lewis dot structure, the shape of a molecule can not be determined. To arrive at an idea of shape of a molecule, the VSEPR theory, i.e., The Valence Shell Electron Pair Repulsion Theory is much useful. On the basis of minimum electrostatic repulsion between the negatively charged electrons in the valence shell of the central atom present as covalent bond pairs or lone pairs of electrons. This theory has been first proposed by Sidgwick and Powell (1940) and developed by Gillespie and Nyholm (1957). The VSEPR theory states that: All the valence shell electron pairs (bonding and nonbonding) are oriented in space around the central atom as far apart as possible to minimise repulsion. It is seen that lone pairs repel stronger than the bonded pairs as lone pairs occupy more space than bonded pairs. The repulsion order is: lone pair-lone pair  $>$  lone pair - bonded pair  $>$  bonded pair bonded pair. It is assumed that the inner electrons of the interacting atoms of the molecule do not take part in repulsion. To determine the geometry of a molecule, following steps are to be adopted: 1. A reasonable Lewis structure of the molecule is to be selected. 2. Total number of lone pairs and number of atoms linked to the central atom is known, irrespective of single or multiple bonds involved in the bonding. 3. In the molecules containing lone pairs, the actual structure is determined by the position of the atoms only. Lone pairs are not included in describing the shape. But the position of the lone pairs and repulsion between the bonds is important to describe the relative positions of the atoms. For a molecule  $AX_m E_n$ , where A = central atom, X = any other atom, E = lone pair on A, the steric number is  $m + n$ , which indicates the coordination number of A. The basic distribution of electron pairs in space around the central atom follows the principle of minimum repulsion. i.e., maximum angular separation as follows :

NSOU | CC-CH-07 41 Steric no. Arrangement Steric no. Arrangement

Type of Molecule	No. of S.N.	Distribution of lone pairs	Shape of Molecule	Examples(s)
$AX_2$	2	0	linear	linear $O=C=O$
$AX_2 E$	3	1	trigonal bent (V-shaped)	$BeCl_2, HgF_2, ZnI_2$
$AX_3$	3	0	trigonal planar	planar shaped
$AX_3 E$	4	1	trigonal pyramidal	trigonal pyramidal
$AX_4$	4	0	tetrahedral	tetrahedral
$AX_4 E$	5	1	trigonal bipyramidal	trigonal bipyramidal
$AX_5$	5	0	trigonal bipyramidal	trigonal bipyramidal
$AX_6$	6	0	octahedral	octahedral

NSOU | CC-CH-07 42  $AX_3 E_2$  trigonal bipyramidal (irregular; sawhorse)  $AX_4 E_2$  octahedral square planar  $AX_5 E$  trigonal bipyramidal (irregular; sawhorse)  $AX_6$  octahedral

Type of Molecule	No. of S.N.	Distribution of lone pairs	Shape of Molecule	Examples(s)
$AX_3 E_2$	5	2	trigonal bipyramidal (irregular; sawhorse)	$BrF_3$
$AX_4 E_2$	6	2	octahedral square planar	$ClF_4, SO_4^{2-}, XeF_4$
$AX_5 E$	6	1	trigonal bipyramidal (irregular; sawhorse)	$TeCl_4$
$AX_6$	6	0	octahedral	octahedral

NSOU | CC-CH-07 43  $AX_5 E$  trigonal bipyramidal  $AX_6$  octahedral  $AX_7$  pentagonal bipyramidal

Type of Molecule	No. of S.N.	Distribution of lone pairs	Shape of Molecule	Examples(s)
$AX_5 E$	6	1	trigonal bipyramidal	$BrF_5, XeOF_4, TeF_6$
$AX_6$	6	0	octahedral	octahedral
$AX_7$	7	0	pentagonal bipyramidal	pentagonal bipyramidal

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NSOU | CC-CH-07 44 Rule I : The number of a bonding pairs will determine the ideal geometry of the species,  $\pi$ -bonding pair will not influence the geometry of the system. The geometry of the molecular species with no lone pairs surrounding the central atom will be determined only by the number of a bonding electron pairs as depicted in Table 1. When the substituents are different in electronegativity as  $CH_2 F_2$ ,  $PCl_3 F_2$ ,  $COCl_2$ ,  $POF_3$  etc. the bond angle changes from regular geometry and can be explained by Bent's rule. Rule II : When central atom bears both bond pairs (b.p.) and lone pairs (l.p.), the structures deviate from regular geometries predicted from Rule I due to difference in the extent of repulsion of the electron

pairs. The order of repulsion varies as: lone pair-lone pair (l.p.-l.p.) > lone pair-bond pair (l.p.-b.p.) > bond pair-bond pair (

b.p.-b.p.). Rule III : The b.p.-b.p. repulsion decreases as the electronegativity of B atom increases in a AB<sub>n</sub> type species where A is the central atom and n is the number of B atoms attached to A. This can be stated as BAB bond angle decreases with increasing electronegativity of B. Rule IV : Multiple bonds do not grossly influence the geometry of a molecular species. Since multiple bonds (σ bonds alongwith π bonds) occupy more space around central atom than simple σ bonds, they create more repulsions than single σ bonds. The magnitude of repulsion follows the sequence multiple bond-multiple bond > multiple bond σ bond > σ bond-σ bond. Rule V : Any repulsive force (l.p.-l.p. or b.p.-b.p.) to contract the bond angle is more significant for the incompletely filled valence shell compared to the completely filled valence shell. For incompletely filled shells, the deviation of bond angle from ideal behaviour is more due to greater flexibility of bonds as there is more space available for central atom compared to filled shells which have greater rigidity of bonds.

2.6 Concept of equivalent and non-equivalent hybridisation and shapes of simple molecules and ions. The formation of a covalent bond involves the concept of overlap between atomic orbitals of combining atoms. Atomic orbitals have definite shape in space (except s-orbital) and so overlap of atomic orbitals must occur in definite direction, and therefore covalent bond must have a directional nature. The directional nature of the covalent bond is a direct consequence of orbital overlap. The resulting covalent bonds will produce a definite geometry of each covalent molecule. It is known that the four C—H bonds in methane are all alike and they are arranged symmetrically around the central carbon atom directed along the four corners of tetrahedron. This leads to the idea of mixing of 2s and 2p orbitals of carbon before overlap. This is called hybridization. Hybridization is a theoretical concept of mixing different atomic orbitals of comparable energy to produce equal number of orbitals of mixed character. The geometry of covalent molecules may be established by different factors: (a) Hybridisation is introduced in VBT to explain the number of bonds formed, equivalence of bonds (with exceptions), the geometry of the molecules, and better overlap of atomic orbitals. (b) Mutual repulsion of bonding electron pairs so as to make the covalent bonds as far apart as possible. (c) Repulsion between non-bonding or unshared pair of electrons greatly influence the geometry of a molecule. The case of methane may be explained. Carbon atom has four valence shell electrons, two paired in 2s orbital and 2 unpaired in 2p orbital. To form four bonds, the two paired electron are to be unpaired first then one of them is to be promoted to the 2p orbital, which can be represented as: ↑ ↑ 6 C 2s 2px 2py 2pz Ground state ↑ ↑ ↑ ↑ sp<sup>3</sup> Excited state ↑ ↓ CH<sub>4</sub> ↑ ↓ ↑ ↓ sp<sup>3</sup> hybridized orbitals Tetrahedral molecule Methane is tetrahedral and the bonded pair of electrons are as far apart as possible. So the energy of the system is minimum. Hybridisation is a process by which pure atomic orbitals will redistribute their energies among themselves so as to make equivalent bonds, before combining with other atoms.

NSOU | CC-CH-07 46 Common hybridization schemes: Interacting orbitals Hybrid orbital Resulting geometry ns, np z sp linear s, p<sub>x</sub>, p<sub>y</sub> sp<sup>2</sup> Triangular planar (XY plane) s, p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub> sp<sup>3</sup> Tetrahedral (Td) (n-1)d, ns, np<sub>x</sub>, np<sub>y</sub> dsp<sup>2</sup> or sp<sup>2</sup> d Square planar (xy plane) ns, np<sub>x</sub>, np<sub>y</sub>, np<sub>z</sub>, 2z nd sp<sup>3</sup> d Trigonal bipyramidal (TBP) ns, np<sub>x</sub>, np<sub>y</sub>, np<sub>z</sub>, 2x y nd<sup>-</sup>, nd<sup>2</sup> sp<sup>3</sup> d<sup>2</sup> or d<sup>2</sup> sp<sup>3</sup> Octahedral (Oh) ns, np<sub>x</sub>, np<sub>y</sub>, np<sub>z</sub>, 2x y nd<sup>-</sup>, d<sup>3</sup> sp<sup>3</sup> or sp<sup>3</sup> d<sup>3</sup> Pentagonal-bipyramidal nd<sup>2</sup>, nd<sup>2</sup> Some examples: sp hybridization: BeCl<sub>2</sub> Be 2s 2p ↑ ↑ sp g.s e.s + + + + + - 2s 2p + - sp + + + + + - 2s 2p sp + + sp - + gs = ground state BeCl<sub>2</sub> - + Cl + + Be + - Cl e.s = excited state sp<sup>2</sup> hybridization BCl<sub>3</sub> B 2s 2p ↑ sp<sup>2</sup> g.s ↑ : ↑ ↑ Cl—B Cl Cl — — e.s

NSOU | CC-CH-07 47 sp<sup>3</sup> hybridization NH<sub>3</sub>, H<sub>2</sub>O 7 N 2s 2p ↑ ↑ sp<sup>3</sup> 6 O ↑ ↑ sp<sup>3</sup> 3 N | H H H — — O H — H — Tetrahedral including Tetrahedral including lone pair of electron two lone pairs of electrons sp<sup>3</sup> d hybridization : PCl<sub>5</sub>, PCl<sub>3</sub> F<sub>2</sub> 15 P 3s 3p 3d ground state ↑ sp<sup>3</sup> d hybridisation 3 ↑ excited state Cl | P | Cl Cl Cl Cl — — — F | P | F Cl Cl Cl — — — more electronegative atoms always occupy the axial position (Bent's Rule) dsp<sup>2</sup> hybridization: 2 4 PtCl<sub>2</sub> — Pt Cl Cl Cl Cl 2- Square planar Pt : Outer electronic configuration : 5d<sup>9</sup> 6s<sup>1</sup> Pt +2 : 5d<sup>8</sup> 6s<sup>0</sup>



NSOU | CC-CH-07 48 5d 6s 6p dsp hybridisation 2 sp<sup>3</sup> d<sup>2</sup> hybridization: SF<sub>6</sub> 6s 3s 3p 3d ↑↓ ↑↑ ↑↑ ground state sp<sup>3</sup> d<sup>2</sup> ↑↑ excited state F | S | F F F F — — F — — sp<sup>3</sup> d<sup>3</sup> hybridization: IF<sub>7</sub> 7s 3d 3 2 5s 5p 5d ↑↑ ↑↑ ↑↑ ground state | F F F F F F F pentagonal bipyramid The concept of hybridization was first introduced to explain the equivalence of the four bonds of CH<sub>4</sub>. Each of the four sp<sup>3</sup> hybrid orbitals of carbon contain 25% s character and 75% p character and are distributed along the four corners of a regular tetrahedron. When there is no lone pair of electron on the central atom then the situation is ideal and all bonds are equivalent. When lone pair of electron is present on the central atom, then the situation of s : p ratio of the sp<sup>3</sup> hybrid change from ideal ratio. In NH<sub>3</sub> and H<sub>2</sub>O there are one and two lone pairs respectively on the central atom. These hybrid orbitals become non-

NSOU | CC-CH-07 49 equivalent hybrid orbitals but still called sp<sup>3</sup> hybrid orbitals. Now it was seen that in some molecules like CH<sub>3</sub>F, CH<sub>3</sub>Cl the bond lengths and bond angles differ from the ideal situation: Molecule Bond length Molecule Bond length CH<sub>3</sub>F C—F 139.1 pm CF<sub>4</sub> C—F 132.3 pm CH<sub>3</sub>Cl C—Cl 170.3 pm CH<sub>2</sub>Cl<sub>2</sub> C—Cl 177.2 pm CF<sub>3</sub>Cl C—Cl 175 pm CHCl<sub>3</sub> C—Cl 176.4 pm C<sub>2</sub>H<sub>6</sub> C—C 153.6 pm CCl<sub>4</sub> C—Cl 176.4 pm C<sub>2</sub>F<sub>6</sub> C—C 151 pm The effect of lone pairs on bonds angles is manifested in the following molecules. The tetrahedral bond angle in methane is 109°5', in ammonia the angle becomes 107° and in water it is further reduced to 104°. H | C | H H H 109°5' CH<sub>4</sub> N | H H H 107°3' NH<sub>3</sub> .. O | H H 104° H O 2 ... In trigonal bipyramidal structure there are two positions to accommodate the lone pair. One in the axial position with nearest bond angle 90° and other in the equatorial position the bond angle is 120°. Therefore the lone pair always prefer the equatorial position, where the repulsion is minimised. There are some special cases, such as in NH<sub>3</sub> &gt; HNH bond angle is 107° whereas in NF<sub>3</sub> < HFH bond angle is 102°. As the bonded atom is more electronegative, bond pair is displaced further from the central atom, and so bp - bp repulsion decreases. In NH<sub>3</sub> < HNH = 107°3' and in PH<sub>3</sub> < HPH = 93°3' Compared to the 1st period elements, the 2nd period elements are larger and the repulsion between lp - bp dominates. In CH<sub>2</sub>F<sub>2</sub> < HCH is 111.9°, whereas < FCF is 108°3', which suggests less than 25% s character is C—F bond. In the sp<sup>3</sup> d<sup>2</sup> and sp<sup>3</sup> d

NSOU | CC-CH-07 50 hybridisation, there are two sets of orbitals shown in the structures below. In structure (a) and (b) sp<sup>3</sup> d<sup>2</sup> i.e. trigonal bipyramid structure, one set is sp<sup>2</sup> oriented in the equatorial position and pd oriented along the vertical position. In the equatorial plane, the orbitals are rich in s-character so the bond lengths are shorter and axial that is vertical bonds are relatively longer. F | P | F F F F 120° 157.7 pm 153.5 pm 90° F | S | F F F 164.6 154.5 . . α β α = 129.3 β = 93.5 (a) (b) The lone pair will always occupy the equatorial position. In compounds like PCl<sub>2</sub>F<sub>3</sub>, PCl<sub>3</sub>F<sub>2</sub> etc. the more electronegative elements will occupy the axial position. (Bent's section 2.9) 2.7 Stereochemically non-rigid molecules Berry's pseudorotation The structures predicted by VSEPR and Bent's rule are structurally rigid or static molecular species. However, there are many molecules which are structurally non-rigid or stereochemically non-rigid. If the rearrangement of structures of a molecule gives configuration which are chemically equivalent having minimum energy and are easily transformed from one form to other, the molecule is said to be 'fluxional'. Fluxional molecules differ from other stereochemically non-rigid molecules in possessing more than a single configuration with minimum energy. Berry's pseudorotation: The structure of PCl<sub>2</sub>F<sub>3</sub> will have two F atoms in axial position and two Cl and one F atom in equatorial position according to Bent's Rule (section 2.9) in a TBP geometry. But NMR studies at various temperatures reveal that all F atoms are equivalent and undergo structural change which is consistent with the time scale of NMR experiment. Interchange of axial and equatorial groups in a trigonal bipyramid (TBP) structure may occur therefore, in some cases. The mechanism was suggested by R.S. Berry and is known as Berry pseudorotation. In a molecule of AX<sub>5</sub> type, without any lone pair on A, the structure is TBP corresponding to sp<sup>3</sup> d<sup>2</sup> hybridisation of the central atom which is not energetically favoured in many cases. Accordingly, a TBP structure may readily



NSOU I CC-CH-07 53 rest of the molecule. This is called hyperconjugation of no bond resonance.  $-A-X-B \leftrightarrow A-X-B$  As in  $ONF_3 \leftrightarrow O=N-F-F-F$  In tautomerism such as keto-enol tautomerism arrangement of atoms change but in Resonance atoms will not change their relative position in the molecule.

2.9 Dipole moments of inorganic molecules and ions The covalent bond between two atoms of the same element is shared equally by the two nuclei concerned. But for bonds between atoms of two different elements, the bonding electrons are not equally distributed between the two nuclei. The electron pair will be shifted towards the more electronegative element. The bond thus gets polar. The polarity is expressed in terms of electric dipole moment vector  $\mu$ .  $\mu = q \cdot d$ . (coulomb metre)  $q + d \leftrightarrow q - d$  and  $q -$  are charges on the atoms sparated by a distance  $d$ . [SI unit is coulomb metre, common unit debye]. 1 Debye =  $10^{-18}$  esu.cm =  $3.33564 \cdot 10^{-30}$  coulomb metre. In a symmetrical heteronuclei molecule bond moments are cancelled ( $O=C=O$ ) i.e.  $\mu = 0$ , where as  $SO_2$  is angular and possesses a positive dipole moment. Lone pairs of electrons also hive some effect on dipole moment.

2.10 VSEPR Theory, Bent's rule and their applications It is seen that the bonding of an electronegative atom or group favours to bind to orbitals having more p-character (or less s-character). The s-orbitals, with greater penetration NSOU I CC-CH-07 54 into inner electron core faces higher effective nuclear charge of the central atom form bonds with less electronegative atoms or groups, whereas electronegative atoms or groups form bonds with orbitals having less s-character (i.e. more p-character). The mismatch of energy results in poor overlap of orbitals. These are summarised in Bent's rules proposed by H.A. Bent in 1960. i) More electronegative substituents prefer hybrid orbitals of the central atom with greater p-character and

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less s-character and more electropositive substituents prefer hybrid orbitals having more s-character.

ii) The central atom involves hybrid orbitals with higher s-character to develop higher covalence, and less s-character in bonds with greater ionic character. iii) The central atom will direct less p-character and greater s-character into the hybrids directed towards less electronegative substituents. In  $PCl_3F_2$ ,  $PF_4(CH_3)$ ,  $PF_3(CH_3)_2$ , the fluorine atoms always occupy the axial position. Again the s-rich covalent bonds require a larger angular volume and leads to widening of bond angle. The Bent's rule gives us an idea about the refinements of bond angle over the VSEPR theory. In TBP  $PCl_3F_2$  molecule for example, the hybridisation is  $sp^3d$  which can be considered as a combination of  $sp^2$  and  $pd$  hybridisation ( $sp^2$  orbitals lie in the  $xy$  equatorial plane and  $2z^2 - x^2 - y^2$  directed mutually  $180^\circ$  in the axial directions i.e. perpendicular to the equatorial plane). The equatorial bonds have s-orbital contribution but axial bonds do not have any s-character. The more electronegative atoms will occupy axial bonds with no s-character, and chlorine atoms will occupy equatorial positions where the hybrid orbitals are  $sp^2$ . For  $sp$  hybrid orbitals where s and p-character are equal (50%–50%), the bond angle is  $180^\circ$ , for  $sp^2$  (s-character 33%, p-character 66%) bond angle is  $120^\circ$ , and  $sp^3$  (s-character 25% – p-character 75%) angle is  $109^\circ 28'$ , for  $p$  (100% p-character) angle is  $90^\circ$ . The greater the s-character greater is the bond angle while greater p-character indicates smaller bond angle.

2.11 Molecular Orbital Theory (MOT) Certain observations of the properties of molecules cannot be adequately explained by VBT. For example, oxygen molecule  $O=O$  should be diamagnetic with each oxygen atom  $sp^2$ -hybridised. Experimentally it is observed that  $O_2$  molecule is paramagnetic with two

NSOU I CC-CH-07 55 unpaired electrons. Same is true for B<sub>2</sub> molecule which should be diamagnetic according to VBT, but actually the molecule is paramagnetic. Such inadequacies have been taken care of in the MOT where the orbitals of the molecule are molecular orbitals and not atomic orbitals as per VBT. VBT uses hybridisation concept to describe the shapes of molecules, but the hybridised orbitals are still atomic orbitals. Each electron in a molecule is described by a certain wave function  $\psi$  which represents the orbit of the electron in a molecule, and is called molecular orbital. When two individual hydrogen atoms comes closer and closer from a very large distance from each other, the nucleus of each atom will start to attract the electrons originally associated solely with the other atom. The change in energy of the system as a function of distance shown is in the following curve (known as Morse Curve). When the distance of separation of the nuclei is near the bonding range, two electrons in the system are both associated with the two nuclei. The original atomic orbitals on the two atom will be associated to one molecular orbital. Thus a molecular orbital is formed from the combination of two atomic orbitals.  $r$  equilibrium Internuclear distance ( $r_0$ )  $E + + + H A H B + H 2$  Fig. 3. The Morse Curve for Fig. 4. Addition of two 1s Hydrogen Molecule atomic orbitals The molecular orbital thus formed, is a result of linear combination of atomic orbitals. When one atom has the wave function  $\phi_A$  and the other atom possess wave function  $\phi_B$  In this case the linear combination (like simple addition or subtraction) of atomic orbitals (LCAO) will produce the molecular orbital wave function  $\psi_{MO}$ .  $b A B MO \psi = \phi + \phi$  and  $a A B MO \psi = \phi - \phi$  ( $b =$  bonding,  $a =$  antibonding)

NSOU I CC-CH-07 56 For effective combination of  $\phi_A$  and  $\phi_B$  the following conditions should be maintained: i) The energies of  $\phi_A$  and  $\phi_B$  should be of comparable magnitude. This is called energy condition and therefore best combination will occur between 1s and 1s, 3p and 3p etc. but combination between 1s and 5s, 3p and 5p will be less probable. ii)  $\phi_A$  and  $\phi_B$  should have the same symmetry relation to the molecular axis of molecule AB. So s-type atomic orbital will not combine with pz type orbital if x is the molecular axis.  $A + + + + B + - - - s p z$  (Non-bonding condition) iii)  $\phi_A$  and  $\phi_B$  should overlap one another as much as possible so that overlap integral  $S_{AB} = \int \phi_A \phi_B d\tau$  and resonance integral  $H_{AB} = \int \phi_A H \phi_B d\tau$  will have maximum value.  $\psi_b MO$  implies that the two electrons in the hydrogen molecule are now shared with both nuclei; that is the MO is bicentric. The MO helps to bond the two hydrogen atoms together ( $b$  indicates the bonding MO). The plus sign in the MO (Fig 4) indicates that the wave function is positive everywhere. Atomic orbitals with same sign will combine to form bonding orbital. There will be no node. (Node is the space where there is minimum probability of finding an electron). In  $\psi_a MO$  ('a' stands for antibonding orbitals) which is produced from  $\phi_A - \phi_B$ , the probability of finding the electrons at exactly half the distance between the nuclei is zero. There is a nodal plane in the M.O.  $E \psi_b ( ) \sigma \phi_B \phi_A \psi_a ( ) \sigma^*$  MO energy diagram of H<sub>2</sub> The LCAO of atomic orbitals may be represented by an energy level diagram.

NSOU I CC-CH-07 57 The energy of the bonding MO orbital is lower than the energies of the atomic orbitals and the energy of antibonding orbital is higher than the atomic orbitals. The bonding MO represents a  $\sigma$ -bonding orbital and the antibonding MO is a  $\sigma^*$  antibonding orbital. Two p orbitals in the similar manner can form bonding orbitals, but there may be two types of overlap.  $- + + + - + + - + + - - + - +$  nodal planes  $\sigma^*$  or  $\sigma$   $\sigma p u \sigma$ -overlap  $+ + + + - - -$  nodal plane  $\pi \pi p$  or  $u + + + - - -$  nodal planes  $\pi \pi^*$  or  $\sigma^* p g \pi$  overlap  $+ - \sigma$  bonding  $\sigma^*$  antibonding  $\pi$  bonding antibonding nodal plane  $\pi^*$  Essential features of MOT 1.

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Molecular orbitals are formed by the combination of atomic orbitals of individual atoms

according to LCAO. The number of molecular orbitals will be equal to the combining atomic orbitals. The combining atomic orbitals must satisfy three conditions to form MO, i.e. energy, overlap and symmetry. 2. An atomic orbital is represented by a wave function. The waves have positive (crest) or negative (trough) phases or amplitude. Two waves may combine constructively (where the wave functions combine with same sign and resultant wave has enhanced amplitude) or destructively (where the wave functions have opposite sign and resultant wave has a reduced amplitude). Therefore, when two atomic orbitals undergo in phase or similar phase addition, the electron density in

NSOU I CC-CH-07 58 between the nuclei increases and a bonding MO results whose energy is lower than the combining atomic orbitals. On the other hand, when the two wave functions combine out of phase (destructively), the electron density in between the nuclei decreases and an antibonding MO is formed which has a higher energy than the combining atomic orbitals. Thus two atomic orbitals combine to form two molecular orbitals—one bonding and the other antibonding. 3. Inner orbitals will not take best in the formation of molecular orbitals as they have smaller radii and do not overlap well with the orbitals of adjacent atoms. 4. The MO's are filled up with electrons following similar rules for filling up of atomic orbitals: (a) Each MO will have a maximum of two electrons (Pauli's exclusion principle) (b) The lower energy MO will be filled up prior to that of higher energy (Aufbau principle). (c) In case of degenerate MO's the electrons remain unpaired as far as possible (Hund's rule of maximum multiplicity).  $\pi^*(2p_x, 2p_y) z 2p_x, 2p_y, 2$

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$p_x y z \pi(2p_x, 2p_y) y z 2p_x, 2p_y, 2p_x y z \sigma^* 2s^* 2p_x \sigma^* 2p$

$x \sigma^* 2p_x \sigma \sigma 2s \sigma^* 1s \sigma^* 1s$  Fig. 6 MO diagram for homonuclear diatomic molecules of second period (x-axis is the molecular axis)

NSOU I CC-CH-07 59 Number 1,2,3 can precede the symmetry symbol which put the MOS of that particular symmetry in ascending energy order So  $\sigma 1s = 1\sigma_g, \sigma 1s^* = 2\sigma_u, \sigma 2s = 2\sigma_g, \pi 2p = 1\pi_u$  etc. Some of the combinations of atomic orbitals are shown in Fig. 5. Those orbitals which are cylindrically symmetrical about the internuclear axis are called  $\sigma$  orbitals, (analogous to s- orbitals). If the internuclear axis lies in a nodal plane, a  $\pi$  bond results. The bonding and antibonding MO arises due to  $\pm$  sign in LCAO i.e.  $\psi_A \pm \psi_B$ .  $\psi_A + \psi_B$  is a bonding combination and  $\psi_A - \psi_B$  is an antibonding combination. All antibonding orbitals possess an additional nodal plane perpendicular to the internuclear axis and lying between the nuclei. In addition, the molecular orbitals may or may not have a centre of symmetry. The subscript 'g' (gerade or even) and 'u' (ungerade or odd) is applied to MOs for a symmetry symbol when the molecule has a centre of symmetry. If a wave function remain unchanged in appearance under the operation of inversion, then it is of 'g' type, if it changes sign then it is 'u' type.  $\sigma$ -bonding MO is designated as  $\sigma_g, \sigma^*$  as  $\sigma_u^*, \pi$  as  $\pi_u$  and  $\pi^*$  as  $\pi_g^*$ . Using Fig. 6 as a guide, we can proceed to build up electronic configurations of various diatomic molecules following the rules for filling up of electrons in MOs. The molecular electronic configurations of homonuclear diatomic molecules: (i)  $H_2 = \sigma 1s^2$  (2 electrons) (ii)  $He_2 = \sigma 1s^2 \sigma 1s^{*2}$  (4 electrons) (iii)  $Li_2 = KK\sigma 2s^2$  (K stands for K (1s) shell where there is no net bonding). (iv)  $Be_2 = KK\sigma 2s^2 \sigma 2s^{*2}$  (v)  $O_2, F_2, Ne_2$ : These three molecules can be treated with the energy diagram depicted in Fig. 6. ( $B_2, C_2, N_2$  require additional considerations).  $O_2 : KK\sigma 2s^2 \sigma 2s^{*2} \sigma 2p^2 \pi 2p^4 \pi 2p^{*2}$  (16 electrons). But  $\pi 2p^*$  orbital (i.e.  $\pi 2p_y, 2p_z$ ) is doubly degenerate and Hund's rule predicts that the two electrons entering  $\pi^*$  level will occupy two different orbitals, and so the electronic configuration of  $O_2$  can be written as  $O_2 = KK\sigma 2s^2 \sigma 2s^{*2} \sigma 2p^2 \pi 2p^4 \pi 2p_y^* 1 \pi 2p_z^* 1$ . [ $O_2$  molecule therefore should be paramagnetic, contrary to conclusions from VBT].  $F_2 : KK\sigma 2$

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$s 2 \sigma 2s^* 2 \sigma 2p^2 \pi 2p^4 \pi 2p^{*4}$  (18 electrons)  $Ne_2 : KK\sigma 2s^2 \sigma 2s^{*2} \sigma 2p^2 \pi 2p^2 \pi 2p^{*4}$

$\sigma 2p^* 2$  (20 electrons) (vi)  $B_2, C_2, N_2$ : Following Fig. 6,  $B_2$  molecule would be predicted to have a single  $\sigma$  bond (see Bond order) and diamagnetic. Experimentally  $B_2$  molecule is found to have 2 unpaired electrons. On the other hand,  $C_2$  molecule would be predicted to be paramagnetic. Experimentally,  $C_2$  in ground state is diamagnetic. Let us consider Fig. 6 where mixing was allowed only between orbitals on the atoms that were identical in energy. Actually, mixing will take place between all orbitals of proper

NSOU I CC-CH-07 60 symmetry, inhibited only by energy mismatch. So there will be no effective mixing of 1s and 2s orbitals (symmetry matches, but energy difference is high). The energy difference between 2s and 2p orbitals is less and varies with the effective nuclear charge. With large  $Z_{\text{eff}}$  as in fluorine, the energy difference is high and mixing can be neglected. The difference in energy between the 2s and 2p levels increases from about 200 KJ mole<sup>-1</sup> in Lithium atom to about 2500 KJ mol<sup>-1</sup> in fluorine. The lower effective nuclear charge allows the 2s and 2p orbitals to come sufficiently close to mix and is equivalent to hybridisation in VBT. Another way to view this phenomenon is to ignore s-p mixing in the initial construction of MO diagram, but then recognise that MOs of the same symmetry will interact if they are close enough in energy. Thus  $\sigma_g$  (2s) and  $\sigma_g$  (2p) MOs in a molecule as B<sub>2</sub> will mix. As a result, the lower energy orbital [ $\sigma_g$  (2s)] will be stabilised and higher energy [ $\sigma_g$  (2p)] will become less stable. This leads to reversal in the energy ordering of the  $\pi_u$  (2p) and  $\sigma_g$  (2p) MOs [Figure 7] compared to MOs where no mixing occurs [Figure 6]. There will be some interaction between  $\sigma_{u^*}$  (2s) and  $\sigma_{u^*}$  (2p) orbitals. However, these orbitals are not close enough in energy and the interaction will be negligible. So, in Fig. 7, it is not appropriate to designate MOs as  $\sigma_g$  (2s) or  $\sigma_g$  (2p) etc. to identify their origin. So the MOs are labelled according to their symmetry and number them in order from most to the least stable.  $2\pi_g, 2p, 2p^*, 2p_x, \sigma_u, \sigma_g, 5\sigma, 1\pi_u, 4\pi_u, 3\sigma_u, 2\sigma_g, 2\sigma$  Figure 7 : Correct MO energy levels for B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>.

NSOU I CC-CH-07 61 The magnetic properties of B<sub>2</sub> and C<sub>2</sub> provide strong experimental verification that their electronic configurations are based on Figure 7 rather than on Figure 6. B<sub>2</sub> :  $KK3\sigma_g, 2, 4\sigma_u, 2, 1\pi_u, 2$  (unpaired) C<sub>2</sub> :  $KK3\sigma_g, 2, 4\sigma_u, 2, 1\pi_u, 4$  (all paired) For N<sub>2</sub> (14 electrons) either diagram would give a bond order of 3 and diamagnetism. Experimental evidence supporting one configuration over the other for N<sub>2</sub> has been sought in photoelectron spectroscopy. The photoelectron spectrum (the method involves ionising electrons in a molecule or atom by subjecting them to radiation of appropriate energy) of N<sub>2</sub> shows the orbital energies of -15.6 and -16.7 eV for  $5\sigma_g$  and  $1\pi_u$  respectively. So s-p mixing (or MO interaction) occurs in this molecule to make  $5\sigma_g$  higher in energy than  $1\pi_u$ . N<sub>2</sub> :  $KK3\sigma_g, 2, 4\sigma_u, 2, 1\pi_u, 4, 5\sigma_g, 2$ .

2.12 Bond Order When two atomic orbitals combine, the result leads to produce two MOs, one bonding (lower energy) and the other antibonding (higher energy). The extent of bond formed between the two nuclei is measured qualitatively by bond order. Bond order is expressed as : Bond order = (number of electrons present in the bonding orbital - number of electrons present in the antibonding orbital) / 2. Thus for hydrogen molecule Bond order = (2 - 0) / 2 = 1. For He<sub>2</sub> molecule, Bond order = (2 - 2) / 2 = 0. So He molecule does not exist.

2.13 Molecular orbitals of heteronuclear diatomic molecules In developing a MO description for heteronuclear diatomic molecules, we need to take into account the difference in electronegativities of the interacting atoms. Heteronuclear bonds will be formed between atoms with orbitals at different energies. When this occurs, the bonding electrons will be more stable in the presence of the nucleus of the atom having greater electronegativity, i.e. the atom having the lower atomic energy levels. The electron cloud will be distorted toward that nucleus and the bonding MO will resemble that AO (of the more electronegative atom) more than the AO on the less electronegative atom. The antibonding MO has more character of the AO of the less electronegative atom and the molecular system assumes some ionic character depending on the electronegativity difference

NSOU I CC-CH-07 62 of the combining atoms. As per LCAO, overlap of the orbitals of combining atoms are less effective (than homonuclear combination) as there is a difference in energies of the AOs. Heteronuclear diatomic molecules have no centre of inversion so that there are no 'g' or 'u' subscript in the MOs. MO diagrams of some heteronuclear diatomic molecules are shown in Figure 8 (CO), Figure 9 (NO), Figure 10 (HF). CO is isoelectronic with CN - with 10 valence electrons (total 14 electrons). The bond order of CO and CN - is 3. NO molecule is odd electron molecule (11 valence electrons). There is one unpaired electron in  $\pi^*$  orbital which is responsible for paramagnetism. Bond order of NO is 2.5. NO + will not have any unpaired electron in  $\pi^*$  and the bond order will be 3 and therefore more stable than NO.  $\sigma, 2s^*, \sigma, 2s, 2s$  Fig. 8 MO diagram of CO Atomic Orbital of Carbon Molecular Orbital CO Atomic Orbitals of oxygen  $\pi, \pi^*, 2p, \pi^*, 2p, y, z, 2p, 2p, x, y, z, 2p, 2p, x, y, z, 2p, 2p, x, y, z$

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$\pi, \pi^*, 2p, \pi^*, 2p, y, z, 2p, 2p, x, y, z, 2p, 2p, x, y, z$



$\pi$   $\pi$   $2p_y$   $2p_z$   $\sigma$   $2p_x$   $\sigma^*$  A.Os of 'N' MOs of NO A.Os of 'O' Fig. 9 MO energy level diagram of NO  $1s$   $2p$   $\sigma$   $\sigma^*$  non-bonding Fig. 10 MO energy level diagram of HF ..... HF F  $2s$  H Molecular orbitals of triatomic molecules or ions H  $2$  O molecule: The molecule is angular and central oxygen atom is  $sp^3$  hybridised with total valence electrons =  $2 + 6 = 8$ . The MO energy level is drawn with the consideration of overlap of four  $sp^3$  hybrid orbitals of oxygen and two  $1s$  orbitals of hydrogen (Figure 11). Two  $3$  nb  $sp^3$  MOs are occupied by lone pairs and the two  $3^*$   $sp^3$   $\sigma$  antibonding orbitals remain unoccupied.

NSOU I CC-CH-07 64  $3^*$   $sp^3$   $\sigma$   $\uparrow$   $\uparrow$   $2H$  O,  $sp^3$   $3$  nb  $sp^3$   $\sigma$   $3$   $sp^3$   $\sigma$  Fig. 11 MO energy level diagram of H  $2$  O BeH  $2$  : BeH  $2$  molecule is linear. The MOs for this molecule are constructed from  $1s$  orbitals of H atoms (labelled H and H') and  $2s$  and one of the  $2p$  orbitals of Be (the one directed along the H—Be—H bond axis). The remaining two  $2p$  orbitals of Be cannot enter into the bonding because they are perpendicular to the molecular axis and have zero net overlap with H orbitals. Four AOs enter into bonding, so four MOs will be formed. The bonding MOs are formed by linear combination of the atomic orbitals to give maximum overlap. Prior to formation of MOs, we can consider that the orbitals of two H-atoms combine into group orbitals. The group orbitals are formed by simply taking linear combinations of  $1s$  orbitals of H and H'. The group orbitals correspond to  $\psi_H + \psi_{H'}$  and  $\psi_H - \psi_{H'}$ . The first one is appropriate to overlap with Be  $2s$  orbital, which is everywhere positive. The second one will form a bonding MO by overlapping with  $2p$  orbital of Be which has one positive and one negative lobe. The antibonding orbitals will be formed by opposite combinations. — H — Be — H — + +  $\sigma$  g — H — Be — H — + -  $\sigma$  u - - + - +  $\sigma^*$  u — H — Be — H — + -  $\sigma$  g \* — Fig. 12 Bonding and Antibonding MOs in BeH  $2$  molecule

NSOU I CC-CH-07 65  $2\sigma$  u  $3\sigma$  g  $2p$   $1\pi$  n b  $2s$   $1s$  H and H'  $1\sigma$  u  $2\sigma$  g Fig. 13 MO energy levels in BeH  $2$  molecule Figure 13 shows both the bonding MOs are delocalised over all three atoms. This is a general result of the MO treatment of polyatomic molecules. The lowest energy orbital,  $1\sigma$  g is not shown in the figure. It would be formed from the  $1s$  orbital on Be, which interacts very little with H orbitals because of large energy difference. This MO is therefore non-bonding and essentially indistinguishable from Be  $1s$  orbital. 2.14 Electron sea model and Band theory Generally metals have very distinctive properties. Specially, they are good electrical and thermal conductors, are very opaque, have high reflecting power i.e. lustrous, generally hard with high density at the same time ductile and malleable, have high melting and boiling points, have properties of alloy formation (i.e. formation of solid solution), photoelectric emission, thermoionic emission, electropositivity etc. All such properties cannot be explained by normal ionic and covalent bond models. A few theories have been proposed to explain the above properties of the metals. 1. Electron sea model (Also known as Drude-Lorentz theory). Generally metals are high density solid crystals. So the atoms are very closely packed and the outer most orbitals containing the valence electrons are not bound to any particular nucleus. The positive cores of the metal atoms constitute a joint lattice, the valence electrons occupy a combined molecular orbital space above the metal ion core to form a sea of electrons and weakly held to the Kernal or core in metals. Thus the free movement of electrons within the metal from one Kernal to other is explained. They are also called electron gas. As the electrons are free from influence of parent metal atom, they conduct electricity easily and

NSOU I CC-CH-07 66 can be easily excited by visible light to give the lustrous nature. The melting point and boiling point of metals may be explained on the basis of cohesive force operated between two adjacent layers of metal lattice. In case of Na, one valence electron per atom contribute to the sea of electrons while Mg and Al contribute two and three valence electrons respectively per atom to the sea of electrons. Therefore the cohesive force between two adjacent layers of the metals is in the order  $\text{Na} > \text{Mg} > \text{Al}$  and so melting point and boiling point will be of the order  $\text{Al} > \text{Mg} > \text{Na}$ . The order of malleability and ductility is opposite to that of cohesive force, i.e. more the cohesive force, less will be the malleability and ductility. Among the above three metals, Al will have the least malleability and ductility while Na will have the highest and the order will be  $\text{Na} > \text{Mg} > \text{Al}$ . This model cannot explain the decrease in conductivity with rise in temperature and non-conductance of some metals in the solid state.

2. Band theory :Band theory can satisfactorily explain many properties of metals. This is an extension of the MO theory for a large number of atoms. For homo nuclear diatomic molecule, two atomic orbitals combine to produce two new sets of orbitals between the two nuclei. This may be extended to a large number of orbitals. If 'n' number of metal atoms, each containing one outermost orbital to combine with other one, there will be produced 'n' number of MO's. Those large number of MO energy levels will be spaced closely one upon another to form an energy band occupied by the valence electrons. A metal thus consists of energy bands formed by mixing the individual atomic orbitals. ++++++ ++++++ ++++++ 'n' a.o s 'n' mos For example the valence electron of sodium atom remains in 3s orbital. When two sodium atoms combine to form MO, two set of new orbital is formed just like hydrogen atoms. For total 'n' number of atomic orbitals, 'n' number of molecular orbitals will be formed half of which will be bonding and other half antibonding. If Avogadro number of Na atoms is present in the metal lattice (one mole) then Avogadro number (N) MOs will NSOU I CC-CH-07 67 be formed. The 3s AO's of Na atoms have one electron each and so 'N' electrons will fill up  $N / 2$  MOs (2 electrons per MO) i.e. the bonding MOs, and  $N / 2$  MOs will remain empty. Fermi level Equivalent to Half unfilled band (ABMOs) Half filled band (BMOs) Na metal therefore will be a conductor of electricity since the lower half filled band transfers electrons to the upper unoccupied half filled band easily. For alkaline earth metals such as Mg with 3s 2 valence electron configuration, both the band (lower BMO and upper ABMO i.e. the 3s band) will be completely occupied and there is no scope for transfer of electrons from lower to upper band. But Mg is a metal and a good conductor of electricity at room temperature. This is due to the fact that the vacant 3p band overlap with 3s band to form an overlap zone and electrons can move easily from 3s to 3p band. For Na metal, as stated above, lower half of 3s band is filled and the upper half empty. This statement is true at absolute zero (0K). At all real temperatures the Boltzmann distribution together with closely spaced energy levels will ensure that the sharp cut-off shown in the figure is somewhat fuzzy. The top of the filled energy levels is termed the Fermi level. As already stated, electrons can also occupy the Mo's formed by the p orbitals. In the case of Be (like Mg discussed earlier) each atom contain two electron in the valence shell. The 2s band will be complete and it will merge with the empty 2p band. Electrons now move to the vacant band on thermal or electrical excitation. The band theory of solids: The band theory may be extended to other non metallic solids. Conduction of electricity are attributed to readily available electrons in their structure. In solid Neon [Ne(c)] atoms are held by weak van der waals force. There is a top level of filled 2p band, a narrow empty band of 3s. Since the bottom 2p band and top 3s bands are NSOU I CC-CH-07 68 widely separated in the case of Neon, the excitation of electrons from 2p to 3s requires high energy. So Ne(s) is expected to be an insulator. Similarly NaCl crystal will be an insulator at ordinary temperature. Molecular crystals will behave in similar manner. Since weak van der waal force within the molecules give rise to narrow band widely separated from one another.

2.15 Classification of Inorganic solids and their conduction properties according to Band theory The difference in energy  $\Delta E$  between the highest occupied band, i.e. valence band, and lowest vacant band (the conduction band) in a solid (Figure 14) may be determined from the lowest frequency of absorption of uv or visible light by the solid. The elements of carbon family show an interesting trend  $\Delta E$ .  $\Delta E$  Empty conduction band (Small energy gap forbidden zone) Filled valence band Figure 14. Energy band diagram of intrinsic semiconductor  $\Delta E$  (eV) C(diamond) C60 Si Ge Sn (grey) Pb 6 1.7 1.2 0.7 0.08 0.0 Lead and tin (Sn) are typical elements whose electrical conductivity decreases with temperature. The band gaps of Si and Ge are small and can be overcome by thermally excited electrons. As T increases more electrons are excited to cross the gap. Therefore they show increase in electrical conductivity with increase in temperature. They are termed as semiconductors. The behaviour of these elements differ from others whose electrical conductivity decrease with temperature. In intrinsic semiconductors the energy gap between a filled band and the next empty band



NSOU I CC-CH-07 69 is very small. The electrons cannot jump across this gap, so the substance behaves like an insulator at absolute zero (0K). As temperature is raised the thermal energy gained by the electrons becomes sufficient to promote them to the next empty band, so conduction can occur. Pure germanium and grey tin are intrinsic semiconductors. Semiconductor behaviour is seen in certain substances by deliberate addition of impurities. Such semiconductors are called extrinsic semiconductors. They are of two types: 1. n-type semiconductors : When arsenic or antimony (with 5 valence electrons) is added (doped) to germanium (4 valence electrons) produces a n-type semiconductor. The deliberately added impurities place a filled energy band just below the empty band of the metal (Ge for example). Electrons from the impurities can be easily excited to the empty metal band. Here the conductivity results from the flow of electrons and hence it is called a negative or n-type semiconductor (Figure 15). Conduction band (Donor levels) Valence band Figure 15. Conduction by electrons in a donor or n-type semiconductor. 2. p-type semiconductors : When Germanium is doped with gallium or indium (with 3 valence electrons), they place an empty band just above the filled metal band. Passage of electrons from germanium to these empty bands results in a number of vacant sites of the electrons on germanium which becomes positively charged. The vacant sites are called 'positive holes'. Adjacent electrons move to fill these positive holes, thus more positive holes are formed behind them. These seem to be that there is a migration of positive holes. Thus a positive or p-type semiconductor results (Figure 16).

NSOU I CC-CH-07 70 Conduction band (Acceptor levels) Valence band Figure 16. Conduction by holes in an acceptor or p-type semiconductor Combination of n-type and p-type semiconductors produces an n-p junction. Electrons can flow from n to p, and holes from p to n and the current passes more easily in one direction than the other. It can act as a diode. Two n-type silicon separated by a weak p-type silicon produces a n-p-n junction or a transistor. 2.16 Hydrogen bonding Hydrogen forms only monovalent compounds. When hydrogen is linked with highly electronegative elements like X=fluorine, oxygen, nitrogen another special situation arises. The bonded pair between H and X is shifted towards X and charge separation occurs. Thus hydrogen acquires a slight positive charge and the negative end of X gets associated with the  $\delta^+$  hydrogen through a weak bond i.e. hydrogen forms a bridge between two highly electronegative atoms. This is called hydrogen bond, which is  $\delta^+ \delta^- \delta^- \delta^- \delta^- \delta^- \delta^- \dots \dots \dots - \dots \dots - H X H X H X H X + - + - + - \rightarrow \rightarrow \rightarrow$  represented by broken line. It is defined as the attractive force which binds hydrogen of one molecule with electronegative atom of another molecule of the same substance. The strength of hydrogen bond may vary widely. The enthalpy change is small for weak interaction (10-50 KJ mol<sup>-1</sup>) and enthalpy change for strong interactions one 50-100 KJ mol<sup>-1</sup>.

NSOU I CC-CH-07 71 Effect of Hydrogen bonding Molecules of water, ammonia, hydrogen fluoride etc. all are associated through hydrogen bonding. The effect is manifested in the boiling points of the molecules compared to the higher congeners of the group. Boiling points (°C) of some Hydrogen bonded compounds Bonded H<sub>2</sub>O 100 HF 19 C<sub>2</sub>H<sub>5</sub>OH 64.5 H<sub>2</sub>S -60 HCl -85 C<sub>2</sub>H<sub>5</sub>SH 5.8 Hydrogen bonds may be of two types: i) Intermolecular ii) Intramolecular i) Hydrogen bonds between several molecules are intermolecular hydrogen bond as in HF, H<sub>2</sub>O, ammonia. ii) Hydrogen bond formed in the same molecule is called intramolecular hydrogen bond, as in o-nitrophenol, salicylic acid etc. O - H N O → = O O - H C = O = OH In the intra molecular hydrogen bonded compounds, there is no association. Thus the boiling point of these compounds are lower than expected. Hydrogen bond in Biological Systems: Hydrogen bond plays an important role in the biological systems. Protein contains chains of amino acid units arranged in a spiral form i.e. like stretched springs. The N-H group of each amino acid unit and the fourth C=O group following it along the chain forms N-H...O hydrogen bond. Thus the spiral structure becomes stable. Nucleic acids also contain hydrogen bond. Hydrogen bonded water also plays a vital role in the life process.

NSOU I CC-CH-07 72 2.17 Vander Waals forces It is believed that there is no attractive force between the gas molecules. But the force though very weak in nature is responsible for liquifaction and solidification of gases. This force cannot be explained by the idea of ionic or co-valent bonds. The existence of a force in the non polar molecules like H<sub>2</sub>, CH<sub>4</sub>, He, Ne etc. was first recognized by van der Waals. So this type of inter molecular force is termed as van der waals forces. The van der Waals forces are best manifested in the molecular crystals of a variety of substances. In graphite the hexagonal framework in one plane is held by covalent bonds but the layers of planes are held by weak van der Waals force. The layers easily slide over one another. Molybdenum sulphide MoS<sub>2</sub> form similar layer structures and used as a lubricant at high temperatures and called 'Moly slip'. The strength of van der Waals force increases as the size of the unit increases. When other forces like Hydrogen bonding are absent this can be appreciated by the comparison of m.p. or b.p. such as PbH<sub>4</sub> < SnH<sub>4</sub> < GeH<sub>4</sub> < SiH<sub>4</sub> < CH<sub>4</sub> and b.p. of Ne 27.2K, He 4.2K etc. Intermolecular forces can originate from a variety of interactions involved between the molecules, such as :

1. Dipole-dipole interaction: The potential energy of interaction between two dipoles having moments  $\mu_A$  and  $\mu_B$  in head to tail arrangement at a distance  $r$  is given by  $E = -(\mu_A \mu_B / 4\pi\epsilon_0 r^3)$  ( $4\pi\epsilon_0$  = permittivity of the medium) The result of higher power of  $r$  in the denominator is a sharper dependence on intermolecular distance and a smaller energy of interaction at ordinary temperature. The expression is comparable to  $KT$  at room temperature, and a realistic assessment of the interaction should allow for a Boltzmann distribution of orientations as the dipole molecules tumble. Using approximation that  $E$  is less than  $KT$ , the average net energy of interaction is given by,  $\langle E \rangle = -\frac{2}{3} \frac{\mu_A \mu_B}{4\pi\epsilon_0 r^3} \left( \frac{1}{KT} \right)$  [K = Boltzmann const. T = Absolute temperature] The dependence of this potential energy has now become  $\propto 1/r^6$  which reduces the

NSOU I CC-CH-07 73 range of interaction sharply.  $E$  (dipole-dipole) is called Keesom energy which is inversely proportional to temperature. At higher temperature, the kinetic energy of the molecules increases and the molecules are randomly oriented, so that dipole-dipole interaction decreases.

Such interaction occur in liquid state HF, NF<sub>3</sub> etc.

2. Ion-dipole interactions: The potential energy of interaction between an ion of charge number  $Z$  with a dipole of moment  $\mu$  at distance  $r$  :  $E = -Z\mu\epsilon_0 / 4\pi r^2$  Such interaction occurs in solvation and dissociation of ionic compounds in polar solvents.
3. Monopole (Ion) — Induced dipole interaction: Charged ions can polarize neutral molecules to change their electronic environment to induce a dipole moment. The energy of such interaction is  $E = \frac{2}{4} \frac{\alpha_0 (Ze)}{2r} \left( \frac{1}{4} \right) - \frac{\pi}{\epsilon}$  The point charge has induced a dipole and the atom is said to be polarised. The induced dipole moment is proportional to the electrical field produced by the point charge and the proportionality constant is polarisability  $\mu_{induced} = \alpha \cdot r$   $Z$  is the numerical charge of the ions,  $r$  the distance between them.  $\alpha$  is the polarisability of the molecule. A strong permanent dipole moment  $\mu$  may also induce a dipole moment in nearby atoms or molecules and may act as an ion.  $E = \frac{2}{6} \frac{\mu \alpha E}{r} (4\pi\epsilon_0) - =$  This effect, like that between thermally averaged permanent dipoles, varies as  $\propto 1/r^6$ , and therefore, the range is extremely short, and energy of interaction is quite small. The force fall rapidly with the distance, involved in the dissolution of ionic or polar compounds in non

NSOU I CC-CH-07 74 polar solvents. 4. Instantaneous dipole, induced dipole interaction, (or Induced dipole-induced dipole interaction) Rapid continuous changes in the intensities of charge concentration in the electron atmosphere may give rise to instantaneous and fluctuating dipoles. These may induce further dipoles in adjacent molecules. The mean instantaneous dipole  $\mu$  and polarizability  $\alpha$  gives the potential energy relation as :  $E = -\frac{1}{4\pi\epsilon_0} \frac{2\mu\alpha}{r^3}$  Or more conveniently as :  $E = -\frac{3}{2} \frac{\mu^2\alpha}{4\pi\epsilon_0 r^6}$  [I = Ionisation energy of the molecule] The resulting weak short ranged force is called London dispersion force or dispersion force. Usually this force is related to molecular weight but polarizability plays an important role. This is only one of the forces considered that can produce a net attraction between two electrically neutral atoms or nonpolar molecules. It constitutes the entire binding energy in genuinely covalent molecular crystals such as those of the noble gases or elemental halogens. So such crystals should sublime or boil at temperatures at which  $KT$  is comparable to this energy. Ar boils at 87K, Kr at 121K, Xe at 165K, At 85K, Cl at 239K. The interaction is independent of temperature and operate at all temperatures in case of real gas molecules. These London forces are responsible for variation of boiling points of inert gases at stated above. It increases with increasing polarisibility of molecules or atoms. The polarisibility depends on molecular or atomic size which in term is related to molecular weight or atomic weight. Boiling point of hydrides of Group 14 are of the order  $CH_4 < SiH_4 < GeH_4 < SnH_4$ . The intermolecular forces that are responsible for non-ideality in gases are limited to those that involve only dipoles and induced dipoles. There are only three of these, all relatively weak. The dipole-dipole interaction, dipole-induced dipole interaction and the London dispersion energy. All of these have  $1/r^6$  dependence, so that they are lumped together as van der Waals forces.

2.18 Summary 1. Lewis Structure, presentation of electrons in a molecule as dot (.). Two dots form a bond. Octet rule is obeyed in the structure (2 for H & He).

NSOU I CC-CH-07 75 2. Formal Charge, i.e. the hypothetical charge acquired by the atom assuming equal sharing of bonding electrons. Calculation of Formal Charge in molecules & ions. 3. Valence bond theory: Idea of bond formation, through spin pairing application of schrödinger wave equation. 4. Directional properties of covalent bond: Hybridisation and shapes of molecules, VSEPR Theory. 5. Concept of Equivalent and non equivalent hybrid orbitals. 6. Stereochemistry of non rigid molecules, Rotation along a bond. Berry pseudorotation in inorganic molecules. 7. Idea of Resonance and dipole moment of inorganic molecules. 8. VSEPR Theory and Bent's rules distribution of ligands along the axis. 9. Molecular orbital theory : Linear combination of atomic orbitals. Bond order. M.O. diagram of homo nuclear diatomic molecules. Hetero nuclear diatomic and some triatomic molecules.  $\sigma$  and  $\pi$  orbitals, non bonding orbitals. 10. Band theory: Conduction band of aggregate of atomic orbitals in closely spaced orbitals. Electron sea model: All the valence electrons are present over the surface of the metal. 11. Classification of inorganic solids: Conductor, semiconductors and transistors. 12. Hydrogen bonding: The interaction of the type  $X-H \cdots Y$  where X and Y are highly electronegative atoms. H-bond is weaker than the covalent bond. Hydrogen bonding is extremely important for the physical properties and structural orientation of molecules. 13. Van der Waals forces: This type of interaction is observed in closed shell

NSOU I CC-CH-07 76 molecules involved in weak interaction between ions or dipoles, London dispersion interaction etc.

2.19 Self Assessment Questions Unit 2 Chemical Bonding II : Covalent Bond. Sub Unit 1 and 2 (Lewis Structure, Formal charge. Q1. a) What is the importance of Octet rule (doublet for H) in the formation of covalent compounds? b) Write down the Lewis dot structures for the following compounds.  $BF_3$ ,  $H_2O$ ,  $CH_4$ ,  $NH_3$ ,  $H_2SO_4$ ,  $HN_3$ ,  $HNO_2$ ,  $H_3PO_3$  and benzene. c) There are many compounds which do not obey the octet rule: explain with examples what are the defects of Lewis dot structure? Q2. Define formal charge. State with example how the formal charge of an atom in a molecule can be calculated. Q3. What is expanded octet. Q4. Draw the Lewis dot structure of  $IO_2F_2^-$  and calculate the formal charge on iodine atom. Q5. Calculate the formal charge on constituent atoms in  $BF_3$ . Sub Unit 3 : VBT Q1 a) State the basic idea of valence bond theory. Explain with diagram, the theoretical energy curves for hydrogen molecule. b) How does the idea of spin pairing appears in the valence bond approach to the  $H_2$  molecule. c) Explain in the light of valence bond theory, the localized bond formed between the two nuclei and that directional character of atomic orbitals gives rise to directional character of the bond. Sub unit : 4 & 5 : Directional properties of covalent. & 6 Equivalent and Non-equivalent hybridization. Q1. State VSEPR theory to predict the shapes of covalent molecules.

NSOU I CC-CH-07 77 Q2. Explain why the repulsion of lonepair-lonepair is greater than that of lonepair- bondpair and bondpair-bondpair. Q3. a) Predict the structure of  $\text{ClF}_3$  according to VSEPR theory. b) What are stereochemically non rigid molecules? Q4. i)  $\text{XeF}_2$  is linear—explain from the VSEPR theory. ii) Describe the molecule geometry of  $\text{XeO}_3\text{F}_2$  in light of VSEPR theory. Q5 Explain : a) In  $\text{NH}_3$  HNH bond angle is  $107.3^\circ$  In  $\text{PH}_3$  HPH bond angle is  $93.3^\circ$  b) In water  $\angle\text{HOH} = 104^\circ$  & in  $\text{H}_2\text{S}$   $\angle\text{HSH} = 92.2^\circ$ . Q6. Establish the idea of hybridization in light of VSEPR Theory. What are equivalent and non-equivalent hybrid orbitals, cite examples. Q7. Explain Berry pseudo rotation with suitable example and mechanism. Submit 7 : Resonance, Dipole moments Q1. State the condition that the different resonating structures should obey. Q2. i) Draw all the canonical forms of  $\text{O}_3$ ,  $\text{N}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CO}$ ,  $\text{CO}_3^{2-}$  and state which one is of lowest energy for each case. ii)  $\text{N}_3^-$  is more resonance stabilized than  $\text{HN}_3$  : Explain Q3. Which of the following molecules are expected to have permanent electrical dipole moment?  $\text{SO}_2$ ,  $\text{SF}_2$ ,  $\text{SF}_4$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{SiF}_4$ ,  $\text{BCl}_3$ ,  $\text{N}_2\text{F}_4$ ,  $\text{PF}_5$ ,  $\text{BrF}_5$ ,  $\text{XeF}_4$ ,  $\text{O}_2$  and  $\text{O}_3$ . Q4. The dipole moment of water is  $6.17 \times 10^{-30}$  Cm. The HOH angle is  $104^\circ$  and O–H distance is 96 pm. Calculate the percent ionic character and bond moment of O – H bond. Q5. The dipole moment of  $\text{CH}_3\text{F}$  and  $\text{CHF}_3$  are comparable—Explain. Q6. Dipole moment of CO molecule is less than expected from the electronegativity difference—explain. Sub unit 8 : (VSEPR Theory and Bent's rules) Q1. In light of VSEPR Theory describe the equivalent and non-equivalent hybrid orbitals.

NSOU I CC-CH-07 78 Q2. State Bent's rules and explain with examples. Q3. The P-F bond lengths in  $\text{PF}_5$  are as follows—axial P – F = 157.7 pm. equatorial P – F = 153.5 pm. — Explain. Q4. In  $\text{CH}_2\text{F}_2$  the HCH angle is  $111.9^\circ$  where as FCF angle is  $108.3^\circ$ —Explain. Q5. Draw the structures of the following molecules according to VSEPR Theory  $\text{SF}_4$ ,  $\text{PCl}_4^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{IF}_5$ ,  $\text{IF}_7$ ,  $\text{ClF}_3$ ,  $\text{IF}_3$ . Sub unit 9 : M.O. Theory Q1. a) What are bonding, anti-bonding and non-bonding molecular orbitals? b) Define bond order. Show that  $\text{He}_2$  molecule does not exist. c) State and explain with reasons the expected change in the bond orders and bond distances in the following isoelectronic species.  $\text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \rightarrow \text{N}_2^+$  d) Draw the MO energy level diagram for HF, CO, NO,  $\text{NO}^+$ ,  $\text{CN}^-$ ,  $\text{H}_2\text{O}$  and  $\text{BeH}_2$ . e) Predict the magnetic properties (paramagnetic or diamagnetic) of  $\text{B}_2$  and  $\text{C}_2$  molecules from M.O. energy level diagram. f) Construct the MO energy level diagram for  $\text{H}_2\text{O}$  molecule and hence predict the nature of bonds formed. Sub unit 10 and 11 : (Band Theory) Q1. Write short accounts on Electron sea model and Band Theory for metals. Q2. What is Fermi Level? What is n-p-n junction? Q3. Define semiconductors. What is Doping? What are n-type and p-type semiconductors? Q4. The solid alkali metals are slightly paramagnetic—explain in the light of band theory. Q5. State and explain the behaviours of metals and semiconductors in respect of their conduction properties when temperature increases.

NSOU I CC-CH-07 79 Sub unit 12 and 13 : (Hydrogen Bonding, Van der Waals forces) Q1. Define hydrogen bonding. Q2. State the effect of hydrogen bonding on the physical properties of compounds, (M.P., B.P., Vaporisation etc.) Q3. What are inter molecular and intra molecular hydrogen bonding? Explain with examples. Q4. State the effect of hydrogen bonding in the biological systems. Q5. Define Van der Waals forces with examples. Q6. What are— a) Dipole-dipole interaction? b) Ion-dipole interaction? c) Ion-induced dipole interaction? d) Instantaneous dipole-induced dipole interaction? What is London force? 2.20 Further Reading 1. General and Inorganic Chemistry, Vol. I and Vol. II, R. P. Sarkar, Books and Allied (P) Ltd. 2. Chemistry of Elements, Greenwood and Earnshaw, Maxwell and MacMillan. 3. Basic Inorganic Chemistry, Cotton, Wilkinson, Gaus, 3rd Ed., Wiley. 4. Inorganic Chemistry, Principle of Structure and Reactivity, Huheey, Keiter and Keiter. 5. Inorganic Chemistry, Miessler and Tarr, Pearson Education. 6. Essential Trend in Inorganic Chemistry, D.M.P. Mingos, Oxford (Indian Ed.) 7. Fundamental Concepts of Inorganic Chemistry, A. K. Das, and M. Das, Volume 4, 1st Ed. 2016. 8. Importance of Anti Bonding Orbital, Jaffe and Orchin, Oxford and IBH Publishing Co. 9. Inorganic Chemistry, G. Wulfsberg, Viva 10. Concepts and Models of Inorganic Chemistry, Douglas, McDaniel, Alexander. Wiley, Students Edition.

NSOU I CC-CH-07 80 Unit 3 □□□□□ Coordination Chemistry-1 3.0 Objectives 3.1 Introduction 3.2 Double Salts Complex Salts 3.3 Werner's theory 3.4 EAN rule 3.5 Classification of ligands and their binding modes 3.6 IUPAC Nomenclature of coordination compounds 3.7 Overall and stepwise stability constants 3.8 Chelates 3.9 Stereochemistry and isomerism of Complexes 3.10 Summary 3.11 Self Assessment Questions 3.12 Further Reading 3.0 Objectives After reading this unit you can be able to know \* definition of double salt and complex salt. \* Details of Werner's theory \* EAN-rule \* Definition of ligands and their classification \* IUPAC nomenclature of coordination compounds \* Concept on stereochemistry and isomerism of complexes. 3.1 Introduction Coordination chemistry is the study of compounds that have a central atom generally metallic surrounded by molecules or anions known as ligands. The ligands are attached to the central atom by dative bonds. Known as coordinate bonds, in which both the electrons in the bond are supplied by the same atom on the ligand. 80

NSOU I CC-CH-07 81 In Coordination chemistry, a ligand is an ion a molecule that binds to a central atom to form a coordination complex. The bonding with the metal generally involves formal donation of one or more of the ligands electron pairs often through Lewis bases.

3.2 Double salts complex salts Double salts: They usually contain two simple salts in equimolar proportions. They exist in the solid state. In aqueous solutions, they dissociate completely into the corresponding ions of the individual components and give the test of all their constituent ions. They don't contain any coordinate bonds since they are ionic in nature. They exhibit properties similar to that of the constituent ions. The metal ions present in double salts show their normal valency. Example:

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KCl MgCl<sub>2</sub> · 6H<sub>2</sub>O, K<sub>2</sub>SO<sub>4</sub> Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 24H<sub>2</sub>O, FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O

etc. Complex salts: The properties of different salts present in a complex salt may or may not be same. The complex salts can exist both in solid state as well as in aqueous solution. Complexes may or may not be ionic but the complex part will always contain coordinate bonds. They exhibit two types of valencies - primary and secondary. A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and complex anion. The term complex compound is used synonymously with the term coordination compound. Example: K<sub>4</sub>[Fe(CN)<sub>6</sub>], [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>6</sub>][Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] etc.

3.3 Werner's theory Alfred Werner in 1823, formulated his theory to describe the structure and formation of complex compounds or coordination compounds. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol CoCl<sub>3</sub> · 6NH<sub>3</sub> (Yellow) → 3 mol AgCl  
 1 mol CoCl<sub>3</sub> · 5NH<sub>3</sub> (Purple) → 2 mol AgCl  
 1 mol CoCl<sub>3</sub> · 4NH<sub>3</sub> (Green) → 1 mol AgCl  
 1 mol CoCl<sub>3</sub> · 4NH<sub>3</sub> (Violet) → 1 mol AgCl

On the basis of the observations Werner postulated the following points. Postulates of Werner's Theory:

1. The central metal ions or the metal atoms in coordination compounds show two types of valency. They are the primary and secondary valency.
2. The primary valency relates to the oxidation state and the secondary valency NSOU I CC-CH-07 82 relates to the coordination number. Primary valency is also called principal, ionisable or ionic valency, and secondary valency is non-ionic or non-ionisable.
3. The number of secondary valences is fixed for every metal atom or ion. It means that the coordination number is fixed.
4. The metal atom or ion works towards satisfying both its primary and secondary valencies. A negative ion satisfies the primary valency. On the other hand, negative ions or neutral molecules satisfy secondary valencies. The ions or molecules which satisfy secondary valency or coordination number are directly attached to metal atom or ion. An anion can

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show a dual behaviour i.e. it may satisfy both primary and secondary valencies. 5.

The secondary valencies point towards a fixed position in space. This is the reason behind the definite geometry of the coordinate compounds. For example, let us consider the case of a metal ion having six secondary valencies. They arrange octahedrally around the central metal ion or atom. If the metal ion has four secondary valencies, they arrange in either tetrahedral or square planar arrangement around the central metal ion or atom. Therefore, we see that the secondary valency determines the stereochemistry of the complex ion. On the other hand, the primary valency is non-directional. Examples Based on Postulates of Werner's Theory Werner's theory is responsible for the formation of structures of various cobalt amines. We will look at its explanation now. Cobalt has a primary valency (oxidation state) of three and exhibits secondary valency (coordination number) of 6. Werner represented the secondary valencies by thick lines (solid lines) and the primary valency by dashed lines (broken lines). 1)  $\text{CoCl}_3 \cdot 6\text{NH}_3$  Complex: In this compound, the coordination number of cobalt (III) is 6 and  $\text{NH}_3$  molecules satisfy all the 6 secondary valencies by binding to the metal centre by coordinate covalent bonds to form the inner coordination sphere Chloride ions satisfy the 3 primary valencies. These are non-directional in character. These chloride ions instantaneously precipitate on the addition of silver nitrate. The total number of ions, in this case, is 4, three chloride ions and one complex ion. The coordination sphere is shown within square bracket [ ] and moieties bound by primary valence outside the bracket in formulation of the compound, which is called outer coordination sphere. 2)  $\text{CoCl}_3 \cdot 5\text{NH}_3$  complex: In this compound- cobalt has coordination number of 6. However, we see that the number of  $\text{NH}_3$  molecules decreases to 5. The chloride ion occupies the remaining one position of coordination. This chloride ion exhibits the dual behaviour as it satisfies the primary as well as the secondary valency. Werner showed its NSOU I CC-CH-07 83 attachment with the central metal ion by a combined dashed—solid line. 3)  $\text{CoCl}_3 \cdot 4\text{NH}_3$  complex: In this compound, two chloride ions exhibit the dual behaviour of satisfying both primary and secondary valencies. This compound gives a precipitate with silver nitrate corresponding to only one chloride ion and the total number of ions in this case, is 2. Hence, we can formulate it as  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ . (See Figure 1) Note : The coordination number of Co (III) (i.e. secondary valency) is always 6.  $\text{Co NH}_3 \text{ NH}_3 \text{ NH}_3 \text{ NH}_3$

40%

MATCHING BLOCK 19/128

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$\text{H}_3\text{N H}_3\text{N Cl Cl Cl CoCl}_3 \cdot 6\text{NH}_3$  or  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   $3\text{Co NH}_3 \text{ NH}_3 \text{ NH}_3 \text{ H}_3\text{N H}_3\text{N Cl Cl Cl Co Cl NH}_3 \text{ NH}_3 \text{ H}_3\text{N H}_3\text{N CoCl}_3 \cdot 4\text{NH}_3$  or  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   $2\text{CoCl}_3 \cdot 5\text{NH}_3$  or  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$

$\text{Cl}_2 \text{ 3 3 5 2+}$  Fig. 1 Designations and formulations of Co (III) ammines on the basis of Werner's theory. 3.4 EAN Rule With the advent of electronic theory of valency, it was considered necessary to make some modifications of Werner's theory. Sidgwick adopted the Lewis concept of two- electron covalent bond between two atoms in a molecule and introduced the new concept of coordinate bond (also called dative bond). The effective atomic number (EAN) of an atom is the number of protons that an electron in the element effectively 'sees' due to screening by inner-shell electrons. It is a measure of the electrostatic interaction between the negatively charged electrons and positively charged protons in the atom. One can view the electrons in an atom as being 'stacked' by energy outside the nucleus with the lowest energy electrons (such as the 1s and 2s electrons) occupying the space closest to the nucleus, and electrons of higher energy are located further from the nucleus. The binding energy of an electron, or the energy needed to remove the electron from the atom, is a function of the electrostatic interaction between the negatively charged electrons and the positively charged nucleus. In iron, atomic number 26, for instance, the nucleus contains 26 protons. The electrons that are closest to the nucleus will 'see' nearly all of them. However, electrons further away are screened from the nucleus by other electrons in between and, feel less electrostatic interaction as a result. The 1s electron of iron (the closest one to the nucleus) sees an effective atomic number (number of protons) of 25. The reason why it is not 26 is because some of the electrons



NSOU I CC-CH-07 84 in the atom end up repelling the others, giving a net lower electrostatic interaction with the nucleus. One way of envisioning this effect is to imagine the 1s electron sitting on one side of the 26 protons in the nucleus, with another electron sitting on the other side; each electron will feel less than the attractive force of 26 protons because the other electron contributes a repelling force. The 4s electrons in iron, which are furthest from the nucleus, feel an effective atomic number of only 5.43 because of the 25 electrons in between it and the nucleus screening the charge. According to Sidgwick's concept, the ligands attached with the central metal ion or atom have atoms which have at least one unshared electron pair and donate this pair to the central metal for attachment. The bond thus established between the ligand and the metal is a coordinate or dative bond. This bond is not different from a covalent bond except that the ligand (donor) has donated the electron pair to the metal ion or atom (acceptor) and represented as  $M \leftarrow L$ . Thus the structure of  $[Co(NH_3)_6]^{3+}$  can be shown as Figure 2.  $Co^{+3}$  the metal ion) [Presently the bonds within the coordination sphere is not designated by an arrow to denote coordinate linkage, but by simple solid lines as given for covalent bonds.] Effective atomic number (EAN) is number that represents the total number of electrons surrounding the nucleus of a metal atom or ion in a metal complex. It is composed of the metal atom's (or ion's) electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. Thus the effective atomic number of the cobalt ion in the complex  $[Co(NH_3)_6]^{3+}$  is 36, the sum of the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair ( $2 \times 6 = 12$ ). EAN 36 of Co (III) is equal to the atomic number of Kr. Generally EAN of central metal will be

**69% MATCHING BLOCK 20/128**

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equal to the number of electrons in the nearest noble gas. If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.

$EAN = [(atomic\ number\ of\ central\ metal\ atom) - (the\ oxidation\ state\ of\ the\ metal) + (the\ number\ of\ electrons\ gained\ by\ the\ metal\ from\ the\ ligands\ through\ co-ordination)]$  or,

NSOU I CC-CH-07 85  $EAN = [Z\ metal - (oxidation\ state\ of\ the\ metal) + 2(coordination\ number\ of\ the\ metal)]$ . Example: 1.  $[Co(NH_3)_6]^{3+} \rightarrow EAN = [27 - 3 + 2(6)] = 36$  2.  $[MnCl_4]^{2-} \rightarrow EAN = [25 - 3 + 8] = 31$  3.  $[Fe(CN)_6]^{4-} \rightarrow EAN = [26 - 2 + 12] = 36$  4.  $[CoF_6]^{3-} \rightarrow EAN = [27 - 3 + 12] = 36$  5.  $[Cr(H_2O)_6]^{3+} \rightarrow EAN = [24 - 3 + 12] = 33$  6.  $Ni(CO)_4 \rightarrow EAN = [28 - 0 + 8] = 36$  7.  $[Cu(NH_3)_4]^{2+} \rightarrow EAN = [29 - 2 + 8] = 35$  8.  $[Pt(NH_3)_4]^{2+} \rightarrow EAN = [78 - 2 + 8] = 84$  9.  $[PtCl_4]^{2-} \rightarrow EAN = [78 - 2 + 8] = 84$  10.  $[PtCl_6]^{2-} \rightarrow EAN = [78 - 4 + 12] = 86$  Exceptions: As seen from the examples not all complexes follow EAN rule. Complexes of Ni(II), Co(II), Ag(I) etc., which have more than one possible coordination number, depending on the nature of the ligand, generally do not follow the rule. 3.5 Classification of ligands and their binding modes: Coordination compounds generally consist of

**100% MATCHING BLOCK 35/128**

**SA** Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)

a central metal atom or ion bonded to a fixed number of ions or molecules

called ligands. The term 'dentate' means 'toothed', i.e. the number of position taken up by the ligand around the central metal atom or ion is its denticity.

Ligands : These are the ions or molecules bound to the

**72% MATCHING BLOCK 21/128**

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central atom/ion in the coordination entity (sphere). They may be simple ions such as  $Cl^-$ , small molecules such as  $H_2O$  or  $NH_3$ , larger molecules such as  $H_2NCH_2CH_2NH_2$  or  $N(CH_2CH_2NH_2)$ ; or even macromolecules, such as proteins. Unidentate or monodentate ligands : When a ligand is bound to a metal ion

or atom

**100% MATCHING BLOCK 22/128**

**W**

through a single donor atom, as with  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the ligand is said to be unidentate.

They coordinate to the central metal atom or ion at one site only. Bidentate ligands :

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When a ligand can bind through two donor atoms as in  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethane- 1,2-diamine) or  $\text{C}_2\text{O}_4^{2-}$  (oxalate), the ligands are said to be bidentate

ligands. They take up two sites around the central metal.  
NSOU | CC-CH-07 86 Polydentate or multidentate ligands :

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When several donor atoms are present in a single ligand as in  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ , the ligand is said to be polydentate.

Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ ) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. Chelating ligands : When

**97% MATCHING BLOCK 25/128**

**W**

a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion

or atom simultaneously and thus produce one or more rings around the central atom or ion, are called chelate (pronounced Kelate) or chelating ligands (from Greek 'crab's claw'). The number of such ligating groups (donor atoms) is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Porphyrins are complexes containing a form of the porphin molecule shown in Figure 3. Important biomolecules like heme and chlorophyll are porphyrins. Chelating ligands form more stable complexes than ordinary ligands. This is also called the chelate effect. The stability of chelate depends upon the number of atoms in the ring.  $\text{H}|\text{N}|\text{N}|\text{H}|\text{N}|\text{N}$  Figure 3 Generally, chelating ligands which do not contain double bonds form stable complexes with five membered rings. On the other hand, the chelating ligands which contain double bonds form stable complexes with six membered rings. Chelating ligands with smaller groups form stable complexes, than with larger and bulky groups. This is because of steric reasons. Ambidentate ligands : Ligands which can ligate through two or more different atoms, but in forming complexes only one donor atom is utilised for attachment at a given time

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are called ambidentate ligands. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate either through nitrogen or

through

**97% MATCHING BLOCK 27/128**

**W**

oxygen to a central metal atom/ion. Similarly.  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom.

Other examples are  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{R}_2\text{SO}$ ,  $\text{SeCN}^-$  etc.



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Coordination number : The coordination number of a metal ion or atom in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded

by  $\sigma$  bonds. For example, in the complex ions,  $[\text{PtCl}_6]^{2-}$  and  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ , the coordination number of Pt (IV) and Ni (II) are 6 and 4 respectively. 3.6 IUPAC nomenclature of coordination compounds: Rules for IUPAC nomenclature of coordination compounds: In a coordination entity 1.

**65% MATCHING BLOCK 29/128**

**W**

The cation is named first in both positively and negatively charged coordination entities. 2. The ligands are named in an alphabetical order before the name of the central atom/ion. The prefixes di, tri, etc. are

not to be considered while determining this alphabetical order. 3.

**91% MATCHING BLOCK 30/128**

**W**

Names of the anionic ligands end in  $-o$ , those of neutral ligands are the same except  $\text{H}_2\text{O}$

which is named aqua,  $\text{NH}_3$  which is named aminine,  $\text{CO}$  which is named carbonyl and  $\text{NO}$  which is named nitrosyl. These are placed within brackets ( $$ ). Positively charged ligands have suffix  $-ium$ , e.g.  $\text{NH}_2\text{NH}_3^+$  is hydrazinium and  $\text{NO}^+$  is nitrosilium. 4.

**91% MATCHING BLOCK 31/128**

**W**

Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. 5. When the names of the ligands include a numerical prefix,

then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parenthesis. 6.

**83% MATCHING BLOCK 32/128**

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Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis ( $$ ). 7. If the complex ion is a cation, the metal is named same as the element. 8.

**100% MATCHING BLOCK 33/128**

**W**

If the complex ion is an anion, the name of the metal ends with the suffix.  $-ate$ . 9. For

some metals, the Latin names are used in the complex anions, e.g.. ferrate for Fe. 10.

**100% MATCHING BLOCK 34/128**

**W**

The neutral complex molecule is named similar to that of the complex cation. 11.

Complexes with two or more metal atoms/ions in the coordination sphere are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphens and adding prefix  $\mu$  before its name.  $\mu$  should be repeated before the name of each bridging group. Two or more bridging groups of the same kind are indicated by di- $\mu$ -, tri- $\mu$ -, etc.

NSOU | CC-CH-07 88 12. A gap should be left between naming of moieties outside and inside the coordination sphere e.g.  $K_2 [CoCl_4]$  is potassium tetrachlorocobaltate (II) or  $[Co(NH_3)_6]Cl_3$  is hexaamminecobalt (III) chloride. No gap is given in naming the moieties within the coordination sphere. Names of Some Common Ligands Anionic Ligands Names Neutral Ligands Names Br – bromo  $NH_3$  ammine F – fluoro  $H_2O$  aqua  $O^{2-}$  oxo NO Nitrosyl OH – hydroxo CO Carbonyl CN – cyano  $O_2$  dioxygen  $C_2O_4^{2-}$  oxalato  $N_2$  dinitrogen  $CO_3^{2-}$  carbonato  $C_5H_5N$  pyridine  $CH_3COO^-$  – acetato  $H_2NCH_2CH_2NH_2$  ethylenediamine. Name of Metals in Anionic Complexes Name of Name in an Name of Name in an Metal Anionic Complex Metal Anionic Complex Iron Ferrate Silver Argenate Copper Cuprate Gold Aurate Lead Plumbate Tin Stannate Examples: Sl. No. Coordination Entity IUPAC Name 1.  $[Cr(NH_3)_3(H_2O)_3]Cl_3$  triamminetriaquachromium(III) chloride 2.  $[Pt(NH_3)_5Cl]Br_3$  pentaamminechloroplatinum(V) bromide 3.  $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$  dichlorobis(ethylenediamine)platinum(IV) chloride 4. [

**100%**

**MATCHING BLOCK 41/128**

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Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)

$Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$  tris(ethylenediamine)cobalt(III) sulfate 5.

$K_4[Fe(CN)_6]$  potassium hexacyanoferrate(II)

NSOU | CC-CH-07 89 6.  $Na_2[NiCl_4]$  sodium tetrachloronickelate(II) 7.  $Pt(NH_3)_2Cl_4$  diamminetetrachloroplatinum(IV) 8.  $Fe(CO)_5$  pentacarbonyliron(0) 9.  $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$  ammonium diaquabis (oxalato) nickelate(II) 10.  $[Ag(NH_3)_2][Ag(CN)_2]$  diamminesilver(I) dicyanoargentate(I) 11.  $[Fe(NH_3)_6](NO_3)_3$  hexaammineiron(III) nitrate 12.  $(NH_4)_2[CuCl_4]$  ammonium tetrachlorocuprate(II) 13.  $Na_3[FeCl(CN)_5]$  sodium monochloropentacyanoferrate(III) 14.  $K_3[CoF_6]$  potassium hexafluorocobaltate(III) 15.  $[CoBr(NH_3)_5]SO_4$  pentaamminebromocobalt (III) sulfate 16.  $[Fe(NH_3)_6][Cr(CN)_6]$  hexaammineiron(III) hexacyanochromate (III) 17.  $[Co(SO_4)(NH_3)_5]_4$  pentaamminesulfatocobalt(III) ion 18.  $[Fe(OH)(H_2O)_5]^{2+}$  pentaqua hydroxoiron(III) ion 19.  $[(NH_3)_5CrCrOH(NH_3)_5]Cl_5$   $\mu$ -hydroxo-bis (pentaamminechromium (III) chloride or, pentamminechromium (III)- $\mu$ -hydroxo- chromium (III) chloride. 20.  $[(NH_3)_4CoCo(NH_3)_4]Cl_3$   $\mu$ -amido- $\mu$ -hydroxo-octaammine dicobalt (iii) chloride. 3.7 Overall and stepwise stability constants:

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The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium.

The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:  $M + 4L \rightleftharpoons ML_4$  (M = metal ion/atom, L = monodentate ligand, 4 = coordination number) then,

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the larger the stability constant, the higher the proportion of  $ML_4$  that exists in solution. Free metal ions

rarely exist in the solution so that

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**MATCHING BLOCK 38/128**

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M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L,

and be successively replaced

NSOU I CC-CH-07 90 by them. For simplicity, we generally ignore these solvent molecules and charge of the complexes

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and write four stability constants as follows:  $1 [M] M L ML; K [M][L] + = f 2 2 2 [M ] ML L ML ; K [ML][L] + = f 3 2 3 3 2 [ML ] ML L ML ; K [ML ][L] + = f 4 3 4 4 3 [M L ] ML L ML ; K [ML ][L] + = f$  where  $K 1 , K 2 , etc.,$  are

referred to as stepwise stability constants.  $[ ]$  represents concentration of the species. Alternatively, we can express

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the stability constants as :  $1 [M] M L ML \beta [M][L] + = f 2 2 2 2 [M L ] M 2L ML \beta [M][L] + = f 3 3 3 3 [M L ] M 3L ML \beta [M][L] + = f 4 4 4 4 [M L ] M 4L ML \beta [M][L] + = f$  where  $\beta 1 , \beta 2$  etc. are called overall stability constants.

The stepwise and overall stability constant are therefore related as follows:  $\beta 4 = K 1 \times K 2 \times K 3 \times K 4$  or more generally,  $\beta n = K 1 \times K 2 \times K 3 \times K 4 \dots K n$  If we take as an example the steps involved in the formation of the cuprammonium ion. we have the following:  $Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}; K 1 2 3 2 3 [Cu(NH_3)] [Cu ][NH ] + + =$   
 $NSOU I CC-CH-07 91 Cu(NH_3)^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}; K 2 2 3 2 2 3 3 [Cu(NH_3)] [Cu(NH_3)] [NH ] + + = [Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+}; K 3 2 3 3 2 3 3 [Cu(NH_3)] [Cu(NH_3)] [NH ] + + = [Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}; K 4 2 3 4 2 3 3 3 [Cu(NH_3)] [Cu(NH_3)] [NH ] + + =$  where  $K 1 , K 2 \dots$  are the stepwise stability constants the overall stability constant is given by  $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}; \beta 4 2 3 4 2 4 3 [Cu(NH_3)] [Cu ][NH ] + + = 3.8$   
 Chelates: When bidentate or polydentate (multidentate) ligands form complexes through chelation, the stability constant increases. This is why, even for similar binding sites, chelating ligands form more stable complexes than non-chelating ligands (i.e. monodentate ligands).

**97% MATCHING BLOCK 42/128**

**SA**

Module-1 Chemistry final (1).docx (D81135194)

Many essential biological chemicals are chelates. Chelates play important roles in oxygen transport and in photosynthesis. Furthermore, many biological catalysts (enzymes) are chelates. In addition to their significance in living organisms, chelates are also economically important, both as products in themselves and as agents in the production of other chemicals. A chelate is a chemical compound composed of a metal ion

or atom

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Module-1 Chemistry final (1).docx (D81135194)

and a chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand. An example of a simple chelating agent is ethylenediamine (

$NH_2CH_2CH_2NH_2$ ). Chelate rings are most stable when they have 5 or 6 members including the metal ion. The enhanced stability of chelate compounds is known as the chelate effect and mainly arises due to favourable entropy effect.

**63% MATCHING BLOCK 44/128**

**SA** Module-1 Chemistry final (1).docx (D81135194)

A single molecule of ethylenediamine can form two bonds to a transition metal ion such as nickel (II), Ni<sup>2+</sup>. The bonds form between the metal ion and the nitrogen atoms of ethylenediamine. The nickel(II) ion can form six such bonds (coordination number 6), so a maximum of three ethylenediamine molecules can be attached to one Ni<sup>2+</sup> ion. NSOU  
CC-NH2 CH2-NH2 OH Ni(OH)2 || OH2 OH2 2+ CH-NH2 CH-NH2 OH Ni(OH)2 || NH2 2+ NH CH2 2- CH-NH2 CH-

NH2 NH Ni NH2 || NH2 2+ NH2 CH2 CH2 CH2 CH2 CH2 chelate with one ethylenediamine ligand chelate with two ethylenediamine ligands chelate with three ethylenediamine ligands In the two structures on the left, the bonding capacity of the Ni<sup>2+</sup> ion (6) is completed by water molecules. Each water molecule forms only one bond to Ni<sup>2+</sup>, so water is not a chelating agent. Because the chelating agent is attached to the metal ion by several bonds, chelates tend to be more stable than complexes formed with monodentate ligands such as water. C=N HN-C C-NH N-C

**51% MATCHING BLOCK 45/128**

**SA** Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)

C-H H-C = H-C C-C = H-C C = H-C = H-C = H-C = H-C H-C = C-H = C-C H-C

porphine C=N N-C C-N N-C  
C-C-

**50% MATCHING BLOCK 47/128**

**SA** MCHE-12.pdf (D112800504)

H-H -C = H-C C-C = H-C 2-C C-C = H-C = CH 2-C = Ch 3-C = CH 3-C CH = CH 2-C = C

H-C C CH 3-C CH=CH 2 heme Fe CH2 COOH HOOCC 2 Porphine is a chelating agent similar to ethylenediamine in that it forms bonds to a metal ion through nitrogen atoms. Each of the four nitrogen atoms in the center of the molecule can form a bond to a metal ion. Porphine is the simplest of a group of chelating agents called porphyrins. Porphyrins have a structure derived from porphine by replacing some of the outside hydrogen atoms with other groups of atoms. One important porphyrin chelate is heme, the central component of hemoglobin, which carries oxygen through the blood from the lungs to the tissues. Heme contains a porphyrin chelating agent bonded to an iron(II) ion. Iron, like nickel, can form six bonds. Four of these bonds tie it to the porphyrin. One of iron's two remaining bonds holds an oxygen molecule as it is transported through the blood. Chlorophyll is another porphyrin chelate. In chlorophyll, the metal at the center of the chelate is a magnesium ion. Chlorophyll, which is responsible for the green color of plant leaves, absorbs the light energy that is converted to chemical energy in the process of photosynthesis. Another biologically significant chelate is vitamin B-12. It is the only vitamin that contains a metal, NSOU  
CC-CH-07 93 a cobalt(II) ion bonded to a porphyrin-like chelating agent. As far as is known, it is required in the diet of all higher animals. It is not synthesized by either higher plants or animals, but only by certain bacteria and molds. These are the sources of the B-12 found in animal products. Because vitamin B-12 is not found in higher plants, vegetarians must take care to include in their diets foods or supplements that contain the vitamin. A chelating agent of particular economic significance is ethylenediaminetetraacetic acid (EDTA). C-CH -N-

**75% MATCHING BLOCK 46/128**

**W**

CH -CH -N-CH -C 2 2 2 2 : : O HO = : CH 2 C O HO : = CH 2 C O

OH : = OH O : = ethylenediaminetetraacetic acid (EDTA)

93%

**MATCHING BLOCK 51/128**

SA

Module-1 Chemistry final (1).docx (D81135194)

EDTA is a versatile chelating agent. It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. EDTA is frequently used in soaps and detergents, because it forms complexes with calcium and magnesium ions. These ions are in hard water and interfere with the cleaning action of soaps and detergents. EDTA binds to them, sequestering them and preventing their interference. In the calcium complex,  $[\text{Ca}(\text{EDTA})]^{2-}$ , EDTA is a tetradentate ligand, and chelation involves the two nitrogen atoms and two oxygen atoms in separate carboxyl ( $-\text{COO}^-$ ) groups. EDTA is also used extensively as a stabilizing agent in the food industry.

Food spoilage is often promoted by naturally-occurring enzymes that contain transition-metal ions. These enzymes catalyze the chemical reactions that occur during spoilage. EDTA deactivates these enzymes by removing the metal ions from them and forming stable chelates with them. It promotes color retention in dried bananas, beans, chick peas, canned clams, pecan pie filling, frozen potatoes, and canned shrimp. It improves flavor retention in canned carbonated beverages, salad dressings, mayonnaise, margarine, and sauces. It inhibits rancidity in salad dressings, mayonnaise, sauces, and sandwich spreads. EDTA salts are used in foods at levels ranging from 33 to 800 ppm. In other applications, EDTA dissolves the  $\text{CaCO}_3$  scale deposited from hard water without the use of corrosive acid. EDTA is used in the separation of the rare earth elements from each other. The rare earth elements have very similar chemical properties, but the stability of their EDTA complexes varies slightly. This slight variation allows EDTA to effectively separate rare-earth ions. EDTA is used as an anticoagulant for stored blood in blood banks; it prevents coagulation by sequestering the calcium ions required for clotting. As an antidote for lead poisoning, calcium disodium EDTA exchanges its chelated calcium for lead, and the resulting lead chelate is rapidly excreted in the urine.

NSOU | CC-CH-07 94 The calcium salt of EDTA, administered intravenously, is also used in the treatment of acute cadmium and iron poisoning. Dimercaprol (2,3-dimercapto-1-propanol) is an effective chelating agent for heavy metals such as arsenic, mercury, antimony, and gold. These heavy metals form particularly strong bonds to the sulfur atoms in dimercaprol.  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SH} + \text{Hg}^{2+} + 2\text{SH} \rightarrow \text{HO}-\text{CH}_2-\text{CH}_2-\text{S}-\text{Hg}-\text{S}-\text{CH}_2-\text{CH}_2-\text{OH} + 2\text{H}^+$   
Dimercaprol was originally employed to treat the toxic effects of an arsenic-containing mustard gas called Lewisite [dichloro(2-chlorovinyl)arsine], which was used in World War I. The chelated metal cannot enter living cells and is rapidly excreted from the body. Since dimercaprol is water insoluble, it is dissolved in an oil base (often peanut oil) and injected intramuscularly.

3.9 Stereochemistry and isomerism of complexes: Isomers are compounds that have the same chemical formulae but different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two main types of isomerism are known among coordination compounds. Each of which can be further subdivided.

1. Structural isomerism

A. Linkage isomerism : It arises in a coordination compound containing ambidentate ligands. A simple example is provided by complexes containing the thioeyanale ligand,  $\text{NCS}^-$ , which may bind through the nitrogen to give  $\text{M}-\text{NCS}$  or through sulphur to give  $\text{M}-\text{SCN}$ . In complexes containing  $\text{NO}_2^-$  ligand,  $\text{NO}_2^-$  may bind through either O-atom or N-atom. Similarly, for  $\text{S}_2\text{O}_3^{2-}$ , the central metal may be coordinated either by S-atom or O-atom. Members of each pair of complex thus formed are linkage isomers to each other.

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Coordination isomerism : This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Both the cation and the anion in the complex compound are complexes themselves and there is an exchange of ligands between the two coordination spheres giving rise to coordination isomers. An example is provided by  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ , in which the

NSOU | CC-CH-07 95  $\text{NH}_3$  ligands are bound to  $\text{Co}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Cr}^{3+}$ . In its coordination isomer  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the  $\text{NH}_3$  ligands are bound to  $\text{Cr}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Co}^{3+}$ .  $[\text{Co}(\text{en})_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)][\text{Cr}(\text{en})(\text{C}_2\text{O}_4)_2]$  are also coordination isomers (en = ethylenediamine,  $\text{C}_2\text{O}_4^{2-}$  = oxalato).

C. Ionization

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isomerism : This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand

in the inner coordination sphere and then become the counter ion. i.e. complexes which have the same empirical formula but give different ions in solution are ionisation isomers. An example is provided by the ionization isomers  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ ,  $[\text{Co}(\text{NH}_3)_4\text{ClNO}_2]\text{Cl}$  etc. D. Solvate isomerism : This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent.

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This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example

is provided by the aqua complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer [

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$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey-green) and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (green) E. Ligand isomerism: Some

ligands themselves are capable of existing as isomers such as 1,2-diaminopropane (pn) and 1,3-diaminopropane (tn). pyridine-2-carboxylate or picnilate (pic) and pyridine-3-carboxylate or nicotinate (nic) n-propylamine (n-pram) and isopropylamine (iso-pram) etc.  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (pn)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (tn)  $\text{NCOO}^-$  (pic)  $\text{NCOO}^-$  (nic)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (n-pram)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (iso-pram)  $\text{NH}_2$  When these ligands form complexes, the complexes are isomers of each other e.g.  $[\text{Co}(\text{pn})_2\text{Cl}_2]^+$  and  $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$  are ligand isomers. F. Coordination position isomerism: In some polynuclear complexes, interchange of ligands between the metal centres within the coordination sphere gives

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rise to coordination position isomerism.  $(\text{H}_3\text{N})_4\text{Co}(\text{III})\text{NH}_2\text{O}_2\text{Co}(\text{IV})(\text{NH})_3\text{Cl}_2 + 2$  and  $\text{Cl}(\text{NH})_3\text{Co}(\text{III})\text{NH}_2\text{O}_2\text{Co}(\text{IV})$

$\text{IV}(\text{NH})_3\text{Cl}_2 + 2$  are

NSOU | CC-CH-07 96 coordination position isomers. 2. Stereoisomerism A. Geometrical isomerism : Geometrical isomers have identical empirical formula but differ in chemical and physical properties because of different arrangement of ligands. i) cis-trans isomerism : Here the isomers differ in the geometrical arrangement of the ligands around the central metal atom or ion. The isomer will be named cis if similar type of ligands occupy positions adjacent to each other and if the similar type of ligands occupy positions diagonally opposite to each other, the isomer is named trans. Example: [

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$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  and  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .  $\text{Pt}(\text{NH}_3)_3\text{Cl}_2$  cis °  $\text{Pt}(\text{NH}_3)_3\text{Cl}_2$  trans °  $\text{Co}(\text{NH}_3)_3\text{Cl}$  cis +  $\text{Cl}(\text{NH}_3)_3\text{Co}(\text{NH}_3)_3\text{Cl}$

trans +  $\text{Cl}(\text{NH}_3)_3\text{NH}_3$

NH<sub>3</sub> Geometrical isomers (cis and trans) Geometrical isomerism cannot arise in a tetrahedral complex because in this geometry all positions are cis to each other. So this isomerism may occur in square planar (C.N = 4) and octahedral (C.N. = 6) complexes. ii) fac-mer isomerism : An isomer becomes facial if three identical ligands occupy the vertices of a octahedron's triangular face (i.e. the ligands are at cis-positions). It becomes meridional if these three ligands form together with the central atom a plane in the octahedron (i.e. when two identical ligands out of three are at the trans positions, it leads to meridional isomers since the three identical ligands are placed along the meridian. They are termed fac-or mer-isomers. Example: [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>], [Pt(NH<sub>3</sub>)<sub>3</sub>Br<sub>3</sub>] + [Ru(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>] etc.

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NH<sub>3</sub> Cl Co NH<sub>3</sub> NH<sub>3</sub> Cl Cl fac-isomer NH<sub>3</sub> Co NH<sub>3</sub> Cl Cl mer-isomer NH<sub>3</sub> Cl

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Optical isomerism : Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers. The molecules or ions that cannot be superimposed are called chiral.

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The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.

No mirror image isomerism is possible with tetrahedral and square planar complexes. In tetrahedral arrangement, as all positions are equivalent, the images are superimposable. For square planar complexes,

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all the four ligands are in the same plane and hence have a plane of symmetry

and are optically inactive. Example : Co(en)<sub>3</sub> dextro laevo en en en mirror 3+ 3+ For octahedral complexes of the type [Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>], [Ma<sub>2</sub>b<sub>2</sub>cd], [Ma<sub>2</sub>bcd<sub>2</sub>] and [Mabcdef] (where a,b,c....etc are different monodentate ligands)

optical isomers are possible. Octahedral complexes with symmetrical bidentate chelating ligands of the type [M(AA)<sub>3</sub>] n+/n-, cis-[M(AA)<sub>2</sub>ef] n±, cis-[M(AA)<sub>2</sub>e<sub>2</sub>] n±, [M(AA)c<sub>2</sub>e<sub>2</sub>] n± are optically active. (AA = symmetrical bidentate i.e. similar donating groups). 3.10 Summary Coordination compounds are of great importance. These compounds provide critical insights into the functioning

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and structures of vital components of biological systems. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.



They are an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in chemical industry and vital insights into the functioning of critical components of biological systems. The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by A. Werner. His theory postulated the use of two types of linkages (primary and secondary) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of Co

NSOU I CC-CH-07 98 isomerism, Werner predicted the geometrical shapes of a large number of coordination entities. The stability of coordination compounds is measured in terms of stepwise or formation constants (K) or overall stability constants ( $\beta$ ). The stabilisation of a coordination compound due to chelation is called the chelate effect. The explanation and interactions of metal ions and ligands and EAN calculation techniques have also been provided in this chapter.

Different types of isomerism possible in the coordination compounds are also discussed. 3.11 Self Assessment Questions

1. Write the differences between complex salts and double salts. 2. Give examples of complex salts and double salts. 3. State and explain Werner's theory. 4. Write the postulates of Werner's theory. 5. What do you mean by EAN rule? 6. Calculate EAN of  $[\text{Ni}(\text{CO})_4]$ ;  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ;  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ . 7. State the exceptions of EAN rule. 8. What do you mean by the term ligand? 9. What are monodentate ligands? Give examples. 10. What are bidentate ligands? Give examples. 11. What are ambidentate ligands? Give examples. 12. What are polydentate ligands? Give examples. 13. Write the IUPAC names of— A.  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}$  B.  $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]\text{Cl}$  C.  $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$  D.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  E.  $\text{Na}_2[\text{NiCl}_4]$  F.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$

NSOU I CC-CH-07 99 G.  $[\text{Fe}(\text{CO})_5]$  14. How are overall and stepwise stability constants related? 15. What are chelates? 16. What do you mean by linkage isomerism? 17. What do you mean by coordination isomerism? 18. What do you mean by ionisation isomerism? 19. What do you mean by solvate isomerism? 20. What do you mean by cis-trans isomerism? 21. What do you mean by fac-mer isomerism? Answer Key 1. See section 3.1 2. See section 3.1 3. See section 3.2 4. See section 3.2 5. See section 3.3 6. See section 3.3 7. See section 3.3 8. See section 3.4 9. See section 3.4 10. See section 3.4

11. See section 3.4 12. See section 3.4 13. See section 3.5 14. See section 3.6 15. See section 3.7 16. See section 3.8 17. See section 3.8 18. See section 3.8 19. See section 3.8 20. See section 3.8 21. See section 3.8 3.12 Further Reading 1. G. B. Kauffman, Classics in Coordination Chemistry, Dover Pub. New York (1995). 2. P. R. Shukla, Advance Coordination Chemistry Himalaya Publishing House. 3. G. A. Lawrance, Introduction to coordination Chemistry, A John Wiley and Sons Ltd., Publication. 4. Basic Inorganic Chemistry, Cotton, Wilkinson, Gaus 3rd Ed. John Wiley and Sons Inc., 2004. 5. Fundamental Concepts of Inorganic Chemistry A. K. Das and M. Das volume 2, First Ed., 2015.

NSOU I CC-CH-07 100 Unit 4 □□□□ Coordination Chemistry-II 4.0 Objectives 4.1 Introduction 4.2 Structure and bonding of coordination compounds on the basis of Valence bond theory and its limitation 4.3 Elementary idea about Crystal Field Theory 4.4 Jahn Teller theorem and applications 4.5 Limitations of CFT 4.6 Nephelauxetic effect 4.7 Stabilisation of unusually high and low oxidation states of 3d transition elements 4.8 Molecular Orbital Theory (elementary idea) 4.9  $\sigma\sigma\sigma\sigma^-$  and  $\pi\pi\pi\pi\pi\pi^-$ -bonding in octahedral complexes (a pictorial approach) 4.10 Colour and electronic spectra of complexes: selection rules for electronic transitions 4.11 Charge transfer transitions (qualitative idea) 4.12 L-S coupling and R-S ground state terms for atomic no. 21 to 30 4.13 Qualitative Orgel diagrams for 3d<sup>1</sup> - 3d<sup>9</sup> ions 4.14 Summary 4.15 Self Assessment Question 4.16 Further Reading 4.0 Objectives After reading this unit you can be able to know— \* Structure and bonding of Coordination Compounds. \* Elementary idea about crystal field theory. 100 NSOU I CC-CH-07 101 \* Jahn Teller theorem and its applications. \* Idea about  $\sigma$ - and  $\pi$ -bonding in octahedral complexes. \* Concept about charge transfer transitions L-S coupling and R-S ground state terms. \* Idea about Orgel diagrams. 4.1 Introduction In order

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to explain the nature of Coordination Compounds generally three theories are considered—Valence bond theory (VBT), crystal field theory (CFT), and molecular orbital theory (



MO). The bonding theory are used described molecules and ions was the VBT which is indeed an essential bonding theory describe the vast majority of molecules and during the year 1930-1950. This theory is based on the orbital overlap model and was developed by Pauling. The inadequacies of VBT arises in case of electron deficient molecule to explain the colour of Coordination complexes. Thus crystal field theory gained ground. The ligand field and crystal field theory were first developed by H. Bethe. The crystal theory strictly valid for ionic complexes, on the otherhand molecular theory explains the covalent bonding in the complexes. 4.2 Structure and bonding of coordination compounds on the basis of Valence Bond Theory (VBT) and its limitations The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902. It was not until 1927, however, that Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the valence-bond theory. The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^2$ , and  $d^2sp^3$  orbitals.

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According to this theory, the metal atom or ion under the influence of ligands can use its ( $ns$ ,  $np$

or  $(n-1)d$ ,  $ns$ ,  $np$ ,  $nd$  orbitals for hybridization

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to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and

so on.

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These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

NSOU I CC-CH-07 102 Coordination Type of Distribution of hybrid Number hybridisation orbitals in space Examples  $4 sp^3$  Tetrahedral  $[Ni(CO)_4]$   $4 dsp^2$  Square planar  $[Ni(CN)_4]^{2-}$   $5 sp^3 d$  Trigonal bipyramidal  $[Fe(CO)]_5$   $6 d^3 sp^3$  Octahedral  $[Co(NH_3)_6]^{3+}$   $6 sp^3 d^2$  Octahedral  $[CoF_6]^{3-}$  It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory. Pauling has made a use of magnetic measurements to find out the number of unpaired electrons in a complex. According to him, the number of unpaired electrons and geometries of the complexes are related to each other (Magnetic criterion of Bond Type).

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In the diamagnetic octahedral complex.  $[Co(NH_3)_6]^{3+}$ , the cobalt ion is in  $+3$  oxidation state and has the

outer electronic configuration  $3d^6 4s^0$ .

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Six pairs of electrons, one from each  $NH_3$ , molecule, occupy the six hybrid orbitals.

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The complex has octahedral geometry and is diamagnetic because of the absence of unpaired

electrons. 3d 4s 4p Co-atom Free Co (III) ion  $\times \times \times \times \times \times \times$  [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> d sp<sup>3</sup> -Hybridisation 2 3  $\times \times$  denotes electron pairs donated by ligands In the formation of this complex, since

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the inner d orbital (3d) is used in hybridisation. the complex, [

Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>

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is called an inner orbital or low spin or spin paired complex. The

NSOU I CC-CH-07 103 paramagnetic octahedral complex, [CoF<sub>6</sub>]<sup>3-</sup>

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uses outer orbital (4d) in hybridisation (sp<sup>3</sup> d<sup>2</sup>). It is thus called outer orbital or high spin or spin free complex.

Co atom Free Co (II) ion  $\times \times \times \times \times \times$  [CoF<sub>6</sub>]<sup>3-</sup> sp<sup>3</sup> d<sup>2</sup>  $\times \times \times \times$  3d 4s 4p F<sup>-</sup> F<sup>-</sup> F<sup>-</sup> F<sup>-</sup> F<sup>-</sup> F<sup>-</sup> In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for [

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NiCl<sub>4</sub>]<sup>2-</sup>. Here nickel is in +2 oxidation state and the ion has the outer electronic configuration 3d<sup>8</sup> 4

s<sup>0</sup>. The hybridisation scheme is as shown in the diagram below. Each Cl<sup>-</sup> ion donates a pair of electrons. Ni atom 3d 4s 4p Free Ni (II) ion 3d 4s 4p [NiCl<sub>4</sub>]<sup>2-</sup> 3d 4s 4p  $\times \times \times \times \times \times$  Cl Cl Cl Cl sp<sup>3</sup>

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The compound is paramagnetic since it contains two unpaired electrons. Similarly, [Ni(CO)<sub>4</sub>] has tetrahedral geometry but is diamagnetic

since nickel is in zero oxidation state and contains no unpaired electrons. In the square planar complexes, the hybridisation involved is dsp<sup>2</sup>. An example is [

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Ni(CN)<sub>4</sub>]<sup>2-</sup>. Here nickel is in +2 oxidation state and has

hybridisation

NSOU I CC-CH-07 104 the outermost electronic configuration 3d<sup>8</sup> 4s<sup>0</sup>. Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron. Ni(CO)<sub>4</sub> Ni atom 3d 4s 4p Ni(O) 3d 4s 4p Ni(CO)<sub>4</sub> 3d 4s 4p  $\times \times \times \times \times \times$  CO CO CO CO sp<sup>3</sup> [Ni(CN)<sub>4</sub>]<sup>2-</sup> Ni atom 3d 4s 4p Free Ni<sup>2+</sup> ion 3d 4s 4p [NiCN<sub>4</sub>]<sup>2-</sup> 3d 4s 4p  $\times \times \times \times \times \times$  CN - CN - CN - CN - dsp<sup>2</sup> It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

NSOU I CC-CH-07 105 Limitations of Valence bond theory:

While the VB theory, to a larger extent,

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explains the formation, structures and magnetic behaviour of coordination compounds, it has many limitations: 1. It involves a number of assumptions. 2. It does not give quantitative interpretation of magnetic data. 3.

Octahedral ( $d^2 sp^3$  or  $sp^3 d^2$ ), tetrahedral ( $sp^3$ ) and square planar ( $dsp^2$ ) complexes of  $d^1$ ,  $d^2$ ,  $d^3$  and  $d^9$  have the same number of unpaired electrons and hence cannot be distinguished from each other merely on the basis on number of unpaired electrons. 4. It cannot explain why square planar complexes like  $[Cu(NH_3)_4]^{2+}$  ( $d^9$  system) and inner orbital  $Co^{+2}$  ( $d^7$ ) complexes are not reducing agents although in both cases promotion of a non-bonding  $d$ -electron to some higher energy level (presumably  $5s$ ) is required. 5. Too much stress has been laid on the metal ion while the importance of ligands are ignored. 6.

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It does not explain the colour exhibited by coordination compounds. 7. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination

compounds and cannot explain reaction rates and mechanism of reactions. 8.

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It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes. It does not distinguish between weak and strong ligands. 4.3

Elementary idea about Crystal Field Theory (CFT) This theory (CFT) largely replaced VB Theory for interpreting the chemistry of coordination compounds. It was proposed by the physicist Hans Bethe in 1929. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications are often referred to as Ligand Field Theory. The interactions between the metal ion (positively charged)

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and the ligands are purely electrostatic (ionic). The ligands are regarded as point charges or point dipoles

is the ligand is negatively charged, ion-ion interaction. If the ligand is neutral, ion-dipole interaction. The electrons on the metal are under repulsion from those on the ligands. It is these repulsive forces that are responsible for causing the splitting of  $d$ -orbitals of the metal centre. According to crystal field theory, the interaction between a transition

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metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the

non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five degenerate d-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion or atom, the electrons from the ligand will be closer to some of the d-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy. Factors affecting crystal field splitting: 1. The nature of the metal ion. 2. The metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field. 3. The arrangement of the ligands around the metal ion. 4. The coordination number of the metal (i.e. tetrahedral, octahedral...) 5. The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands, the greater the difference between the high and low energy d orbitals. The most common type of complex is octahedral in which six ligands form the vertices of an octahedron around the metal centre. The five d-orbitals have been divided into two groups in octahedron symmetry. (i) Group that has the orbitals with their lobes along the axes (axial orbitals). Obviously these are  $d_{z^2}$  and  $2x^2 - y^2$  - and forms a doubly degenerate state. (ii) Group that has the orbitals whose lobes between the axes (non-axial orbitals) They are  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ . In octahedral symmetry, therefore, the d-orbitals split into two sets with an energy difference,  $\Delta_{oct}$  (the crystal-field splitting parameter) where the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals will be lower in energy than the  $d_{z^2}$  and  $d_{x^2 - y^2}$ , which will have higher energy, because the former group is farther from the ligands than the latter and therefore

NSOU I CC-CH-07 107 experiences less repulsion. The three lower-energy orbitals are collectively referred to as  $t_{2g}$  and the two higher-energy orbitals as  $e_g$  (These labels are based on the theory of molecular symmetry). The crystal field splitting energy,  $\Delta_{oct}$  ( $\Delta_o$ ) is also denoted by an energy term,  $10Dq_0$ . If we consider the spherical distribution of ligand charges, then the barycentre (i.e. centre of gravity) of the d-orbitals will be displaced maintaining the degeneracy. If the same amount of spherical charge is redistributed at the six corners of a regular octahedron (with same metal-ligand distance) then the barycentre will be the same as in the case of spherically symmetrical field. Thus the mere redistribution of the spherical charge cannot alter the energy of the system i.e. the barycentre or centre of gravity of d-orbital. So the following condition is obeyed: Destabilisation caused by  $e_g$  set ( $d_{z^2}$  and  $2x^2 - y^2$ ) = Stabilisation caused by  $t_{2g}$  set ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ). If the splitting energy is taken as  $10Dq_0$ , each  $t_{2g}$  electron (in any of the three degenerate orbitals) is stabilised by  $4Dq_0$  and each  $e_g$  electron (in any of the two degenerate orbitals) destabilised by  $6Dq_0$  with respect to the energy of the electrons in the pre-splitting condition. Similarly it can be known that if  $\Delta_0$  is taken as the splitting energy, then the  $t_{2g}$  set is stabilised by  $2/5 \Delta_0$  ( $0.4 \Delta_0$ ) and  $e_g$  set destabilised by  $3/5 \Delta_0$  ( $0.6 \Delta_0$ ) relative to the d-orbitals in the pre-splitting condition (i.e. barycentre). Metal d-orbitals Average energy of the d-orbitals in spherical crystal field  $d_{z^2}$ ,  $d_{x^2 - y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  Energy  $d_{z^2}$ ,  $d_{x^2 - y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  Splitting of d-orbitals in octahedral crystal field  $t_{2g}$   $e_g$   $\Delta_o$   $3/5$   $2/5$  Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal centre. In a tetrahedral crystal field splitting, the d-orbitals again split into two groups, with an energy difference of  $\Delta_{tet}$  ( $\Delta_t$ ). The lower energy orbitals will be  $d_{z^2}$  and  $d_{x^2 - y^2}$ . and the higher energy orbitals will be  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  opposite to the octahedral case. The geometry of tetrahedron within a cube have the four negative ligands at the alternate corners of the cube and are lying between the three axes (x,y,z). The  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  orbitals have lobes between the axes and face the ligands more

NSOU I CC-CH-07 108 directly than  $d_{z^2}$  and  $d_{x^2 - y^2}$ . So they face greater repulsion from ligands than the other two. So the former three orbitals will be raised in energy ( $t_{2g}$  set in tetrahedral symmetry) and the latter two ( $e_g$  set) will be stabilised with respect to the barycentre. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d-orbitals, the energy splitting will be lower than in the octahedral i.e.  $\Delta_t < \Delta_o$ . It can be shown that  $\Delta_t = 4/9 \Delta_o$ . 'g' is omitted in tetrahedral case as this geometry do not have a centre of symmetry. Square planar and other complex geometries can also be described by CFT. d-orbitals free ion Average energy

**75%**

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of the d-orbitals in spherical crystal field Splitting of d-orbitals in tetrahedral

crystal field [ ] [ ] Energy [ ]  $d, d x^2 - y^2 z^2$  [ ]  $d d d xy yz xz$  , ,  $t_2g - 5 \Delta 1 e_g - 5 \Delta 1 \Delta t e$  The size of the gap  $\Delta$  between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of  $\Delta$ , while others always give a large splitting. The reasons behind this can be explained by ligand field theory. Spectrochemical Series: The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting  $\Delta$  that they produce (

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small  $\Delta$  to large  $\Delta$ ):  $I - Br - \text{I}^-$ ;  $S^{2-}$ ;  $SCN^-$ ;  $Cl^-$ ;  $NO_3^-$ ;  $N_3^-$ ;  $F^-$ ;  $OH^-$ ;  $C_2O_4^{2-}$ ;  $H_2O$ ;  $NCS^-$ ;  $CH_3CN$ ;  $py$ ;  $NH_3$ ;  $en$ ; 2,2-bipyridine;  $phen$ ;  $NO_2^-$ ;  $PPh_3$ ;  $CN^-$ ;  $CO$

It is useful to note that the ligands producing the largest splitting are those that can engage in metal to ligand back-bonding. The oxidation state of the metal also contributes to the size of  $\Delta$  between the high and low energy levels. As the oxidation state increases for a given metal, the magnitude of  $\Delta$  increases. A  $V^{3+}$  complex will have a larger  $\Delta$  than a  $V^{2+}$  complex for a given set of ligands, as the difference in charge density allows the ligands to be closer to a  $V^{3+}$  ion than to a  $V^{2+}$  ion. The smaller distance between the ligand and the metal ion results in a larger  $\Delta$  because the ligand and metal electrons are closer together and therefore repel more.

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Ligands which cause a large splitting  $\Delta$  of the d-orbitals

NSOU | CC-CH-07 109 are referred to

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as strong-field ligands such as  $CN^-$  and  $CO$  from the spectrochemical series. In complexes with these ligands, it is unfavourable to put electrons into the high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets

starts according to the Aufbau principle. Complexes such as these are called "low spin" (spin-paired complexes).

**89% MATCHING BLOCK 82/128**

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For example,  $NO_2^-$  is a strong-field ligand and produces a large  $\Delta$ . The octahedral ion  $[Fe(NO_2)_6]^{3-}$ , which has 5 d-electrons, would have the all the five electrons in the  $t_2g$  level.

This low spin state therefore does not follow Hund's rule. Conversely,

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ligands (like  $I^-$  and  $Br^-$ ) which cause a small splitting  $\Delta$  of the d-orbitals are referred to as weak-field ligands. In this case, it is easier to put electrons into the higher energy set of orbitals than it is to put two into the same low-energy orbital, because two electrons in the same orbital repel each other. So, one electron is put into each of the five d-orbitals in accordance with Hund's rule, and "high spin" complexes (

or spin-free complexes) are formed before any pairing occurs.

**72% MATCHING BLOCK 84/128**

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For example, Br<sup>-</sup> is a weak-field ligand and produces a small  $\Delta_{oct}$ . So, the ion  $[FeBr_6]^{3-}$ , again with five d-electrons, would have all five orbitals (

t<sub>2g</sub> and e<sub>g</sub>) singly occupied.

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In order for low spin to occur, the energy cost of placing an electron into an already singly occupied orbital must be less than the cost of placing the additional electron into an e<sub>g</sub> orbital at an energy cost of  $\Delta$ .

As noted above, e<sub>g</sub> refers to the d<sub>z<sup>2</sup></sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> which are higher in energy than the t<sub>2g</sub> in octahedral complexes.

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If the energy-required to pair two electrons is greater than

$\Delta$ , the energy cost of placing an electron in an e<sub>g</sub> is more appropriate and a high spin complex is formed. The crystal field splitting energy for tetrahedral metal complexes (four ligands) is referred to as  $\Delta_{tet}$  ( $\Delta_t$ ) and is roughly equal to  $4/9\Delta_{oct}$  (for the same metal and same ligands). Therefore, the energy required to pair two electrons is typically higher than the energy required for placing electrons in the higher energy orbitals. Thus, tetrahedral complexes are usually high-spin.

Thus if  $\Delta_o > P$ ; ( $P$ = pairing energy)

**76% MATCHING BLOCK 85/128**

**W**

the fourth electron enters one of the e<sub>g</sub> orbitals giving the configuration t<sub>2g</sub><sup>3</sup> e<sub>g</sub><sup>1</sup>. Ligands for which  $\Delta_o > P$  are known as weak field ligands and form high spin complexes, whereas, if  $\Delta_o < P$ , it becomes more energetically favourable for the fourth electron to occupy a t<sub>2g</sub> orbital

resulting in a

**100% MATCHING BLOCK 86/128**

**W**

configuration t<sub>2g</sub><sup>4</sup> e<sub>g</sub><sup>0</sup>. Ligands which produce this effect are known as strong field ligands and form low spin complexes

or spin-paired complexes. Distribution of electrons in octahedral field in presence of strong field and weak field ligands: The use of these splitting diagrams can aid in the prediction of magnetic properties of coordination compounds. A compound that has unpaired electrons in its splitting diagram NSOU LCC-CH-07 110 will be paramagnetic and will be attracted by magnetic fields, while a compound that lacks unpaired electrons in its splitting diagram will be diamagnetic and will be weakly repelled by a magnetic field.

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The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the d-orbitals are split in a ligand field (as described above), some of them become lower in energy than before

with respect to a spherical field known as the barycenter in which all five d-orbitals are degenerate.

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For example, in an octahedral case, the  $t_{2g}$  set becomes lower in energy

than the orbitals in the barycenter. As a result of this,

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if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field

relative to the barycenter by an amount known as the CFSE (Crystal Field Stabilisation Energy). Conversely, the  $e_g$  orbitals (in the octahedral case) are higher in energy than in the barycenter, so putting electrons in these reduces the amount of CFSE. Examples: For  $d^1$  metal ion in octahedral field, the electron occupies a  $t_{2g}$  orbital with an energy of  $-0.4 \Delta_0$  ( $-4Dq$ ) relative to the barycentre of d-orbitals, (negative sign denotes stabilisation relative to barycentre). The complex can thus be said to be stabilised to the extent of  $0.4 \Delta_0$  or  $4Dq$ . For  $d^4$  (high spin)  $t_{2g}^3 e_g^1$  configuration,  $CFSE = (3 \times -0.4 \Delta_0) - (1 \times 0.6 \Delta_0) = -1.8 \Delta_0$ . For  $d^4$  (low spin)  $t_{2g}^4$  configuration,  $CFSE = (4 \times -0.4 \Delta_0) = -1.6 \Delta_0$  (or,  $-4 \Delta_0$ ) =  $16 \Delta_0$ . The CFSE can be stated as  $-0.6 \Delta_0$  or,  $-1.6 \Delta_0$  (negative sign indicates stabilisation) or by  $CFSE = 0.6 \Delta_0$  or  $1.6 \Delta_0$  denotes (with nonnegative sign) stabilisation by that amount. It pairing is considered, pairing of electrons would destabilise the system because of electronic repulsion and CFSE should be  $1.6 \Delta_0 - P$  or  $16 Dq - P$ . If CFSE is denoted by negative sign or  $-1.6 \Delta_0$  ( $-16 Dq$ ) then CFSE is given as  $-1.6 \Delta_0 + P$  ( $-16 Dq + P$ ). Positive sign denotes destabilisation. When calculating CFSE, for weak field cases, comparison is made with free ion configuration, so number of electron pairs are same in both cases and  $P$  (pairing energy) can be omitted. For strong field cases, comparison is made with weak field (i.e. free ion) and extra pairs are subtracted from CFSE. If CFSE is stated as positive and added if CFSE is stated as negative. For example high spin  $d^7$  metal ion has configuration  $t_{2g}^5 e_g^2$  and  $CFSE = 0.8 \Delta_0 - 2P$  (or sometimes  $-0.8 \Delta_0 + 2P$ ). Low spin  $d^7$  will have the configuration  $t_{2g}^6 e_g^1$  and  $CFSE = 1.8 \Delta_0 - 3P$  (or  $-1.8 \Delta_0 + 3P$ ). In comparison to WF case (or free ion) SF configuration has one extra 'pair' of electrons. So the CFSE can be NSOU I CC-CH-07 111 written as  $1.8 \Delta_0 - P$  (or  $-1.8 \Delta_0 + P$ ). (Note in terms of  $Dq$ , the CFSE's will be  $-8 Dq + 2P - 18 Dq + 3p$  (or  $8 Dq - 2P, 18 Dq - 3P$ ) and so on. Strong field (SF) Weak field (WF) d 1 Strong field (SF) Weak field (WF) d 2 Strong field (SF) Weak field (WF) d 3 d 8 2u.e. 4u.e. 1u.e. 5u.e. 0u.e. 4u.e. 1u.e. 3u.e. 2 u.e. 2 u.e. d 9 1 u.e. 1 u.e. d 10 0 u.e. 0 u.e. (SF) (WF) (SF) (WF) (SF) (WF) (SF) (WF) (SF) (WF) (SF) (WF) (SF) (WF) (SF) (WF) u.e. = unpaired electrons Octahedral field Tetrahedral field High spin Low spin High spin Low spin d-system Configu- CFSE Configu- CFSE Configu- CFSE ration ration ration

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$d^1 t_{2g}^1 e_g^0$   $0.4 \Delta_0$   $t_{2g}^1 e_g^0$   $0.4 \Delta_0$   $e^1 t_{2g}^0$   $0.6 \Delta_0$   $t_{2g}^2 e_g^0$   $0.8 \Delta_0$   $t_{2g}^2 e_g^0$   $0.8 \Delta_0$   $e^2 t_{2g}^0$   $1.2 \Delta_0$   $t_{2g}^3 e_g^0$   $1.2 \Delta_0$   $t_{2g}^3 e_g^0$   $1.2 \Delta_0$   $e^2 t_{2g}^1$   $0.8 \Delta_0$   $t_{2g}^4 e_g^0$   $1.6 \Delta_0$   $t_{2g}^4 e_g^0$   $1.6 \Delta_0$   $e^2 t_{2g}^2$   $0.4 \Delta_0$  NSOU I CC-CH-07 112  $d^5 t_{2g}^3 e_g^2$   $0.0 \Delta_0$   $t_{2g}^5 e_g^0$   $2.0 \Delta_0$   $e^2 t_{2g}^3$   $0.0 \Delta_0$   $t_{2g}^6 e_g^0$   $2.4 \Delta_0$   $e^3 t_{2g}^3$   $0.6 \Delta_0$   $t_{2g}^7 e_g^0$   $2.8 \Delta_0$   $t_{2g}^6 e_g^1$   $1.8 \Delta_0$

$\Delta_0 e^4 t_{2g}^3$   $1.2 \Delta_0$   $t_{2g}^3$

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$d^8 t_{2g}^6 e_g^2$   $1.2 \Delta_0$   $t_{2g}^6 e_g^2$   $1.2 \Delta_0$   $e^4 t_{2g}^4$   $0.8 \Delta_0$   $t_{2g}^9 e_g^2$   $3.0 \Delta_0$   $t_{2g}^6 e_g^3$   $0.6 \Delta_0$   $e^4 t_{2g}^5$   $0.4 \Delta_0$   $t_{2g}^{10}$   $0.0 \Delta_0$   $t_{2g}^6 e_g^4$   $0.0 \Delta_0$

$\Delta_0 e^4 t_{2g}^6$   $0.0 \Delta_0$

t 4.4 Jahn Teller theorem and applications Hermann Jahn and Edward Teller in 1937,



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postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," with regard to its electronic state. This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecraft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy. "This is most commonly observed with transition metal octahedral complexes.

In the octahedral system, if the two trans ligands lying along the Z-axis are compressed or elongated compared to other four ligands in the xy-plane, a tetragonally distorted octahedrons are obtained.

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However, it can be observed in tetrahedral compounds as well.

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The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.

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For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels:  $t_{2g}$  ( $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ ) and  $e_g$  ( $d_{z^2}$  and  $d_{x^2-y^2}$ ). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the ligand bonds.

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**SA** Coordination (Theory).pdf (D98069410)

M L L L L L L Elongated M L L L L L L

Compressed When an octahedral complex exhibits elongation (z-out),

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the axial bonds are longer than the equatorial bonds. For a compression (

z-in)

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it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Thus distortion will occur if only the splitted energy levels can yield an additional stabilisation through distortion. For octahedral complexes, if distortion occurs due to uneven occupancy of electrons in the  $e_g$  set (eg 1 or eg 3), it is more severe than cases where uneven occupancy is in  $t_2g$  set, since the interaction of electrons with legands is more direct (along the axis) in the  $e_g$  set. For tetrahedral complexes, the J.T. elistortion is significant if  $t_2$  set is unsymmetrically filled up. z x y

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$d, d_{x^2-y^2}, z^2, \Delta, d_{xy}, yz, dxz, E, \dots, z, xy, d, d_{x^2-y^2}, z^2, d, d_{xy}, xz, yz, \dots, z, z^2, d, d, d, d, x^2-y^2$

xz yz xy (z-in) (Z-out)  
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Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, (

due to lower repulsion with ligands)

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while the orbitals without a z component are destabilized (higher in energy).

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This is due to the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the  $d_{x^2-y^2}$  orbital is antibonding, it is expected to increase in energy due to elongation. The

$d_{xy}$

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orbital is still nonbonding, but is destabilized due to the interactions.

J.T. distortion in octahedral geometry.  $d^1, d^4$  (h.s.),  $d^7$  (l.s.),  $d^9, d^6$  (h.s.) Tetrahedral:  $d^3, d^4, d^8, d^9$  occupation of electrons in  $t_2$  level). Jahn-Teller elongations are well-documented for copper(II) ( $d^9$ ),

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octahedral compounds. A classic example is that of copper(II) fluoride.

Some examples of Jahn-Teller distorted complexes are  $K_2CuF_4$  and  $KCuAlF_6$ . In the former, four F atoms are at 191 pm and two F atoms are at 237 pm and in the latter, two F atoms are at 188 pm and four F atoms are at 220 pm. 237 pm 191 pm F Cu 2+ 4.5 Limitations of CFT The crystal field theory suffers from the following limitations: 1. The CFT cannot explain the colour of substances with a full or empty d orbital.  $KMnO_4$  is one such substance in which the d orbital is empty. 2. There is another kind of electron transfer called Charge Transfer(CT) which is more powerful than d-d transfer and is between metal and ligand. This type of electron transfer is not covered in crystal field theory and can only be explained using MOT. 3. It treats metal ligand interactions as purely ionic. Hence it cannot be used for sulfides as sulfides form mostly covalent bonds.

NSOU | CC-CH-07 115 4. It cannot satisfactorily explain chemical bonding. Complexes may also be formed between neutral metal atoms and neutral or cationic ligands. Crystal Field Theory is poorly suited to explain such interactions. 5. Crystal Field Theory fails in explaining why a neutral ligand such as CO can cause a very large crystal field splitting, as it does not consider formation of  $\pi$ -bonds in complexes. Molecular Orbital Theory explains why the CO ligand leads to a higher crystal field splitting. 6. It does not explain why the anionic ligands are present at low end of the spectrochemical series, and why  $H_2O$ , a neutral ligand, appears in the spectrochemical series as a stronger ligand than  $OH^-$ . 4.6 Nephelauxetic effect Nephelauxetic effect ( $\beta$ ) generally denotes the decrease in the Racah interelectronic repulsion parameter (B) which

**100%**

**MATCHING BLOCK 107/128**

**SA** MCHE-12.pdf (D112800504)

indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than there is in the respective  $M^{n+}$  gaseous metal ion, which in turn implies that the size of the orbital is larger in the complex. This electron cloud expansion effect may occur for one (or both) of two reasons. One is that the effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d-orbitals can expand slightly. The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals. The

name "nephelauxetic" comes from the Greek for 'cloud-expanding'. The presence of this effect brings out the disadvantages of crystal field theory, as this accounts for somewhat covalent character in the metal-ligand interaction.

**68%**

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The reduction of B from its free ion value is given as complex free ion(gaseous)  $B \beta B =$  Experimentally, it is observed that size of the nephelauxetic parameter always follows a certain trend with respect to the nature of the ligands present. The

value depends on the extent of covalency in metal-ligand bond and depends on the nature of both the metal and the ligand. The metal ions are arranged in terms of nephelauxetic effect as follows (with a particular ligand):

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**58%**

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$Mn(II) \approx Ni(II) \approx Co(II) \approx Mo(II) \approx Re(IV) \approx Fe(III) \approx Ir(III) \approx Co(III) \approx Mn(IV)$

The ligands are arranged in terms of increasing nephelauxetic effect as follows.  $F^-$ ;  $H_2O$ ;  $NH_3$ ;  $en$ ;  $NCS^-$ ;  $Cl^-$ ;  $CN^-$ ;  $Br^-$ ;  $N_3^-$ ;  $1-\beta$  can never be greater than unity ( $\beta \leq 1$ ).  $\beta = 1$  indicates 100% ionic interaction in the metal-ligand. For non-polarisable ligands like  $F^-$ ,  $\beta$  is close to unity and for polarisable ligands as  $I^-$ ,  $S^{2-}$   $\beta$  is less than unity. The nephelauxetic series of metal ions also depends on the covalent bond forming power of the metal ions. 4.7 Stabilisation of unusual high and low oxidation states of 3d transition elements The chemical environment required to stabilise high oxidation states from that required in stabilising low oxidation states : Metal ions in higher oxidation states become oxidising, and so for stabilisation of the higher state, the surrounding environment must be resistant to prevent oxidation. The ligands must be non-oxidisable and non-polarisable. Low oxidation states (can be zero or even negative) are sensitive to oxidation by atmospheric  $O_2$  or ligands. Synthesis of such compounds are carried out in  $O_2$  free environment. The ligands should produce a reducing environment around the metal centre. So large ligands as  $I^-$ ,  $S^{2-}$  etc. are suitable for stabilising low oxidation states. For the stable halides of the 3d series of transition metals, the highest oxidation numbers are achieved in  $TiX_4$  (tetrahalides),  $VF_5$  and  $CrF_6$ . The +7 state for Mn is not represented in simple halides but  $MnO_3F$  is known, and beyond Mn no metal has a trihalide except  $FeX_3$  and  $CoF_3$ . The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of  $CoF_3$ , or higher bond enthalpy terms for the higher covalent compounds, e.g.,  $VF_5$  and  $CrF_6$ . Although V +5 is represented only by  $VF_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $VOX_3$ . Another feature of fluorides is their instability in the low oxidation states e.g.,  $VX_2$  ( $X = Cl, Br$  or  $I$ ) and the same applies to  $CuX$ .  $F^-$  is the least polarisable ion. Oxidation number +6 +5 +4 +3 +2 +1 4 - -  $TiX_4$   $TiX_3$   $TiX_2$  - 5 -  $VF_5$   $VX_4$   $VX_3$   $VX_2$  - 6  $CrF_6$   $CrF_5$   $CrX_4$   $CrX_3$   $CrX_2$  - G r o u p s

NSOU LCC-CH-07 117 7 - -  $MnF_4$   $MnF_3$   $MnX_2$  - 8 - - -  $FeX_3$   $FeX_2$  - 9 - - -  $CoX_3$   $CoX_2$  - 10 - - - -  $NiX_2$  - 11 - - - -  $CuX_2$   $CuX$  12 - - ? "  $ZnX_2$  - On the other hand, all Cu(II) halides are known except the iodide. In this case,  $Cu^{2+}$  oxidises  $I^-$  to  $I_2$ . However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation. The stability of  $Cu^{2+}$  (aq) rather than  $Cu^+$  (aq) is due to the much more negative hydration energy than  $Cu^+$ , which more than compensates for the second ionisation enthalpy of Cu. The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides coincides with the group number and is attained in  $Sc_2O_3$  to  $Mn_2O_7$ . Oxidation number +7 +6 +5 +4 +3 +2 -1 3 - - - -  $Sc_2O_3$  - - 4 - - -  $TiO_2$   $Ti_2O_3$   $TiO$  - 5 - -  $V_2O_5$   $V_2O_4$   $V_2O_3$   $VO$  - 6 -  $CrO_3$  -  $CrO_2$   $Cr_2O_3$   $CrO$  - 7  $Mn_2O_7$  - -  $MnO_2$   $Mn_2O_3$ ,  $MnO$  -  $Mn_3O_4$  8 - - - -  $Fe_2O_3$ ,  $FeO$  -  $Fe_3O_4$  9 - - - -  $Co_3O_4$   $CoO$  - 10 - - - - -  $NiO$  - 11 - - - - -  $CuO$   $Cu_2O$  12 - - - - -  $ZnO$  - Beyond Group 7, no higher oxides above  $Fe_2O_3$  and  $Co_3O_4$ , are known. Although ferrates  $Fe(VI)O_4^{2-}$  are formed in alkaline media, they readily decompose to  $Fe_2O_3$  and  $O_2$ . G r o u p s G r o u p s

NSOU LCC-CH-07 118 Besides the oxides, oxocations stabilise V(V) as  $VO_3^+$ , V(IV) as  $VO_2^+$  and Ti(IV) as  $TiO_2^+$ . The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$ . The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide  $Mn_2O_7$ , each Mn is tetrahedrally surrounded by O's including a Mn-O-Mn bridge. The tetrahedral  $[MO_4]^{n-}$  ions are known for V(V), Cr(VI), Mn(V), Mn(VI) and Mn(VII). Examples of complexes with low oxidation states:  $[Ti(CO)_6]^{2-}$  (-2),  $[V(CO)_6]^{3-}$  (-3),  $[Cr(C_6H_6)_2]$  (0),  $[Cr(bpy)_3]$  (0),  $[Mn(bpy)_3]$  (-1),  $[Mn(CO)_5]^-$  (-1),  $[Fe(bpy)_3]$  (0),  $[Fe(CO)_4]^{2-}$  (-2),  $[Co(CO)_4]^-$  (-1),  $[Ni(bpy)_2]$  (0),  $Ni(CO)_4$  (0),  $[Cu(CN)_2]^-$  (+1),  $[Cu(CN)_4]^{3-}$  (+1) etc. 4.8 Molecular orbital theory (elementary idea) The crystal field theory fails to explain many physical properties of the transition metal complexes because it does not consider the interaction between the metal and ligand orbitals. The molecular orbital theory can be very well applied to transition metal complexes to rationalize the covalent as well as the ionic character in metal-ligand bond. A transition metal ion or atom has nine valence atomic orbitals which consist of five nd, three (n+1)p, and one (n+1)s orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The

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s orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The

molecular orbital theory is highly dependent on the geometry of the complex and can successfully be used for describing octahedral, tetrahedral and square-planar complexes. The main features of molecular orbital theory for metal complexes are as follows: 1. The atomic orbital of metal centre and of surrounding ligands combine to form new orbitals, known as molecular orbitals. Combination is the symmetry permitted overlap between the metal atomic orbitals and suitable ligand group orbitals (LGOs). In the resultant MOs, electrons are placed in terms of their energy as usual. 2. The number of molecular orbitals formed is same as that or number of atomic orbitals combined. 3. The additive overlap results in the bonding molecular orbitals while the subtractive overlap results in the anti-bonding overlap. 4. The energy of bonding molecular orbitals is lower than their nonbonding counterparts while the energy of anti-bonding molecular orbitals is higher than that of non-bonding orbitals. 5. The energy of non-bonding orbitals remains the same. NSOU I CC-CH-07 119 6. The ionic character of the covalent bond arises from the difference in the energy of combining orbitals. 7. If the energy of a molecular orbital is comparable to an atomic orbital, it will not be very much different in nature from atomic orbital. Some typical explanations in the view of MO-theory are: i) Spin only magnetic moments ii) 18-electron rule iii) The splitting of d-orbital iv) High spin - low spin complexes 4.9  $\sigma\sigma\sigma\sigma$  and  $\pi\pi\pi\pi\pi\pi$  bonding in octahedral complexes (a pictorial approach) The  $\sigma$  and  $\pi$  bonding in octahedral complexes is depicted using the following diagrams. 1.  $\sigma\sigma\sigma\sigma$  - bonding in octahedral ML 6 complexes (excluding  $\pi\pi\pi\pi\pi\pi$ -bonds.)  $\Delta$  Energy ML 6 a g 1

<b>70%</b>	<b>MATCHING BLOCK 111/128</b>	<b>SA</b>	Coordination (Theory).pdf (D98069410)
t u 1 e g t 2g e* g a* 1g t* 1u t u 1 a g 1 e + t g 2 g a g, e, t u 1			

g 1 6  
L (LGO) a g =  
s t u = p ,p ,p

<b>58%</b>	<b>MATCHING BLOCK 112/128</b>	<b>SA</b>	Coordination (Theory).pdf (D98069410)
t g = d d d e = d d ,d 1 1 x y z 2 xy, yz, zx g x2, y2			

z2 - - - - - M  
NSOU I CC-CH-07 120 The 6 bonding MO s (BMO s ) (t 1u , eg, a 1g ) are relatively energetically closer to the ligand orbitals and are attracted more towards the ligands to have polar character. Three metal orbitals of t 2g set remain non-bonding. The 6 AB MO's are relatively closer to metal orbitals i.e. they are more enriched with with metal orbital character. 2.  $\pi\pi\pi\pi\pi\pi$ -bonding in octahedral ML 6 complexes The orbitals on the metal centre which can participate in  $\pi$ -bonding are t 1 u and t 2 g sets. The t 1 u set can also participate in  $\sigma$ -bonding (see for  $\sigma$ -interaction). The  $\sigma$ -bonds being stronger than  $\pi$ -bonds, the metal p orbitals (t 1 u set) prefer to form  $\sigma$ -bonds and do not participate in  $\pi$ -bonding interaction. The ligands can provide the following orbitals for  $\pi$ -bonding: (i) p $\pi$ -orbitals perpendicular to M-L  $\sigma$ -bond (ii) d $\pi$  orbitals (iii) suitable MOs as  $\pi^*$  in polyatomic ligands such as CO, CN - etc. The ligands that form  $\pi$ -bonds with metals are generally of two types: (a)  $\pi\pi\pi\pi\pi\pi$ -donor ligands (Filled ligand  $\pi$ -orbitals of lower energy than metal t 2g orbitals).  $\pi$ -LGOs from 12p $\pi$  orbitals of 6 ligands (2 perpendicular  $\pi$ -orbitals per ligand) form t 1g + t 1u + t 2g + t 2u . LGOs t 1g , t 2u and t 1u remain non-bonding and t 2g interacts with metal t 2g orbitals (same symmetry). (i.e. t 2g orbitals of  $\sigma$ -complex with essentially metal character).  $\Delta$  0

<b>100%</b>	<b>MATCHING BLOCK 113/128</b>	<b>SA</b>	Coordination (Theory).pdf (D98069410)
e * g t * 2 g $\Delta$ 0 t 2g t 2g t 2g (			

a)  $\alpha$ -complex (b) Ligand p-orbitals (Ligand may be F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> etc.) (c) MO diagram for the  $\pi$ -donor interaction (Ligand t 2g orbitals lower than  $\sigma$ -complex t 2g orbitals). (a) MO's for  $\sigma$ -system of complex (b) MO's after  $\pi$ -interaction (c) LGO's of t 2g symmetry.

NSOU | CC-CH-07 121 ( $\pi$ -t 1 u, t 1 g, t 2 u non-bonding excluded for clarity).  $\pi^*$ -t 2g MO has more metal orbital character while  $\pi$ -t 2g (BMO) is enriched with more ligand orbital (LGO) character. The energy difference between  $\sigma$ -eg\* and  $\pi$ -t 2 g\* gives the new  $\Delta_0$  value which is smaller compared to that found in absence of  $\pi$ -bonding i.e. only  $\sigma$ -bonding). b)  $\pi$  acceptor ligands t \* 2 g  $\Delta_0$  t 2g t 2g t 2g (a)  $\alpha$ -complex (b) Ligand -orbitals (Ligand may be CO, PR CN<sup>-</sup> etc.)  $\pi$  3 (c) e\* g t 2 g e\* g  $\Delta_0$  MO diagram for the  $\pi$ -acceptor interaction (Ligand t 2g orbitals higher in energy than  $\sigma$ -complex t 2g orbitals). (a) MO's for  $\sigma$ -system of complex (b) MO's after  $\pi$ -interaction (c) LGO's of t 2g symmetry.  $\pi$ -t 2 g LGO's are higher in energy than Ligand  $\sigma$ -complex t 2 g orbitals (essentially metal t 2 g in  $\sigma$ -complex). The  $\pi$ -t 2 g (BMO) has more metal t 2 g character and ABMO  $\pi^*$ -t 2g becomes enriched with more ligand character. So p-t 2g BMO is lower in energy than metal t 2g for  $\sigma$ -only bonding and the energy difference between  $\pi$ -t 2 g and  $\sigma$ - eg \* gives the new  $\Delta_0$  which is greater than the value with no  $\pi$ -bonding.

4.10 Colour and electronic spectra of complexes: selection rules for electronic transitions The origin of colors in substances can be explained in such a way that when a sample absorbs light, what we see is the sum of the emitted colors that strikes our eyes. If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample, and then NSOU | CC-CH-07 122 the sample appears black. If the sample absorbs no visible light, it is white or colorless. When the sample absorbs a photon of visible light, it is its complementary color we actually see.

Red Orange Violet Blue Green For example, if the sample absorbed orange color, it would appear blue; blue and orange are said to be complementary colors. The visible part of the electromagnetic spectrum contains light of wavelength 380-750 nm. The color wheel above gives information on the wavelength of different color and also the complementary color. For example: if red light is absorbed, the complex appears green; if purple light is absorbed, the complex appears yellow. Colour of absorbed light Range in nm Colour of emitted light Red 700 to 620 Green Orange 620 to 580 Blue Yellow 580 to 560 Violet Green 560 to 490 Red Blue 490 to 430 Orange Violet 430 to 380 Yellow Selection Rules for Electronic Transitions The Selection Rules governing transitions between electronic energy levels of transition metal complexes are: 1. The Orbital Rule or Laporte rule  $\Delta L = \pm 1$  2. The Spin Rule  $\Delta S = 0$  Yellow

NSOU | CC-CH-07 123 1. Laporte rule Statement: Only allowed transitions are those occurring with a change in parity (flip in the sign of one spatial coordinate). In other words, during an electronic transition, the azimuthal quantum number can change only by  $\pm 1$  ( $\Delta l = \pm 1$ ) The Laporte selection rule reflects the fact that for light to interact with a molecule and be absorbed, there should be a change in dipole moment. The Laporte rule is a spectroscopic selection rule that only applies to centro symmetric molecules (those with an inversion centre) and atoms. It states that electronic transitions that conserve parity, either symmetry or antisymmetry with respect to an inversion centre - i.e., g (gerade = even (German))  $\rightarrow$  g, or u (ungerade = odd)  $\rightarrow$  u respectively—are forbidden. Allowed transitions in such molecules must involve a change in parity, either  $g \rightarrow u$  or  $u \rightarrow g$ . As a consequence,

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if a molecule is centrosymmetric, transitions within a given set of p or d orbitals (i.e., those that only involve a redistribution of electrons within a given subshell) are forbidden. Allowed transitions are

those which occur between gerade to ungerade or ungerade to gerade orbitals Allowed  $g \rightarrow u$  &  $u \rightarrow g$  Not allowed (FORBIDDEN)  $g \rightarrow g$  &  $u \rightarrow u$  t 2 g  $\rightarrow$  e g is forbidden OR d  $\rightarrow$  d transitions are not allowed A designation of g for an orbital means there is symmetry with respect to an inversion center. That is, if all the atoms are inverted across the inversion center, the resulting orbital would look exactly the way it did before having inversion applied to it. (This includes same orientation in space). A designation of u means the orbital is antisymmetric with respect to the inversion center, and changes sign everywhere upon inversion. The rule originates from a quantum mechanical selection rule that, during an electron transition, parity should be inverted.

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However, forbidden transitions are allowed if the centre of symmetry is disrupted,

and indeed, such apparently forbidden transitions are then observed in experiments. Disruption of the centre of symmetry occurs for various reasons, such as the Jahn-Teller effect and asymmetric vibrations. Complexes are not perfectly symmetric all the time.

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Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions, such

as those caused by

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vibronic coupling. Through such asymmetric vibrations, transitions that would theoretically be forbidden, such as a  $d \rightarrow d$  transition, are weakly allowed.

NSOU I CC-CH-07 124 The rule is named after Otto Laporte It is relevant, in particular,  $\leftarrow$  to  $\leftarrow$  the electronic spectroscopy of transition metals. Octahedral complexes have a center of symmetry (exact or approximate) so that  $d \rightarrow d$  transitions are forbidden by the Laporte rule and are observed to be quite weak. However tetrahedral complexes have no center of symmetry so that the Laporte rule does not apply, and have more intense spectra. 2. Spin selection rule Statement: This rule states that transitions that involve a change in spin multiplicity are forbidden. According to this rule, any transition for which  $\Delta S = 0$  is allowed and  $\Delta S \neq 0$  is forbidden. During an electronic transition, the electron should not change its spin — — — — — — — — [GS] [ES] [GS] [ES]  $\Delta S=0$  Allowed  $\Delta \neq S 0$  Forbidden — — — — — — — —  $\Delta \neq S 0$  Forbidden d High spin (e.g.  $[\text{Mn}(\text{H}_2\text{O})]^{2+}$ )  $5 2+ 2 6 e g e g h\nu$  — — t 2g t 2g Relaxation of the Rates can occur through: 1. Spin-Orbit coupling - this gives rise to weak spin forbidden bands 2. Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible. 3.  $\pi$ -acceptor and  $\pi$ -donor ligands mix with d-orbitals so transitions are not purely d-d. 4.11 Charge transfer transitions (qualitative idea) A charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, or of different parts of one large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. The nature of the attraction in a charge-transfer



NSOU I CC-CH-07 125 complex is not a stable chemical bond, and is thus much weaker than covalent forces. Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electromagnetic spectrum, which produces the characteristic intense color for these complexes. These optical absorption bands are often referred to as charge-transfer bands (CT bands). Optical spectroscopy is a powerful technique to characterize charge-transfer bands. Charge-transfer complexes exist in many types of molecules, inorganic as well as organic, and in solids, liquids and solutions. A well-known example is the complex formed by iodine when combined with starch, which exhibits an intense blue charge-transfer band. Most charge-transfer complexes involve electron transfer between metal atoms and ligands. CT bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character. If the transfer occurs from the MO with ligand-like character to the metal-like one, the complex is called a ligand-to-metal charge-transfer (LMCT) complex. If the electronic charge shifts from the MO with metal-like character to the ligand-like one, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, a MLCT results in oxidation of the metal center, whereas a LMCT results in the reduction of the metal center. Resonance Raman spectroscopy is also a powerful technique to assign and characterize CT bands in these complexes. Energy of charge transfer transitions: The absorption wavelength of charge-transfer bands, i.e., the charge-transfer transition energy, is characteristic of the specific type of donor and acceptor entities. The electron donating power of a donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the highest occupied molecular orbital (HOMO). The electron accepting power of the electron acceptor is determined by its electron affinity, which is the energy released when filling the lowest unoccupied molecular orbital (LUMO). The overall energy balance ( $\Delta E$ ) is the energy gained in a spontaneous charge transfer. It is determined by the difference between the acceptor's electron affinity ( $E_A$ ) and the donor's ionization potential ( $E_I$ ), adjusted by the resulting electrostatic attraction ( $J$ ) between donor and acceptor.  $\Delta E = E_A - E_I + J$  The positioning of the characteristic CT bands in the electromagnetic spectrum is directly related to this energy difference and the balance of resonance contributions of non-bonded and dative states in the resonance equilibrium.

NSOU I CC-CH-07 126 Identification of the charge transfer bands: 1. Color: The color of CT complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor. 2. Solvatochromism: In solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variations in shifts of electron density as a result of the transition. This distinguishes it from the  $\pi \rightarrow \pi^*$  transitions on the ligand. 3. Intensity: CT absorption bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For inorganic complexes, the typical molar absorptivities,  $\epsilon$  are about  $50000 \text{ L mol}^{-1} \text{ cm}^{-1}$ , that are orders of magnitude higher than typical  $\epsilon$  of  $20 \text{ L mol}^{-1} \text{ cm}^{-1}$  or lower, for d-d transitions (transition from  $t_2g$  to  $e_g$ ). This is because the CT transitions are spin-allowed and Laporte-allowed. However, d-d transitions are potentially spin-allowed but always Laporte-forbidden. LMCT MLCT \* e.g. transfer of an electron from  $p$ -\* e.g. transfers of electron from orbital on a chloride ( $u$  symmetry) to metal's d-orbital to  $\pi^*$  orbital of CO a metal's d-orbital ( $g$  symmetry) ligand. \* Favourable when metal centre is in \* Favoured electron rich metal centres a high oxidation state and those ligated by  $\pi$ -acceptors \* Common for  $\pi$ -donor ligands ( $F^-$ , \* Often higher in energy (in the UV  $O^{2-}$ ,  $N^{3-}$ ,  $OH^-$ ) region) \* e.g. color of  $KMnO_4$  ( $d^0$  complex) Ligand-to-metal (ion) charge transfer: LMCT complexes arise from transfer of electrons from MO with ligand-like character to those with metal-like character. This type of transfer is predominant if complexes have ligands with relatively high-energy lone pairs (example S or Se) or if the metal has low-lying empty orbitals. Many such complexes have metals in high oxidation states (even  $d^0$ ). These conditions imply that the acceptor level is available and low in energy. Metal (ion)-to-ligand charge transfer: Metal (ion)-to-ligand charge-transfer (MLCT) complexes arise from transfer of electrons from MO with metal-like character to those with

NSOU | CC-CH-07 127 ligand-like character. This is most commonly observed in complexes with ligands having low-lying  $\pi^*$  orbitals, especially aromatic ligands. The transition will occur at low energy if the metal ion has a low oxidation number, for its d orbitals will be relatively high in energy. 4.12 L-S coupling and R-S ground state terms for atomic no. 21 to 30 LS-coupling: When there are unfilled shells in an atom, there may be possibilities to form wave functions that correspond to different electronic states for a given configuration. To get a good understanding of the electronic structure, we must be able to define these states and determine how they are energetically ordered. The answers are found by investigating the non-central contributions to the field and the spin-orbit coupling. The Hamiltonian to be considered is defined by the difference between the full operator and  $H_0$ , i.e.  $H = H_0 + H' + H'' + H''' + \dots$ . We assume that the central contributions to the integral from the first term and substantial parts of the second have been obtained by the SCF (self-consistent field) procedure. Alternatively, we may simply neglect them, since in this connection we are only interested in describing the splitting of a configuration into different electronic states. The interesting part of  $H'$  is now rather small and may be treated as a perturbation operator. To proceed systematically, we treat the influence of electron-electron interaction and spin-orbit coupling separately. We start by the former, i.e. consider such atoms where the spin-orbit coupling is considered to be small compared to the electron-electron interaction  $H_{ee} = \sum_{i < j} \frac{e^2}{r_{ij}}$ . Russell Saunders coupling The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterize the electronic states of atoms. The interactions that can occur are of three types: A) spin-spin coupling B) orbit-orbit coupling C) spin-orbit coupling R-S scheme assumes: spin-spin coupling &lt; orbit-orbit coupling &lt; spin-orbit coupling.

NSOU | CC-CH-07 128 This is found to give a good approximation for first row transition series where spin-orbit (J) coupling can generally be ignored. However for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used. Spin-Spin coupling: S—the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual  $m_s$  values together and is a result of coupling of spin quantum numbers for the separate electrons. Orbit-Orbit coupling: L—the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows: Total orbital angular momentum L 0 1 2 3 4 5 Orbital S P D F G H Spin-Orbit coupling: Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula  $(2S+1)$ . Terms for 3d n free ion configurations Configuration Ground state term Excited state term

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d 1, d 9 2 D - d 2, d 8 3 F 3 P, 1 G, 1 D. 1 S d 3, d 7 4 F 4 P, 2 H, 2 G, 2 F, 2 D 1, 2 D. 2 P d 4, d 6 5 D 3 H, 3 G, 2 F 1, 3 F, 3 D, 3 P 1, 3 P, 1 1, 1 G 1, 1 G, 1 F, 1 I, 1 D 1, 1 D. 1 S, 1 S d 5 6 S 4 G, 4 F, 4 D, 4 P, 2 I, 2 G 1, 2 H, 2 G, 2 F 1, 2 F. 2 D 1, 2 D. 2 P, 2 S The

Russell Saunders term symbol that results from these considerations is given by:  $(2S+1)L$

NSOU | CC-CH-07 129 Configua- Example Ground m 1 ration state term 2 1 0 -1 -2 M L M s d 1 Ti 3+ 2 D  $\uparrow 2 1 2 d 2 V 3+ 3 F \uparrow \uparrow 3 1 d 3 Cr 3+ 4 F \uparrow \uparrow \uparrow 3 1 1 2 d 4 Cr 2+ 5 D \uparrow \uparrow \uparrow \uparrow 2 2 d 5 Mn 2+ 6 S \uparrow \uparrow \uparrow \uparrow 0 1 2 2 d 6 Fe 2+ 5 D \uparrow \uparrow \uparrow \uparrow 2 2 d 7 Co 2+ 4 F \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow 3 1 1 2 d 8 Ni 2+ 3 F \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow 3 1 d 9 Cu 2+ 2 D \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow 2 1 2$

4.13 Qualitative Orgel diagram for 3d 1 - 3d 9 ions

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Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams. They are named after their creator, Leslie Orgel. Orgel diagrams are restricted to only weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams; also, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry designations.

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In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are two Orgel diagrams, one for d 1, d 4, d 6 and d 9 and the other with d 2, d 3, d 7 and d 8 configurations.

NSOU | CC-CH-07 130 T 2 T 2 E E O D q D q D Energy 4D q 6D q T 1 (P) A 2 O D q D q F Energy O T 1 (F) P T 2 10D q A 2 10D q T 1 (P) 8D q T 1 (F) T 2 d 1, d 6 (tetrahedron) d 1, d 6 (octahedron) d 2, d 7 (tetrahedron) d 2, d 7 (Octahedron) d 4, d 9 (octahedron) d 4, d 9 (tetrahedron) d 3, d 8 (octahedron) d 3, d 8 (tetrahedron) The inverse relationship between the two symmetries (Oct and tet) arises because a tetrahedral field is in effect, a negative octahedral field. For the second diagram, the effect of mixing of terms is represented. As a general rule, terms having identical symmetry will mix, with the extent of mixing being inversely proportional to the energy difference between them. For d 7 the terms involved are the two T 1 (tet) and T 1 g (Oct.) levels. The upper level is raised in energy while the lower level falls. This is represented in the diagram as diverging lines for the pairs of T 1 g and T 1 levels. The terms include 'g' in oct. field, but not in tet. field. For example for the first diagram on the left hand side, the d 1, d 6 (tet) have the terms E and T 2, but for d 4, d 9 (oct.) the terms are E<sub>g</sub> and T 2<sub>g</sub>. 4.14 Summary Coordination compounds is the study of complexes of transition metals and different interactions of these complexes under different conditions. In this chapter the structure and bonding of coordination compounds on the basis of valence bond theory along with its limitations are discussed briefly. Valence bond theory does not differentiate between the strong and weak ligands and hence the same is explained later by Crystal Field Theory. It is mainly based on the splitting of metal d orbitals in presence of ligands. The Jahn Teller theorem and its applications are also discussed accordingly. The limitations of Crystal Field Theory along with nephelauxetic effect are also discussed in detail. The different aspects

NSOU | CC-CH-07 131 for stabilization of unusually high and low oxidation states of 3d series elements is discussed. Elementary idea about molecular orbital theory is given. Transition metals are responsible for colours in substances. This is being explained using the Newton's colour disc. The CT, L-S and R-S ground state term symbols are discussed along with Orgel diagrams. Their explanation and diagrams are also provided in this chapter. 4.15 Self Assessment Questions 1. State Valence bond theory. 2. Predict the hybridisation, shape and nature of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ . 3. State the limitations of Valence bond theory. 4. State crystal field theory. 5. Write the factors affecting crystal field theory. 6. Show crystal field splitting in octahedral and tetrahedral fields. 7. What do you mean by Jahn Teller distortion? 8. State the limitations of crystal field theory. 9. What is nephelauxetic effect? 10. Write the main features of MOT. 11. Why do transition metals and their complexes show colours? 12. State the Selection Rules for Electronic Transitions. 13. Write the statement of Laporte rule. 14. Write the statement for spin selection rule. 15. What do you mean by charge transfer spectra? 16. How can the CT bands be identified? 17. Write the differences between LMCT and MLCT. 18. What do you mean by R-S coupling? 19. What do you mean by Orgel diagrams? 20. Draw the Orgel diagrams for d 1, d 4, d 6, and d 4 configurations.

NSOU I CC-CH-07 132 21. Draw the Orgel diagrams for d 2 , d 3 , d 7 , and d 8 configurations. Answer 1. See section 4.1 2. See section 4.1 3. See section 4.1 4. See section 4.2 5. See section 4.2 6. See section 4.2 7. See section 4.3 8. See section 4.4 9. See section 4.5 10. See section 4.7 11. See section 4.9 12. See section 4.9 13. See section 4.6 14. See section 4.9 15. See section 4.10 16. See section 4.10 17. See section 4.10 18. See section 4.11 19. See section 4.12 20. See section 4.12 21. See section 4.12 4.16 Further Reading 1. Essential Trend in Inorganic Chemistry, Mingos, Oxford University Press, 2004 2. Basic Inorganic Chemistry, Cotton, Wilkinson, Gans 3rd Ed. John Wiley Sons, Inc., 2004. 3. Fundamental Concepts of Inorganic Chemistry, A. K. Das and M. Das, Volume-2, First Ed., 2015.

NSOU I CC-CH-07 133 Unit 5 □□□□ Reaction Kinetics and Mechanism 5.0 Objectives 5.1 Introduction to Inorganic reaction mechanisms 5.2 Substitution reactions in square planar complexes 5.3 Trans-effect-theories and applications 5.4 Lability and inertness in octahedral complexes towards substitution reactions 5.5 Elementary concept of cis-effect 5.6 Summary 5.7 Self Assessment Questions 5.8 Further Reading 5.0 Objectives After reading this unit you can be able to know the following factors— \* Definition of substitution reaction and its application in square planar complexes. \* Trans effect theories and applications. \* Elementary concept of Cis-effect. 5.1 Introduction to Inorganic reaction mechanisms Transition metal Ions and complexes play a fundamental role in at least three areas of research: (i) bioinorganic chemistry and molecular biology, in investigating the functions of metal complex metalloproteins (ii) industrial chemistry, in exploiting metal complexes as homogeneous catalysts for the optimization of very important commercial processes, such as polymerization, hydroformylation, hydrogenation, oxidation of olefins, etc. (iii) environmental and medicinal chemistry. Understanding the mechanism of the reactions at transition metal sites is then crucial in designing new inorganic materials, developing industrial homogeneous catalysts and gaining insight into the role of metalloenzymes in biological processes and metals in medicine. The old motto "every little reaction has a mechanism all its own" appears to be incorrect because, at the present time, the mechanistic tools developed for the analysis of kinetic and extra kinetic data have proved their worth in the classification of a wide range of reaction types in coordination, organometallic and bioinorganic chemistry. A mechanism is then a predictive theoretical construction that must account for all the kinetic, spectroscopic and theoretical information currently available on a reaction. The mechanistic picture is always on trial and it can or cannot survive to future results coming 133

NSOU I CC-CH-07 134 from the use of more sophisticated experimental and theoretical techniques. In this chapter a description is reported of some fundamental reactions in transition metal chemistry that have established the pattern of reactivity on which contemporary studies are based. Monitoring the rate of a reaction occurring in solution usually requires the measure of a physical property of the system directly related to the concentration changes of reactant or products by the use of simple or of sophisticated methods. Any measurement that gives the amount of material as a function of time can be used to generate kinetic data. A variety of spectroscopic techniques are appropriate to the purpose such as ultraviolet/visible (UV/VIS) or infrared (IR) spectroscopy, fluorescence, circular dichroism (CD), nuclear magnetic resonance (NMR), etc. and the choice will depend upon the type of reaction and the rate of reaction. 5.2 Substitution reactions in square planar complexes Square planar is the common geometry for the d 8 metal ions. Much of the discussion in this section deals with Pt(II) square-planar complexes. For square planar both bond- breaking and bond making are important in the reaction mechanism and the mechanism is an associative mechanism. entering group can approach from top or bottom since sq. planar is easy to get into M L 3 L 2 L 1 X Y M L 3 L 2 L 1 X M L 3 L 2 L 1 Y Y making breaking Leaving group TbP transition state + X Stereospecific - X (leaving group) is trans to L 2 and so is Y (entering group) Incoming ligand attacks from above the square plane Plane containing Pt(II) and four ligands. Incoming ligand attacks from below the square plane

NSOU I CC-CH-07 135 Pt L 1 L 2 L 3 X Y Pt L 1 L 2 L 3 X -x Pt L 1 L 2 L 3 Y Y Initial attack by the entering group at a square planar Pt(II) centre is from above or below the plane. Nucleophile Y then coordinates to give a trigonal bipyramidal intermediate species which loses X with retention of stereochemistry. The incoming ligand approaches a vacant axial site of the square planar complex to form a square pyramidal intermediate (or transition state).

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L 1 L 2 L 3 X M L 1 L 2 L 3 X + Y Y M L 1 L 2 L 3 Y M L 1 L 2 L 3

Y X M Y X L 1 L 2 L 3 -

X Intramolecular rearrangement via a trigonal bipyramid generates a different square pyramidal structure with the incoming ligand now in the basal plane. (This motion is closely related to the Berry pseudorotation). The reaction is completed by the leaving group departing from an axial site. Note that the stereochemistry of the complex is retained during the substitution process. Therefore the substitution in square planar complexes generally proceeds by bimolecular displacement (S<sub>N</sub>2) mechanism. Examples: 1.1 Solvent 2.2 MLX L MLL X L ??? → + Factors affecting rate of Substitution: 1. Role of the Entering Group The rate of substitution is proportional to the nucleophilicity of entering group, i.e. for most reactions of Pt(II), the rate constant increases in the order: H<sub>2</sub>O < NH<sub>3</sub> < py < Br<sup>-</sup> < I<sup>-</sup> < CN<sup>-</sup>. The ordering is consistent with Pt(II) being a soft metal centre. NSOU | CC-CH-07 136 2. The Role of The Leaving Group For the reaction [Pt(dien)X] + py → [Pt(dien)(py)] + X<sup>-</sup> In H<sub>2</sub>O at 25°C the sequence of lability of X<sup>-</sup> (leaving group) is: H<sub>2</sub>O < Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup> < N<sub>3</sub><sup>-</sup> < SCN<sup>-</sup> < NO<sub>2</sub><sup>-</sup> < CN<sup>-</sup> with a spread of over 10<sup>6</sup> in rate across series. The leaving group does not affect the nucleophiles discrimination factors, only the intrinsic reactivity. The series tend to parallel the strength of the Metal-ligand bond. 3. The Nature of the Other Ligands in the Complex Trans effect (discussed later) 4. Effect of the Metal Centre The order of reactivity of a series of isovalent ions is: Ni(II) < Pd(II) < Pt(II). This order of reactivity is the same order as the tendency to form 5-coordinate complexes. More is it easier for the formation of a 5-coordinate intermediate complex, greater is the stabilization of the transition state and so the greater the bimolecular rate enhancement. 5.3 Trans effect - theories and applications The trans effect is best defined as

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the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it

or the ability of a ligand in a square planar complex to direct the replacement of the ligand trans to it. By measuring rates a series of ligands can be put into an order of decreasing trans-effect. The approximate order of decreasing trans-effect of some common ligands is: The trans effect is given as the following series: CN<sup>-</sup> < NO<sub>2</sub><sup>-</sup> < I<sup>-</sup> = SCN<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup> < py < NH<sub>3</sub> < H<sub>2</sub>O The Trans Effect in Practice 1. [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> + 2Cl<sup>-</sup> → trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] why the different isomers? 2. [PtCl<sub>4</sub>]<sup>2-</sup> + 2NH<sub>3</sub> → cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] } NSOU | CC-CH-07 137 Reaction 1 Pt NH<sub>3</sub> NH<sub>3</sub> NH<sub>3</sub> NH<sub>3</sub> Pt

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NH<sub>3</sub> Cl NH<sub>3</sub> NH<sub>3</sub> + Cl<sup>-</sup> → NH<sub>3</sub> Pt NH<sub>3</sub> Cl Cl NH<sub>3</sub> + Cl<sup>-</sup> → NH<sub>3</sub> Very good at directing incoming Cl trans to it. - trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] 3 2 2 [Pt(NH<sub>3</sub>)<sub>2</sub>Cl]<sub>3</sub> 3 + [Pt(NH<sub>3</sub>)<sub>2</sub>Cl]<sub>3</sub> 4 2 + Reaction 2 less trans directing ability than Cl<sup>-</sup>. 3 - NH<sub>3</sub> - Cl Cl Cl Pt Cl Cl + ??? → 3 - 3 NH<sub>3</sub> - Cl Cl NH<sub>3</sub> Pt Cl Cl + ??? → 3 3 Cl NH<sub>3</sub> Pt Cl

NH<sub>3</sub> [PtCl<sub>4</sub>]<sup>2-</sup> [Pt(NH<sub>3</sub>)Cl<sub>3</sub>]<sup>-</sup> cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]

Feature's: • Cl<sup>-</sup> has a greater trans directing effect than NH<sub>3</sub>. • Trans directing series Cl<sup>-</sup> < NH<sub>3</sub> • Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(II) complexes. E.g. consider the preparation of cis and trans [PtCl<sub>2</sub>l(py)]<sup>-</sup> from [PtCl<sub>4</sub>]<sup>2-</sup>, I<sup>-</sup> and py. Cl Cl

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Cl Cl Pt + I<sup>-</sup> - Cl<sup>-</sup> Cl Cl I Cl Pt + py - Cl<sup>-</sup> Cl py

I Cl Pt Higher than Cl<sup>-</sup> in the trans directing series directs py trans to it Trans [PtCl<sub>4</sub>]<sup>2-</sup> [PtCl<sub>3</sub>l]<sup>-</sup> 2- Trans-[PtCl<sub>2</sub>l(py)]<sup>-</sup>

NSOU | CC-CH-07 138 Cl Cl Cl Cl Pt +py -Cl<sup>-</sup> Cl py Cl Cl Pt +I<sup>-</sup> -Cl<sup>-</sup> Cl py I Cl Pt lower than Cl<sup>-</sup> in the trans directing series Cl<sup>-</sup> directs I<sup>-</sup> trans to it Cis [PtCl<sub>4</sub>] 2- [PtCl<sub>3</sub>(py)] - Cis-[PtCl<sub>2</sub>l(py)] - Polarization Theory: The Pt(II) cation induces a dipole in the polarizable trans- directing ligand A. The induced dipole in ligand A induces a dipole in the polarizable Pt(II) cation. The chloride anion trans to A is more easily released due to the extra repulsive forces between its negative charge and the induced dipole of the Pt(II) cation. Support for this theory is demonstrated by looking at the trans directing series. The more polarizable ligands such as SCN<sup>-</sup>, and I<sup>-</sup> and the ligands containing π-clouds e.g. CN<sup>-</sup> are high in the series, whereas less polarizable ligands such as ammonia or water are lower in the series. Additional support comes from the observation that Pt(II) complexes demonstrate a more pronounced trans effect than those of the less polarizable Pd(II) and Ni(II) cations. δ+ δ- A + + + + - - - - δ+ δ- Pt 2+ + + + + - - - - Cl<sup>-</sup> A Pt 2+ Cl<sup>-</sup> δ+ δ- A + + + + - - - - Pt 2+ Cl<sup>-</sup> Cl<sup>-</sup> to be displaced Trans directing ligand + + + + - - - - - Polarised or distorted Pt(II) ion Polarised or distorted (attraction to Pt(II) reduced due to repulsion of charges).

NSOU | CC-CH-07 139 Other contributing factors to the trans-effect: In the trigonal plane of the 5-coordinate transition state or intermediate, a π- bonding interaction can occur between a metal d-orbital (e.g. d<sub>xy</sub>) and suitable orbitals (p atomic orbitals, or molecular orbitals of p-symmetry) of ligand L<sub>2</sub> (the ligand trans to the leaving group) and Y (the entering group). These 3 ligands and the metal centre can communicate electronically through π-bonding only if they all lie in the same plane in the transition state or intermediate. This implies the 5-coordinate species must be trigonal pyramidal. Pt L<sub>1</sub> L<sub>2</sub> L<sub>3</sub> X Y Pt L<sub>2</sub> X Y trigonal bipyramidal transition state or intermediate π-bonding in the trigonal plane  
Rules: 1. It is easier to replace Cl<sup>-</sup> than most other ligands. 2. To displace some other ligands with Cl<sup>-</sup>, a huge excess of Cl<sup>-</sup> must be added. 3. If there is more than one possibility for replacing the Cl<sup>-</sup>, the one that is replaced is the one trans to the ligand higher in the series. 4. Part of the general order for the trans effect (the ability of ligands to direct trans-substitution) is : CN<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > I<sup>-</sup> > SCN<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > py > NH<sub>3</sub> > H<sub>2</sub>O 5. A strong π-acceptor e.g.

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CN<sup>-</sup> will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal

centre, and will thereby facilitate substitution at the site trans to it. The vacant π or π\* orbital of π-bonding ligands accept

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a pair of electrons from filled d-orbitals of the metal to form

metal ligand π-bond (either dπ-pπ or dπ-dπ). The formation of π-bond in the complex increases the electron density in the direction of L<sub>2</sub> and diminishes it in the direction of X trans to L<sub>2</sub>. So Pt-X bond weakens. (x = leaving group y = entering group)



NSOU I CC-CH-07 140 5.4 Lability and inertness in octahedral complexes towards substitution reactions The concept of lability and inertness was first explained by Henry Taube (Nobel Prize, 1983). He tried to understand lability by comparing the factors that govern bond strengths in ionic complexes to observations about the rates of reaction of coordination complexes. He saw some things that were surprising. Taube observed that many  $M^{+1}$  ions ( $M$  = metal) are more labile than many  $M^{3+}$  ions, in general. That is not too surprising, since metal ions function as Lewis acids and ligands function as Lewis bases in forming coordination complexes. In other words, metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly. However, there were exceptions to that general rule. For example, Taube also observed that  $Mo(V)$  compounds are more labile than  $Mo(III)$  compounds. That means there is more going on here than just charge effects. Another factor that governs ionic bond strengths is the size of the ion. Typically, ions with smaller ionic radii form stronger bonds than ions with larger radii. Taube observed that  $Al^{3+}$ ,  $V^{3+}$ ,  $Fe^{3-}$  and  $Ga^{3+}$  ions are all about the same size. All these ions exchange ligands at about the same rate. The transformation of one complex into other is determined by thermodynamic stability when the system has reached equilibrium while kinetic stability refers to the speeds at which these take place. The stability depends upon the difference in energy of the reactant and product. If the product has less energy than that of reactant, it will be more stable as compared to reactant. Thermodynamic stability of metal complexes is calculated by the overall formation constant (stability constant). The kinetic stability of the complex depends upon the activation energy of the reaction, If the activation energy barrier is low, reaction will take place at higher speed. These types of complexes are also called kinetically unstable or labile. If the activation energy barrier is high, the substance will react slowly and will be called as kinetically stabilized or inert. There is no correlation between thermodynamic and kinetic stability. Thermodynamically stable product may labile or inert and the vice versa is also true. In accordance to valence bond theory, octahedral metal-complexes can be divided into two types. A. Outer orbital complexes: Complexes with  $sp^3d^2$  hybridization are generally labile in nature. Valence bond theory proposed that the bonds in this hybridization are

NSOU I CC-CH-07 141 generally weaker than  $d^2sp^3$  and therefore they show labile character. B. Inner orbital complexes: Since  $d^2sp^3$  hybrid orbitals have six electron pairs donated by the ligands, hence these hybrid orbitals can form both inert and labile complexes. In terms of CFT any increase in the crystal field stabilization energy will make a complex labile while the decrease in CFSE will make complex inert. The calculation of CFSE is done by using the following: 1. Complexes with coordination number six should be treated as perfect octahedral even if mixed ligands are present. 2. Inter-electronic repulsive forces should be neglected 3.  $\Delta_o$  -Magnitude for reacting as well as the intermediate complexes are assumed to be same though they might have considerably different values. 4. JahnTeller distortion is to be neglected in all evidences for the lability and inertness. Table I. CFSE values of high-spin (HS) and low-spin (LS) octahedral complexes undergoing ligand displacement reactions through  $SN_1$  mechanism (Dissociation Mechanism)  $MX_5Y + Z \rightarrow MX_5Z + Y$  (Intermediate is 5-coordinate of sq. py. or tbp geometry). Configuration CFSE for CFSE for square Gain or loss of Kinetic octahedral pyramidal CFSE stability (Coordination intermediate Negative=gain No - 6) (Dq) (Coordination Positive=loss No - 5) (Dq) (Dq) d 0 0 0 0 Labile d 1 -4 -4.57 -0.57 Labile d 2 -8 9.14 -1.14 Labile d 3 -12 10 +2.00 Inert d 4 (HS) -6 -9.14 -3.14 Labile d 4 (LS) -16 -14.57 +1.4.3 Inert d 5 (HS) 0 0 0 Labile NSOU I CC-CH-07 142 d 5 (LS) -20 -19.4 +0.86 Inert d 6 (HS) -4.00 -4.57 -0.57 Labile d 6 (LS) -24 -20 +4.00 Inert d 7 (HS) -8 -9.14 -1.14 Labile d 7 (LS) -18 -19.14 -1.14 Labile d 8 -12 -10 +2.00 Inert d 9 -6 -9.14 -3.14 Labile d 10 0 0 0 Labile Table 2. CFSE values of high-spin (HS) and low spin (LS) octahedral complexes undergoing ligand displacement reactions through  $S_n2$  mechanism (Associative Mechanism)  $MX_5Y + Z \rightarrow MX_5YZ \rightarrow MX_5Z + Y$  (Intermediate is 7-coordinate). Configuration CFSE for CFSE for Gain or loss of Kinetic octahedral octahedral-wedge CFSE stability reactant intermediate Negative=gain (Coordination (Coordination Positive=loss No - 6) (Dq) No - 7) (Dq) (Dq) d 0 0 0 0 Labile d 1 4 6.08 -2.08 Labile d 2 -8 -8.68 -0.68 Labile d 3 -12 -10.20 +1.80 Inert d 4 (HS) -6 -8.79 -2.79 Labile d 4 (LS) -16 -16.26 -0.26 Labile Configuration CFSE for CFSE for square Gain or loss of Kinetic octahedral pyramidal CFSE stability (Coordination intermediate Negative=gain No - 6) (Dq) (Coordination Positive=loss No - 5) (Dq) (Dq) NSOU I CC-CH-07 143 d 5 (HS) 0 0 0 Labile d 5 (LS) -20 -18.86 +1.14 Inert d 6 (HS) -4 -6.08 -2.08 Labile d 6 (LS) -24 -20.37 +3.63 Inert d 7 (HS) -8 -8.68 -0.68 Labile d 7 (LS) -18 -18.98 -0.98 Labile d 8 -12 -10.20 +1.80 Inert d 9 -6 -8.79 -2.79 Labile d 10 0 0 0 Labile Factors affecting kinetic stability and lability of non-transition metal complexes: 1.



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Charge on the central metal ion. 2. Radii of the central metal ion. 3.

Ratio of charge to ionic size 4. Molecular geometry of the complex 5.5 Elementary concept of cis-effect Cis effect is defined as the labilization (making unstable) of CO ligands that are cis to other ligands. CO is a well-known strong pi-accepting ligand in organometallic chemistry that will labilize in the cis position when adjacent to ligands due to steric and electronic effects. The system most often studied for the cis effect is an octahedral complex  $M(CO)_5X$  where X is the ligand that will labilize a CO ligand cis to it. Unlike trans effect, where this property is most often observed in 4-coordinate square planar complexes, the cis effect is observed in 6-coordinate octahedral transition metal complexes. It has been determined that ligands that are weak sigma donors and non-pi acceptors seem to have the strongest Configuration CFSE for CFSE for Gain or loss of Kinetic octahedral octahedral-wedge CFSE stability reactant intermediate Negative=gain (Coordination Positive=loss No - 6) (Dq) No - 7) (Dq) (Dq)  
NSOU I CC-CH-07 144 cis-labilizing effects. Therefore, the cis effect has the opposite trend of the trans-effect, which effectively labilizes ligands that are trans to strong pi accepting and sigma donating ligands. M  
CO m CO X OC OC

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W

CO M CO X OC OC CO M CO CO X OC CO -CO -CO M CO Y X OC OC CO M CO CO X Y OC CO +

Y +Y Group 6 and group 7 transition metal complexes  $[M(CO)_5X]$  have been found to be the most prominent with regard to dissociation of the CO cis to ligand X. CO is a neutral ligand that donates 2 electrons to the complex, and therefore lacks anionic or cationic properties that would affect the electron count of the complex. For transition metal complexes that have the formula  $M(CO)_5X$ , group 6 metals ( $M^0$ , where the oxidation state of the metal is zero) paired with neutral ligand X, and group 7 metals ( $M^+$ , where the oxidation state of the metal is +1), paired anionic ligands, will create very stable 18 electron complexes. Transition metal complexes have 9 valence orbitals, and 18 electrons will in turn fill these valence shells, creating a very stable complex, which satisfies the 18-electron rule. The cis-labilization of 18 e- complexes suggests that dissociation of ligand X in the cis position creates a square pyramidal transition state, which lowers the energy of the  $M(CO)_4X$  complex, enhancing the rate of reaction. The scheme shows the dissociation pathway of a CO ligand in the cis and trans position to X, followed by the association of ligand Y. This is an example of a dissociative mechanism, where an 18 e- complex loses a CO ligand, making a 16 e- intermediate, and a final complex of 18 e- results from an incoming ligand inserting in place of the CO. This mechanism resembles the  $S_N1$  mechanism in organic chemistry, and applies to coordination compounds as well. The order of ligands which possess cis-labilizing effects are as follows:

NSOU | CC-CH-07 145 CO, AuPPh<sub>3</sub>, H<sup>-</sup>, SnPh<sub>3</sub>, GePh<sub>3</sub>, M(CO)<sub>n</sub> &gt; P(O)Ph<sub>3</sub> &gt; PPh<sub>3</sub> &gt; I<sup>-</sup> &gt; CH<sub>3</sub>SO<sub>2</sub><sup>-</sup>, NC<sub>5</sub>H<sub>5</sub> &gt; CH<sub>3</sub>CO &gt; Br<sup>-</sup>, NCO<sup>-</sup> &gt; Cl<sup>-</sup> &gt; NO<sub>3</sub><sup>-</sup> Anionic ligands such as F<sup>-</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, and SH<sup>-</sup> have particularly strong CO labilizing effects in [M(CO)<sub>5</sub>L]<sup>-</sup> complexes. This is because these ligands will stabilize the 16 e<sup>-</sup> intermediate by electron donation from the p-pi lone pair donor orbital. Other sulfur-containing ligands, particularly thiobenzoate, are other examples of particularly useful CO cis-labilizing ligands, which can be explained by stabilization of the intermediate that results upon CO dissociation. This can be attributed to the partial interaction of the oxygen from the thiobenzoate and the metal, which can eliminate solvent effects that can occur during ligand dissociation in transition metal complexes.

5.6 Summary Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction. The inorganic reaction mechanism and kinetics involve detailed studies about the cis and trans effects. The details of substitution reactions involved associative and dissociative mechanisms. The lability and inertness of octahedral complexes have also been discussed in this chapter.

5.7 Self Assessment Questions

1. What do you mean by inorganic reaction mechanism?
2. Explain the mechanism of substitution reactions in square planar complexes.
3. State the factors affecting rate of substitution reactions.
4. What is trans effect?
5. Mention the features of trans effect.
6. Explain lability and inertness of octahedral complexes towards substitution reactions.
7. What do you mean by cis effect?

NSOU | CC-CH-07 146 Answer Key

1. See section 5.1
2. See section 5.2
3. See section 5.2
4. See section 5.3
5. See section 5.3
6. See section 5.4
7. See section 5.5

5.8 Further Reading

1. Comprehensive Coordination Chemistry, S.P. Banerjee, Books & Allied Publication.
2. Fundamental Concepts of Inorganic Chemistry, A.K. Das and M. Das, Volume- 2, First Ed., 2015
3. Essential Trend in Inorganic Chemistry, Mingos, Oxford University Press (Ind. Ed.) 2004.





<b>2/128</b>	<b>SUBMITTED TEXT</b>	67 WORDS	<b>74% MATCHING TEXT</b>	67 WORDS
<p><math>A + A + B - B - A + B - A + B - A + A + B - A + B - A + B - A + B - B - A + A + B - B - A + B - A + B - A + A + B - A + B - A + B -</math></p>		<p><math>a^1 - a^2 + b^1 - b^2) - (4a^1 b^1 - 4a^2 b^2 + a^2 1 - a^2 2 + (a^2 1 b - a^2 2 b^2) = 0</math> i.e. <math>AX^2 + BX + C = 0</math> Where, <math>A = 4(a^1 - a^2 + b^1 - B = (4(a^1 b^1 - 4a^2 b^2 + a^2 1 - a^2 2) b^1 (4b^1) - b^2 (4a^2 + b^2)</math></p>		
<p><b>W</b> <a href="http://mpbou.edu.in/slm/mscche1p1.pdf">http://mpbou.edu.in/slm/mscche1p1.pdf</a></p>				
<b>3/128</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>95% MATCHING TEXT</b>	10 WORDS
<p>prefer octahedral holes in a closest packed lattice of chloride ions. a</p>				
<p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>				
<b>4/128</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>84% MATCHING TEXT</b>	14 WORDS
<p>Lattice Energy: It is the amount of energy required for complete separation of</p>				
<p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>				
<b>5/128</b>	<b>SUBMITTED TEXT</b>	7 WORDS	<b>70% MATCHING TEXT</b>	7 WORDS
<p>F F F F : : : F : SF 6 PF 5 F : I : F F F F : : : F : IF 7 F :</p>				
<p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>6/128</b>	<b>SUBMITTED TEXT</b>	45 WORDS	<b>76% MATCHING TEXT</b>	45 WORDS
<p><math>\psi = \psi A (1) \psi B (2) + \psi A (2) \psi B (1) + \lambda \psi A (1) \psi A (2) + \lambda \psi B (1) \psi B (2).</math></p>				
<p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>				
<b>7/128</b>	<b>SUBMITTED TEXT</b>	3 WORDS	<b>86% MATCHING TEXT</b>	3 WORDS
<p>F F F F — 6 PCl — F F F F F F F F F</p>				
<p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				

<b>8/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>42% MATCHING TEXT</b>	18 WORDS
<p>pairs. The order of repulsion varies as: lone pair-lone pair (l.p.-l.p.)&amp;lt;&amp;lt; lone pair-bond pair (l.p.-b.p.)&amp;lt;&amp;lt; bond pair-bond pair (</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>9/128</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>87% MATCHING TEXT</b>	21 WORDS
<p>C O C O C O - + + - = ↔ ≅ ↔ - :C::O C::O : :C :O: - + + - ↔ ↔</p> <p><b>SA</b> Chp01.pdf (D97925379)</p>				
<b>10/128</b>	<b>SUBMITTED TEXT</b>	7 WORDS	<b>91% MATCHING TEXT</b>	7 WORDS
<p>O - C O O - - - - O = C O - O - - - O - - C O - O - - -</p> <p><b>SA</b> Chp01.pdf (D97925379)</p>				
<b>11/128</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>less s-character and more electropositive substituents prefer hybrid orbitals having more s-character.</p> <p>less s character and more electropositive substituents 'prefer' hybrid orbitals having more s character."</p> <p><b>W</b> <a href="http://mpbou.edu.in/slm/mscche1p1.pdf">http://mpbou.edu.in/slm/mscche1p1.pdf</a></p>				
<b>12/128</b>	<b>SUBMITTED TEXT</b>	26 WORDS	<b>87% MATCHING TEXT</b>	26 WORDS
<p>in case of undissociated hydrazoic acid, structure (II) contributed less compared to the structures (I) and (III). 2 H N N N H N N N H N N N (</p> <p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>				
<b>13/128</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>88% MATCHING TEXT</b>	13 WORDS
<p>Molecular orbitals are formed by the combination of atomic orbitals of individual atoms</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				

<b>14/128</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>47% MATCHING TEXT</b>	21 WORDS
	<p><math>p \times y \times z \pi(2p, 2p) y z 2p, 2p, 2p \times y \times z \sigma^* 2s^* 2p \times \sigma^* 2p</math></p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>			
<b>15/128</b>	<b>SUBMITTED TEXT</b>	46 WORDS	<b>69% MATCHING TEXT</b>	46 WORDS
	<p><math>s 2 \sigma 2s^* 2 \sigma 2p 2 \pi 2p 4 \pi 2p^* 4</math> (18 electrons) Ne 2 : KK<math>\sigma</math>  <math>2s 2 \sigma 2s^* 2 \sigma 2p 2 \pi 2p 2 \pi 2p^* 4</math></p> <p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>			
<b>16/128</b>	<b>SUBMITTED TEXT</b>	57 WORDS	<b>76% MATCHING TEXT</b>	57 WORDS
	<p>KCl MgCl<sub>2</sub> · 6H<sub>2</sub>O, K<sub>2</sub>SO<sub>4</sub> Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 24H<sub>2</sub>O, FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O</p> <p>KCl MgCl<sub>2</sub> 6H<sub>2</sub>O. K<sub>2</sub>SO<sub>4</sub> + Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 24H<sub>2</sub>O ? K<sub>2</sub>SO<sub>4</sub> · Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 24H<sub>2</sub>O 2</p> <p><b>W</b> <a href="https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf">https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf</a></p>			
<b>17/128</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>100% MATCHING TEXT</b>	13 WORDS
	<p>show a dual behaviour i.e. it may satisfy both primary and secondary valencies. 5.</p> <p>show a dual behaviour, i.e. it may satisfy both primary and secondary valencies</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>			
<b>18/128</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>42% MATCHING TEXT</b>	27 WORDS
	<p><math>p \times y, 2p z</math> NSOU I CC-CH-07 63 <math>\pi \pi^* 2p, ^* 2p y z 2p, 2p</math>  <math>x y, 2p z 2p, 2p x y, 2p z</math></p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>			
<b>19/128</b>	<b>SUBMITTED TEXT</b>	66 WORDS	<b>40% MATCHING TEXT</b>	66 WORDS
	<p>H<sub>3</sub>NH<sub>3</sub>N Cl Cl Cl CoCl<sub>2</sub> · 6H<sub>2</sub>O or [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> Cl<sub>3</sub> 3 6 3          3+ Co NH<sub>3</sub> NH<sub>3</sub> NH<sub>3</sub> H<sub>3</sub>NH<sub>3</sub>N Cl Cl Cl Co Cl NH<sub>3</sub>          NH<sub>3</sub> H<sub>3</sub>NH<sub>3</sub>N CoCl<sub>2</sub> · 4H<sub>2</sub>O or [Co(NH<sub>3</sub>)<sub>4</sub>Cl]<sub>2</sub> Cl<sub>2</sub> 3 3 4          + Cl CoCl<sub>2</sub> · 5H<sub>2</sub>O or [Co(NH<sub>3</sub>)<sub>5</sub>Cl]</p> <p><b>SA</b> Chp01.pdf (D97925379)</p>			



<b>20/128</b>	<b>SUBMITTED TEXT</b>	34 WORDS	<b>69% MATCHING TEXT</b>	34 WORDS
<p>equal to the number of electrons in the nearest noble gas. If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.</p> <p><b>SA</b> Final Cpoy HCT-1.1.pdf (D143811609)</p>				
<b>21/128</b>	<b>SUBMITTED TEXT</b>	87 WORDS	<b>72% MATCHING TEXT</b>	87 WORDS
<p>central atom/ion in the coordination entity (sphere). They may be simple ions such as <math>\text{Cl}^-</math>, small molecules such as <math>\text{H}_2\text{O}</math> or <math>\text{NH}_3</math>, larger molecules such as <math>\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2</math> or <math>\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3</math>; or even macromolecules, such as proteins. Unidentate or monodentate ligands : When a ligand is bound to a metal ion</p> <p>central metal atom or ion in the coordination entity are called ligands. may be simple ions such as <math>\text{Br}^-</math>, small molecules such as <math>\text{H}_2\text{O}</math> or <math>\text{NH}_3</math>, larger molecules such as <math>\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2</math> or <math>\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3</math> or even macromolecules such as proteins. When a ligand is attached to a metal ion</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>22/128</b>	<b>SUBMITTED TEXT</b>	26 WORDS	<b>100% MATCHING TEXT</b>	26 WORDS
<p>through a single donor atom, as with <math>\text{Cl}^-</math>, <math>\text{H}_2\text{O}</math> or <math>\text{NH}_3</math>, the ligand is said to be unidentate.</p> <p>through a single donor atom, as with <math>\text{Cl}^-</math>, <math>\text{H}_2\text{O}</math> or <math>\text{NH}_3</math>, the ligand is said to be unidentate.</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>23/128</b>	<b>SUBMITTED TEXT</b>	46 WORDS	<b>71% MATCHING TEXT</b>	46 WORDS
<p>When a ligand can bind through two donor atoms as in <math>\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2</math> (ethane-1,2-diamine) or <math>\text{C}_2\text{O}_4^{2-}</math> (oxalate), the ligands are said to be bidentate</p> <p>when a ligand is bound through two donor atoms (in a single ligand), as in <math>\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2</math> (ethane-1,2-diamine) or <math>\text{C}_2\text{O}_4^{2-}</math> (oxalate), the ligand is said to be bidentate</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>24/128</b>	<b>SUBMITTED TEXT</b>	35 WORDS	<b>91% MATCHING TEXT</b>	35 WORDS
<p>When several donor atoms are present in a single ligand as in <math>\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3</math>, the ligand is said to be polydentate.</p> <p>when several donor atoms are present in a single ligand as in <math>\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3</math> or ethylenediaminetetraacetic acid (EDTA), the ligand is said to be polydentate.</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundenglishpc2016-2pdf-pdf-free.html</a></p>				

<b>25/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>97% MATCHING TEXT</b>	18 WORDS
	a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion		a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion	
	<b>W</b> <a href="https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf">https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf</a>			
<b>26/128</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>90% MATCHING TEXT</b>	29 WORDS
	are called ambidentate ligands. Examples of such ligands are the NO <sub>2</sub> <sup>-</sup> and SCN <sup>-</sup> ions. NO <sub>2</sub> <sup>-</sup> ion can coordinate either through nitrogen or		are called ambidentate ligands. Examples of such ligands are the NO <sub>2</sub> <sup>-</sup> and SCN <sup>-</sup> ions. NO <sub>2</sub> <sup>-</sup> ion can coordinate through either the nitrogen or	
	<b>W</b> <a href="https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf">https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf</a>			
<b>27/128</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>97% MATCHING TEXT</b>	20 WORDS
	oxygen to a central metal atom/ion. Similarly. SCN <sup>-</sup> ion can coordinate through the sulphur or nitrogen atom.		oxygen atoms to a central metal atom/ion. Similarly, SCN <sup>-</sup> ion can coordinate through the sulphur or nitrogen atom.	
	<b>W</b> <a href="https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf">https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf</a>			
<b>28/128</b>	<b>SUBMITTED TEXT</b>	31 WORDS	<b>58% MATCHING TEXT</b>	31 WORDS
	Coordination number : The coordination number of a metal ion or atom in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded		Coordination compound 5 The coordination number (CN) CN of a metal ion in a complex is defined as the number of ligand donor atoms to which the metal is directly bonded. [	
	<b>W</b> <a href="https://slideplayer.com/slide/6819642/">https://slideplayer.com/slide/6819642/</a>			
<b>29/128</b>	<b>SUBMITTED TEXT</b>	34 WORDS	<b>65% MATCHING TEXT</b>	34 WORDS
	The cation is named first in both positively and negatively charged coordination entities. 2. The ligands are named in an alphabetical order before the name of the central atom/ion. The prefixes di, tri, etc. are		The cation is named first in both positively and negatively charged coordination complexes. 3. dissimilar ligands are named in an alphabetical order before the name of central metal atom or ion. 4. For more than one similar the prefixes di, tri, tetra, are	
	<b>W</b> <a href="https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20%20...">https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20%20...</a>			

<b>30/128</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>91% MATCHING TEXT</b>	21 WORDS
<p>Names of the anionic ligands end in –o, those of neutral ligands are the same except H<sub>2</sub>O</p>		<p>Names of the anionic ligands end in –o and those of neutral ligands are the same except aqua for H<sub>2</sub>O,</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>31/128</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>91% MATCHING TEXT</b>	29 WORDS
<p>Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. 5. When the names of the ligands include a numerical prefix,</p>		<p>Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>32/128</b>	<b>SUBMITTED TEXT</b>	36 WORDS	<b>83% MATCHING TEXT</b>	36 WORDS
<p>Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis (.). 7. If the complex ion is a cation, the metal is named same as the element. 8.</p>		<p>Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal. (vi) 6 Coordination Compounds (vii) (viii) (If the complex ion is a cation, the metal is named same as the element.</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>33/128</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>100% MATCHING TEXT</b>	19 WORDS
<p>If the complex ion is an anion, the name of the metal ends with the suffix. –ate. 9. For</p>		<p>If the complex ion is an anion, the name of the metal ends with the suffix - ate. For</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>34/128</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>100% MATCHING TEXT</b>	14 WORDS
<p>The neutral complex molecule is named similar to that of the complex cation. 11.</p>		<p>The neutral complex molecule is named similar to that of the complex cation.</p>		
<p><b>W</b> <a href="https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf">https://kupdf.net/download/resonance-booklet-of-coordination-compounds_5a5447a3e2b6f51a7fb09d1f_pdf</a></p>				

<b>35/128</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>a central metal atom or ion bonded to a fixed number of ions or molecules</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>36/128</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>93% MATCHING TEXT</b>	23 WORDS
<p>The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium.</p> <p><b>W</b> <a href="https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;%2">https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;%2</a> ...</p>				
<b>37/128</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>63% MATCHING TEXT</b>	21 WORDS
<p>the larger the stability constant, the higher the proportion of ML<sub>4</sub> that exists in solution. Free metal ions</p> <p><b>W</b> <a href="https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c">https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c</a> ...</p>				
<b>38/128</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>62% MATCHING TEXT</b>	16 WORDS
<p>M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L,</p> <p><b>W</b> <a href="https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c">https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c</a> ...</p>				
<b>39/128</b>	<b>SUBMITTED TEXT</b>	53 WORDS	<b>59% MATCHING TEXT</b>	53 WORDS
<p>and write four stability constants as follows: <math>1 \text{ [ML] M L ML; } K \text{ [M][L] } + = f \text{ } 2 \text{ } 2 \text{ } 2 \text{ [ML] ML L ML; } K \text{ [ML][L] } + = f \text{ } 3 \text{ } 2 \text{ } 3 \text{ } 3 \text{ } 2 \text{ [ML] ML L ML; } K \text{ [ML][L] } + = f \text{ } 4 \text{ } 3 \text{ } 4 \text{ } 4 \text{ } 3 \text{ [ML] ML L ML; } K \text{ [ML][L] } + = f</math> where <math>K_1, K_2, \dots</math> are</p> <p><b>W</b> <a href="https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c">https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c</a> ...</p>				

<b>40/128</b>	<b>SUBMITTED TEXT</b>	46 WORDS	<b>30% MATCHING TEXT</b>	46 WORDS
<p>the stability constants as : <math>1 [ML] M L ML \beta [M][L] + = f 2 2</math>  <math>2 2 [ML] M 2L ML \beta [M][L] + = f 3 3 3 3 [ML] M 3L ML \beta</math>  <math>[M][L] + = f 4 4 4 4 [ML] M 4L ML \beta [M][L] + = f</math> where <math>\beta</math>  <math>1, \beta 2</math> etc. are called overall stability constants.</p>		<p>the four stability constants as follows: <math>?? ? ?? ? 1 M + L</math>  <math>ML K = M L ? ? ? ? ? 2 2 2 ML + L ML K = ML / ML L ? ? ?</math>  <math>?? ? 2 3 3 3 2 ML + L ML K = ML / ML L ? ? ? ? ? 3 4 4 4 3</math>  <math>ML + L ML K = ML L</math> where <math>1 2 K, K,</math> etc are known as  stepwise stability constants.</p>		
<b>W</b>	<a href="https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c...">https://www.vedantu.com/content-files-downloadable/revision-notes/cbse-class-12-chemistry-notes-c ...</a>			

<b>41/128</b>	<b>SUBMITTED TEXT</b>	33 WORDS	<b>100% MATCHING TEXT</b>	33 WORDS
<p><math>Co(H 2 NCH 2 CH 2 NH 2 ) 3 ] 2 (SO 4 ) 3</math>  tris(ethylenediamine)cobalt(III) sulfate 5.</p>				
<b>SA</b>	<a href="#">Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</a>			

<b>42/128</b>	<b>SUBMITTED TEXT</b>	58 WORDS	<b>97% MATCHING TEXT</b>	58 WORDS
<p>Many essential biological chemicals are chelates.  Chelates play important roles in oxsgen transport and in  photosynthesis. Furthermore, many biological catalysts  (enzymes) are chelates. In addition to their significance in  living organisms, chelates are also economically  important, both as products in themselves and as agents  in the production of other chemicals. A chelate is a  chemical compound composed of a metal ion</p>				
<b>SA</b>	<a href="#">Module-1 Chemistry final (1).docx (D81135194)</a>			

<b>43/128</b>	<b>SUBMITTED TEXT</b>	38 WORDS	<b>100% MATCHING TEXT</b>	38 WORDS
<p>and a chelating agent. A chelating agent is a substance  whose molecules can form several bonds to a single  metal ion. In other words, a chelating agent is a  multidentate ligand. An example of a simple chelating  agent is ethylenediamine (</p>				
<b>SA</b>	<a href="#">Module-1 Chemistry final (1).docx (D81135194)</a>			

<b>44/128</b>	<b>SUBMITTED TEXT</b>	88 WORDS	<b>63% MATCHING TEXT</b>	88 WORDS
<p>A single molecule of ethylenediamine can form two bonds to a transitionmetal ion such as nickel (II), Ni<sup>2+</sup>. The bonds form between the metal ion and the nitrogen atoms of - ethylenediamine. The nickel(II) ion can form six such bonds (coordination number 6), so a maximum of three ethylenediamine molecules can be attached to one Ni<sup>2+</sup> ion.</p> <p>NSOU   CC-CH-07 92 CH -NH 2 2 CH -NH 2 2 OH Ni OH 2 2    OH 2 OH 2 2+ CH -NH 2 2 CH -NH 2 2 OH Ni OH 2 2    NH C 2 - H 2 2+ NH CH 2 2 - CH -NH 2 2 CH -</p>				
<p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				
<b>45/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>51% MATCHING TEXT</b>	18 WORDS
<p>C-H H-C = = H-C C C = H C C = H C = H C = H C = H C H C = C H = C C H C H</p>				
<p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>46/128</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>75% MATCHING TEXT</b>	15 WORDS
<p>CH -CH -N-CH -C 2 2 2 2 :: O HO = : CH 2 C O HO : CH 2 CH 2 N CH 2 C O O CH 2 C O O N CH 2 C O = CH 2 C O</p>				
<p><b>W</b> <a href="https://theuranium.org/content-images/01-coordination-complex-compounds-plus2-2nd-year.pdf">https://theuranium.org/content-images/01-coordination-complex-compounds-plus2-2nd-year.pdf</a></p>				
<b>47/128</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>50% MATCHING TEXT</b>	24 WORDS
<p>H H-C = = H-C C C = H C 2 C C = H C = CH 2 C = Ch 3 C = CH 3 C CH =CH 2 C = C</p>				
<p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>48/128</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>94% MATCHING TEXT</b>	25 WORDS
<p>Coordination isomerism : This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.</p> <p>Coordination isomerism This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex,</p>				
<p><b>W</b> <a href="https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;%20...">https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;%20...</a></p>				

<b>49/128</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>75% MATCHING TEXT</b>	25 WORDS
<p>isomerism : This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>		<p>isomerism : This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand</p>		
<b>50/128</b>	<b>SUBMITTED TEXT</b>	35 WORDS	<b>95% MATCHING TEXT</b>	35 WORDS
<p>This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>		<p>This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. For example,</p>		
<b>51/128</b>	<b>SUBMITTED TEXT</b>	112 WORDS	<b>93% MATCHING TEXT</b>	112 WORDS
<p>EDTA is a versatile chelating agent. It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. EDTA is frequently used in soaps and detergents, because it forms complexes with calcium and magnesium ions. These ions are in hard water and interfere with the cleaning action of soaps and detergents. EDTA binds to them, sequestering them and preventing their interference. In the calcium complex. <math>[\text{Ca}(\text{EDTA})]^{2-}</math>, EDTA is a tetradentate ligand, and chelation involves the two nitrogen atoms and two oxygen atoms in separate carboxyl (<math>-\text{COO}^-</math>) groups. EDTA is also used extensively as a stabilizing agent in the food industry.</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				
<b>52/128</b>	<b>SUBMITTED TEXT</b>	40 WORDS	<b>59% MATCHING TEXT</b>	40 WORDS
<p><math>\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}</math> (grey-green) and <math>[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}</math> (green) E. Ligand isomerism: Some</p> <p><b>SA</b> UnitIII-CoordinationCompunds4.pdf (D17589551)</p>				

<b>53/128</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>47% MATCHING TEXT</b>	42 WORDS
<p>rise to coordination position isomerism. (H 3 N) 4 Co III            NH<sub>2</sub>O<sub>2</sub>Co IV (NH)<sub>3</sub>2Cl<sub>2</sub>+ 2 and Cl(NH)<sub>3</sub>3Co III            NH<sub>2</sub>O<sub>2</sub>Co Cl</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>54/128</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>58% MATCHING TEXT</b>	14 WORDS
<p>NH<sub>3</sub>ClCo NH<sub>3</sub>NH<sub>3</sub>ClCl fac-isomer NH<sub>3</sub>Co NH<sub>3</sub>Cl NH<sub>3</sub>4Cl<sub>2</sub>]Cl.NH<sub>3</sub>(2) [Co(NH<sub>3</sub>)<sub>4</sub>Cl]Cl<sub>2</sub>. NH<sub>3</sub>(3)            Cl mer-isomer NH<sub>3</sub>Cl [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>(4) [Co(NH<sub>3</sub>)<sub>3</sub>Cl]<sub>3</sub>.2</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>55/128</b>	<b>SUBMITTED TEXT</b>	28 WORDS	<b>87% MATCHING TEXT</b>	28 WORDS
<p>Optical isomerism : Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers. The molecules or ions that cannot be superimposed are called chiral.</p> <p>optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral.</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>56/128</b>	<b>SUBMITTED TEXT</b>	42 WORDS	<b>90% MATCHING TEXT</b>	42 WORDS
<p>The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.</p> <p>The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, ? to the left).            Octahedral complex : Optical isomerism is common in octahedral complexes involving didentate ligands.</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>57/128</b>	<b>SUBMITTED TEXT</b>	38 WORDS	<b>36% MATCHING TEXT</b>	38 WORDS
<p>Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] and [pt (NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. Pt HN<sub>3</sub>HN<sub>3</sub>Cl            Cl cis ° Pt HN<sub>3</sub>NH<sub>3</sub>Cl Cl trans ° Co NH<sub>3</sub>Cl cis + Cl NH<sub>3</sub>            3 NH<sub>3</sub>NH<sub>3</sub>Co NH<sub>3</sub>Cl</p> <p><b>SA</b> Chp01.pdf (D97925379)</p>				



<b>58/128</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>92% MATCHING TEXT</b>	20 WORDS
<p>and structures of vital components of biological systems. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.</p>		<p>and structures of vital components of biological systems. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry. 2.1</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>59/128</b>	<b>SUBMITTED TEXT</b>	20 WORDS	<b>59% MATCHING TEXT</b>	20 WORDS
<p>to explain the nature of Coordination Compoundsgenerally three theoriesare considered –Valence bond theory (VBT), crystal field theory (CFT), and molecular orbital theory (</p>		<p>to explain the nature of bonding in coordination compounds; these are valence bond theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>60/128</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>75% MATCHING TEXT</b>	19 WORDS
<p>According to this theory, the metal atom or ion under the influence of ligands can use its (ns, np</p>		<p>According to the Valence Bond Theory (VBT), the metal atom or ion under the influence of the ligands can use its (n-1)d, ns, np</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>61/128</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>73% MATCHING TEXT</b>	17 WORDS
<p>to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and</p>		<p>to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>62/128</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>91% MATCHING TEXT</b>	16 WORDS
<p>These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.</p>		<p>These hybrid orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				

<b>63/128</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>100% MATCHING TEXT</b>	29 WORDS
<p>In the diamagnetic octahedral complex. <math>[\text{Co}(\text{NH}_3)_6]^{3+}</math>, the cobalt ion is in +3 oxidation state and has the</p>		<p>In the diamagnetic octahedral complex, <math>[\text{Co}(\text{NH}_3)_6]^{3+}</math>, the cobalt ion is in +3 oxidation state and has the</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>64/128</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>81% MATCHING TEXT</b>	16 WORDS
<p>all the four ligands are in the same plane and hence have a plane of symmetry</p>				
<p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>65/128</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>100% MATCHING TEXT</b>	14 WORDS
<p>The complex has octahedral geometry and is diamagnetic because of the absence of unpaired</p>		<p>the complex has octahedral geometry and is diamagnetic because of the absence of unpaired</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>66/128</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>the inner d orbital (3d) is used in hybridisation. the complex, [</p>		<p>the inner d-orbital (3d) is used in hybridisation, the complex</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>67/128</b>	<b>SUBMITTED TEXT</b>	14 WORDS	<b>100% MATCHING TEXT</b>	14 WORDS
<p>is called an inner orbital or low spin or spin paired complex. The</p>		<p>is called an inner orbital or low spin or spin paired complex. The</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>68/128</b>	<b>SUBMITTED TEXT</b>	27 WORDS	<b>97% MATCHING TEXT</b>	27 WORDS
<p>uses outer orbital (4d) in hybridisation (<math>sp^3d^2</math>). It is thus called outer orbital or high spin or spin free complex.</p>		<p>uses outer orbital (4d) in hybridisation (<math>sp^3d^2</math>); it is thus called as outer orbital or high spin or spin free complex.</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				

<b>69/128</b>	<b>SUBMITTED TEXT</b>	28 WORDS	<b>81% MATCHING TEXT</b>	28 WORDS
<p>NiCl<sub>4</sub>]<sup>2-</sup>. Here nickel is in +2 oxidation state and the ion has the outer electronic configuration 3d<sup>8</sup> 4</p>		<p>NiCl<sub>4</sub>]<sup>2-</sup>, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d<sup>8</sup>.</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>70/128</b>	<b>SUBMITTED TEXT</b>	22 WORDS	<b>89% MATCHING TEXT</b>	22 WORDS
<p>The compound is paramagnetic since it contains two unpaired electrons. Similarly, [Ni(CO)<sub>4</sub>] has tetrahedral geometry but is diamagnetic</p>		<p>The compound is paramagnetic since it contains two unpaired electrons. Similarly complex [Ni(CO)<sub>4</sub>] has tetrahedral geometry and is diamagnetic</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>71/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>100% MATCHING TEXT</b>	18 WORDS
<p>Ni(CN)<sub>4</sub>]<sup>2-</sup>. Here nickel is in +2 oxidation state and has</p>		<p>Ni(CN)<sub>4</sub>]<sup>2-</sup> (here nickel is in +2 oxidation state and has</p>		
<p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>72/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>85% MATCHING TEXT</b>	18 WORDS
<p>Six pairs of electrons, one from each NH<sub>3</sub>, molecule, occupy the six hybrid orbitals.</p>				
<p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>73/128</b>	<b>SUBMITTED TEXT</b>	29 WORDS	<b>79% MATCHING TEXT</b>	29 WORDS
<p>explains the formation, structures and magnetic behaviour of coordination compounds, it has many limitations: 1. It involves a number of assumptions. 2. It does not give quantitative interpretation of magnetic data. 3.</p>				
<p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				

<b>74/128</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>98% MATCHING TEXT</b>	25 WORDS
<p>It does not explain the colour exhibited by coordination compounds. 7. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				
<b>75/128</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>85% MATCHING TEXT</b>	16 WORDS
<p>and the ligands are purely electrostatic (ionic). The ligands are regarded as point charges or point dipoles</p> <p>and the ligands is purely electrostatic(ionic). The ligands are regarded as point charges(ionic ligands) or point dipoles{</p> <p><b>W</b> <a href="https://theuranium.org/content-images/01-coordination-complex-compounds-plus2-2nd-year.pdf">https://theuranium.org/content-images/01-coordination-complex-compounds-plus2-2nd-year.pdf</a></p>				
<b>76/128</b>	<b>SUBMITTED TEXT</b>	24 WORDS	<b>100% MATCHING TEXT</b>	24 WORDS
<p>It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes. It does not distinguish between weak and strong ligands. 4.3</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				
<b>77/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>60% MATCHING TEXT</b>	18 WORDS
<p>metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>78/128</b>	<b>SUBMITTED TEXT</b>	9 WORDS	<b>75% MATCHING TEXT</b>	9 WORDS
<p>of the d-orbitals in spherical crystal field Splitting of d-orbitals in tetrahedral</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				

<b>79/128</b>	<b>SUBMITTED TEXT</b>	105 WORDS	<b>71% MATCHING TEXT</b>	105 WORDS
<p>small <math>\Delta</math> to large <math>\Delta</math>): I – Br – &amp;gt; S 2– &amp;gt; SCN – &amp;gt; Cl – NO 3 – &amp;gt; N 3 – &amp;gt; F – &amp;gt; OH – &amp;gt; C 2 O 4 2– &amp;gt; H 2 O &amp;gt; NCS – &amp;gt; CH 3 CN &amp;gt; py &amp;gt; NH 3 &amp;gt; en &amp;gt; 2,2-bipyridine &amp;gt; phen &amp;gt; NO 2 – &amp;gt; PPh 3 &amp;gt; CN – &amp;gt; CO</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>80/128</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>Ligands which cause a large splitting <math>\Delta</math> of the d-orbitals</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>81/128</b>	<b>SUBMITTED TEXT</b>	43 WORDS	<b>61% MATCHING TEXT</b>	43 WORDS
<p>as strong-field ligands such as CN – and CO from the spectrochemical series. In complexes with these ligands, it is unfavourable to put electrons into the high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>82/128</b>	<b>SUBMITTED TEXT</b>	50 WORDS	<b>89% MATCHING TEXT</b>	50 WORDS
<p>For example. NO 2 – is a strong-field ligand and produces a large <math>\Delta</math>. The octahedral ion <math>[\text{Fe}(\text{NO}_2)_6]^{3-}</math>, which has 5 d-electrons. would have the all the five electrons in the t 2 g level.</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				

83/128	SUBMITTED TEXT	82 WORDS	95% MATCHING TEXT	82 WORDS
	<p>ligands (like I – and Br – ) which cause a small splitting <math>\Delta</math> of the d- orbitals are referred to as weak-field ligands. In this case, it is easier to put electrons into the higher energy set of orbitals than it is to put two into the same low-energy orbital, because two electrons in the same orbital repel each other. So, one electron is put into each of the five d-orbitals in accordance with Hund's rule, and "high spin" complexes (</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>			
84/128	SUBMITTED TEXT	35 WORDS	72% MATCHING TEXT	35 WORDS
	<p>For example, Br – is a weak-field ligand and produces a small <math>\Delta_{oct}</math>. So, the ion <math>[FeBr_6]^{3-}</math>, again with five d-electrons, would have all five orbitals (</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>			
85/128	SUBMITTED TEXT	63 WORDS	76% MATCHING TEXT	63 WORDS
	<p>the fourth electron enters one of the <math>e_g</math> orbitals giving the configuration <math>t_{2g}^3 e_g^1</math>. Ligands for which <math>\Delta_o &gt; P</math> are known as weak field ligands and form high spin complexes, whereas, if <math>\Delta_o &lt; P</math>, it becomes more energetically favourable for the fourth electron to occupy a <math>t_{2g}</math> orbital</p> <p><b>W</b> <a href="https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;2">https://www.spsrohini.com/sites/default/files/12%20Chemistry-Coordination%20Compounds-Notes%20&amp;2 ...</a></p>		<p>the fourth electron enters one of the <math>e_g</math> orbitals giving the configuration <math>t_{2g}^3 e_g^1</math>. Ligands for which <math>\Delta_o &gt; P</math> are known as weak field ligands and form high spin complexes. If <math>\Delta_o &lt; P</math>, it becomes more energetically favourable for the fourth electron to occupy a <math>t_{2g}</math> orbital</p>	
86/128	SUBMITTED TEXT	25 WORDS	100% MATCHING TEXT	25 WORDS
	<p>configuration <math>t_{2g}^4 e_g^0</math>. Ligands which produce this effect are known as strong field ligands and form low spin complexes</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>		<p>configuration <math>t_{2g}^4 e_g^0</math>. Ligands which produce this effect are known as strong field ligands and form low spin complexes.</p>	

<b>87/128</b>	<b>SUBMITTED TEXT</b>	40 WORDS	<b>91% MATCHING TEXT</b>	40 WORDS
<p>In order for low spin to occur, the energy cost of placing an electron into an already singly occupied orbital must be less than the cost of placing the additional electron into an lg orbital at an energy cost of <math>\Delta</math>.</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>88/128</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>If the energy-required to pair two electrons is greater than</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>89/128</b>	<b>SUBMITTED TEXT</b>	53 WORDS	<b>92% MATCHING TEXT</b>	53 WORDS
<p>The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the d-orbitals are split in a ligand field (as described above), some of them become lower in energy than before</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>90/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>100% MATCHING TEXT</b>	18 WORDS
<p>For example, in an octahedral case, the t<sub>2g</sub> set becomes lower in energy</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>91/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>100% MATCHING TEXT</b>	18 WORDS
<p>if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				

92/128	SUBMITTED TEXT	251 WORDS	35% MATCHING TEXT	251 WORDS
<p>d 1 t 2 g 1 eg 0 0.4 Δ 0 t 2 g 1 eg 0 0.4 Δ 0 e 1 t 2 0 0.6 Δ t  d 2 t 2 g 2 eg 0 0.8 Δ 0 t 2 g 2 eg 0 0.8 Δ 0 e 2 t 2 0 1.2 Δ t  d 3 t 2 g 3 eg 0 1.2 Δ 0 t 2 g 3 eg 0 1.2 Δ 0 e 2 t 2 1 0.8 Δ t  d 4 t 2 g 3 eg 1 0.6 Δ 0 t 2 g 4 eg 0 1.6 Δ 0 e 2 t 2 2 0.4 Δ t  NSOU I CC-CH-07 112 d 5 t 2 g 3 eg 2 0.0 Δ 0 t 2 g 5 eg 0  2.0 Δ 0 e 2 t 2 3 0.0 Δ t d 6 t 2 g 4 eg 2 0.4 Δ 0 t 2 g 6 eg  0 2.4 Δ 0 e 3 t 2 3 0.6 Δ t d 7 t 2 g 5 eg 2 0.8 Δ 0 t 2 g 6 eg  1 1.8</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				

93/128	SUBMITTED TEXT	103 WORDS	51% MATCHING TEXT	103 WORDS
<p>d 8 t 2 g 6 eg 2 1.2 Δ 0 t 2 g 6 eg 2 1.2 Δ 0 e 4 t 2 4 0.8 Δ t  d 9 t 2 g 6 eg 3 0.6 Δ 0 t 2 g 6 eg 3 0.6 Δ 0 e 4 t 2 5 0.4 Δ t  d 10 t 2 g 6 eg 4 0.0 Δ 0 t 2 g 6 eg 4 0.0</p> <p><b>SA</b> Module-1 Chemistry final (1).docx (D81135194)</p>				

94/128	SUBMITTED TEXT	91 WORDS	95% MATCHING TEXT	91 WORDS
<p>postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," with regard to its electronic state. This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecraft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy. "This is most commonly observed with transition metal octahedral complexes.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				

95/128	SUBMITTED TEXT	11 WORDS	100% MATCHING TEXT	11 WORDS
<p>However, it can be observed in tetrahedral compounds as well.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				



96/128	SUBMITTED TEXT	58 WORDS	100% MATCHING TEXT	58 WORDS
	<p>The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>			
97/128	SUBMITTED TEXT	99 WORDS	95% MATCHING TEXT	99 WORDS
	<p>For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t<sub>2g</sub> (d<sub>xz</sub>, d<sub>yz</sub>, d<sub>xy</sub>) and e<sub>g</sub> (d<sub>z<sup>2</sup></sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub>). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the ligand bonds.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>			
98/128	SUBMITTED TEXT	3 WORDS	86% MATCHING TEXT	3 WORDS
	<p>M L L L L L L Elongated M L L L L L L</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>			
99/128	SUBMITTED TEXT	12 WORDS	100% MATCHING TEXT	12 WORDS
	<p>the axial bonds are longer than the equatorial bonds. For a compression (</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>			

<b>100/128</b>	<b>SUBMITTED TEXT</b>	61 WORDS	<b>100% MATCHING TEXT</b>	61 WORDS
<p>it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn- Teller effect to be observed.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>101/128</b>	<b>SUBMITTED TEXT</b>	26 WORDS	<b>37% MATCHING TEXT</b>	26 WORDS
<p>d , d x 2 -y 2 z 2 Δ d d xy yz d xz E - - - - - z x y d d x 2            -y 2 z 2 d d d xy xz yz - - - - - z z 2 d d d d x 2            -y 2</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>102/128</b>	<b>SUBMITTED TEXT</b>	23 WORDS	<b>97% MATCHING TEXT</b>	23 WORDS
<p>Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, (</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>103/128</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>100% MATCHING TEXT</b>	12 WORDS
<p>while the orbitals without a z component are destabilized (higher in energy).</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>104/128</b>	<b>SUBMITTED TEXT</b>	50 WORDS	<b>95% MATCHING TEXT</b>	50 WORDS
<p>This is due to the dxy and d x 2 -y 2 orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d x 2 -y 2 orbital is antibonding, it is expected to increase in energy due to elongation. The</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				

<b>105/128</b>	<b>SUBMITTED TEXT</b>	11 WORDS	<b>100% MATCHING TEXT</b>	11 WORDS
<p>orbital is still nonbonding, but is destabilized due to the interactions.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>106/128</b>	<b>SUBMITTED TEXT</b>	10 WORDS	<b>100% MATCHING TEXT</b>	10 WORDS
<p>octahedral compounds. A classic example is that of copper(II) fluoride.</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>107/128</b>	<b>SUBMITTED TEXT</b>	117 WORDS	<b>100% MATCHING TEXT</b>	117 WORDS
<p>indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than there is in the respective <math>M^{n+}</math> gaseous metal ion, which in turn implies that the size of the orbital is larger in the complex. This electron cloud expansion effect may occur for one (or both) of two reasons. One is that the effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d-orbitals can expand slightly. The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals. The</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>108/128</b>	<b>SUBMITTED TEXT</b>	38 WORDS	<b>68% MATCHING TEXT</b>	38 WORDS
<p>The reduction of B from its free ion value is given as complex free ion(gaseous) <math>B \beta B =</math> Experimentally, it is observed that size of the nephelauxetic parameter always follows a certain trend with respect to the nature of the ligands present. The</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				

<b>109/128</b>	<b>SUBMITTED TEXT</b>	17 WORDS	<b>58% MATCHING TEXT</b>	17 WORDS
<p>Mn(II) &amp;gt; Ni(II) ≈ Co(II) &amp;gt; Mo(II) &amp;gt; Re(IV) &amp;gt; Fe(III) &amp;gt; Ir(III) &amp;gt; Co(III) &amp;gt; Mn(IV)</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>110/128</b>	<b>SUBMITTED TEXT</b>	15 WORDS	<b>100% MATCHING TEXT</b>	15 WORDS
<p>s orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The</p> <p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>111/128</b>	<b>SUBMITTED TEXT</b>	18 WORDS	<b>70% MATCHING TEXT</b>	18 WORDS
<p>t u 1 e g t 2 g e* g a* 1 g t* 1 u t u 1 a g 1 e + t g 2 g a g, e, t u 1</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>112/128</b>	<b>SUBMITTED TEXT</b>	19 WORDS	<b>58% MATCHING TEXT</b>	19 WORDS
<p>t g = d d d e = d d , d 1 1 x y z 2 xy, yz, zx g x2, y2</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>113/128</b>	<b>SUBMITTED TEXT</b>	12 WORDS	<b>100% MATCHING TEXT</b>	12 WORDS
<p>e* g t* 2 g Δ 0 t 2 g t 2 g t 2 g (</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>114/128</b>	<b>SUBMITTED TEXT</b>	31 WORDS	<b>89% MATCHING TEXT</b>	31 WORDS
<p>if a molecule is centrosymmetric, transitions within a given set of p or d orbitals (i.e., those that only involve a redistribution of electrons within a given subshell) are forbidden. Allowed transitions are</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				

**115/128 SUBMITTED TEXT** 12 WORDS **87% MATCHING TEXT** 12 WORDS

However, forbidden transitions are allowed if the centre of symmetry is disrupted,

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**116/128 SUBMITTED TEXT** 17 WORDS **97% MATCHING TEXT** 17 WORDS

Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions, such

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**117/128 SUBMITTED TEXT** 231 WORDS **48% MATCHING TEXT** 231 WORDS

d 1, d 9 2 D - d 2 , d 8 3 F 3 P, 1 G, 1 D. 1 S d 3 , d 7 4 F 4 P, 2 H, 2 G, 2 F, 2 D 1 , 2 D. 2 P d 4 , d 6 5 D 3 H, 3 G, 2 F 1 , 3 F, 3 D, 3 P 1 , 3 P, 1 I, 1 G 1 , 1 G, 1 F, 1 I, 1 D 1 , 1 D, 1 S, 1 S d 5 6 S 4 G, 4 F, 4 D, 4 P, 2 I, 2 G 1 , 2 H, 2 G, 2 F 1 , 2 F. 2 D 1 , 2 D. 2 P, 2 S The

d 7 d 4 , d 6 d 5 2 D 3 F 4 F 5 D 6 S 3 P, 1 G, 1 D, 1 S 4 P, 2 H, 2 G, 3 F, 2 x 2 D, 2 P 3 H, 3 G, 2 x 3 F, 3 D, 2 x 3 P, 1 I, 2 x 1 G, 1 F, 2 x 1 D, 2 x 1 S 4 G, 4 F, 4 D, 4 P, 2 I, 2 H, 2 G, 2 x 2 F, 3 x 2 D, 2 P, 2 S 92 the

**W** <http://mpbou.edu.in/slm/mscche1p1.pdf>

**118/128 SUBMITTED TEXT** 22 WORDS **92% MATCHING TEXT** 22 WORDS

vibronic coupling. Through such asymmetric vibrations, transitions that would theoretically be forbidden, such as a  $d \rightarrow d$  transition, are weakly allowed.

**SA** Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)

<b>119/128</b>	<b>SUBMITTED TEXT</b>	97 WORDS	<b>99% MATCHING TEXT</b>	97 WORDS
<p>Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams. They are named after their creator, Leslie Orgel. Orgel diagrams are restricted to only weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams; also, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry designations.</p>				
<p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>120/128</b>	<b>SUBMITTED TEXT</b>	89 WORDS	<b>99% MATCHING TEXT</b>	89 WORDS
<p>In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are two Orgel diagrams, one for d 1 , d 4 , d 6 and d 9 and the other with d 2 , d 3 , d 7 and d 8 configurations.</p>				
<p><b>SA</b> MCHE-12.pdf (D112800504)</p>				
<b>121/128</b>	<b>SUBMITTED TEXT</b>	25 WORDS	<b>62% MATCHING TEXT</b>	25 WORDS
<p>L 1 L 2 L 3 X M L 1 L 2 L 3 X +Y Y M L 1 L 2 L 3 Y M L 1 L 2 L 3</p>				
<p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>122/128</b>	<b>SUBMITTED TEXT</b>	16 WORDS	<b>68% MATCHING TEXT</b>	16 WORDS
<p>the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it</p>				
<p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				

<b>123/128</b>	<b>SUBMITTED TEXT</b>	58 WORDS	<b>25% MATCHING TEXT</b>	58 WORDS
<p>NH<sub>3</sub> Cl NH<sub>3</sub> NH<sub>3</sub> +Cl – –NH<sub>3</sub> Pt NH<sub>3</sub> Cl Cl NH<sub>3</sub> +Cl            – –NH<sub>3</sub> Very good at directing incoming Cl trans to it. –            trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl]<sub>2</sub> [Pt(NH<sub>3</sub>)<sub>2</sub>Cl]<sub>3</sub> + [Pt(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub><sup>+</sup>            Reaction 2 less trans directing ability than Cl – . 3 – NH            –Cl Cl Cl Pt Cl Cl + ???→ 3 – 3 NH –Cl Cl NH Pt Cl Cl +            ???→ 3 3 Cl NH Pt Cl</p> <p><b>SA</b> Chp01.pdf (D97925379)</p>				
<b>124/128</b>	<b>SUBMITTED TEXT</b>	5 WORDS	<b>100% MATCHING TEXT</b>	5 WORDS
<p>Cl Cl Pt +I<sup>-</sup> –Cl<sup>-</sup> Cl Cl I Cl Pt +py –Cl<sup>-</sup> Cl py</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>125/128</b>	<b>SUBMITTED TEXT</b>	21 WORDS	<b>80% MATCHING TEXT</b>	21 WORDS
<p>CN – will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				
<b>126/128</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>76% MATCHING TEXT</b>	13 WORDS
<p>a pair of electrons from filled d-orbitals of the metal to form</p> <p><b>SA</b> Coordination (Theory).pdf (D98069410)</p>				
<b>127/128</b>	<b>SUBMITTED TEXT</b>	3 WORDS	<b>44% MATCHING TEXT</b>	3 WORDS
<p>CO M CO X OC OC CO M CO CO X OC CO –CO –CO M CO CO OC CO OC CO CO Co 7. (a) OC Co Co CO OR            CO Y X OC OC CO M CO CO X Y OC CO + Co OC CO OC CO CO CO OC CO</p> <p><b>W</b> <a href="https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html">https://pdfcoffee.com/download/coordination-compoundsenglishpc2016-2pdf-pdf-free.html</a></p>				
<b>128/128</b>	<b>SUBMITTED TEXT</b>	13 WORDS	<b>87% MATCHING TEXT</b>	13 WORDS
<p>Charge on the central metal ion. 2. Radii of the central metal ion. 3.</p> <p><b>SA</b> Course HCT 2.1 (Inorganic Chemistry).pdf (D157336879)</p>				

