

(Deemed to be University) (Under Section 3 of UGC Act 1956) KARPAGAM ACADEMY OF HIGHER EDUCATION (Deemed University Established Under Section 3 of UGC Act 1956) COIMBATORE-21 DEPARTMENT OF CHEMISTRY

B.Sc Chemistry Syllabus

Semester - V15CHU502INORGANIC CHEMISTRYSemester - VInstruction Hours/week:L: 5 T:0 P:0Marks: Internal:40 External: 60 Total:100

Scope

The course in chemistry is useful for the students in various aspects of inorganic chemistry and offers them with bright career. The course helps the students in improving their diverse skills in various areas such as laboratory skills, numerical and computing skills, ability to approach to the problems both analytically and logically, etc. The principles in this course are used in almost every field such as medicines, food products, and electronics and even in construction industry.

Programme outcome

The student will be able

- 1. To learn the principles of radioactivity.
- 2. To understand the fundamentals of acids and bases.
- 3. To understand about the structure of metals and alloys.
- 4. To learn about different aspects of solvents

Programme learning outcome

Students understood the principles of radiochemistry and thereby capable of recognizing risks of radiation in their environment. Students know different fundamental theories of acids and bases. Student will have an ability to read the types, properties and reactivity of different type of solvents.

UNIT-I

Structure of metals and alloys - substitutional and interstitial solid solutions - Hume -Rothery ratios - metallic bonding -theories-Valence Bond Theory (VBT), Molecular Orbital Theory

(MOT) and free electron theory- electrical, optical and mechanical properties of metals -semi conductors, intrinsic and extrinsic – uses, Crystal defects.

UNIT - II

Radio activity – General properties of Radio activity radiations, detection and measurement of radio activity. Natural radio activity & artificial radioactivity: Artificial transmutation of new elements, synthesis of radio isotopes of elements. Nuclear fission and fusion. Nuclear reactors - principles of working - production of electrical energy. Atomic energy projects in Industries - Safety measures, pollution, disposal of reactor wastes.

UNIT - III

Nature of isotopes and isobars - Detection and isolation of isotopes- various methods-importance of discovery of isotopes - uses of isotopes in various fields. Nuclear stability n/p ratio,magic numbers, C-12 and C-14 and nuclear binding energies. Nuclear reactions, mechanism and different types. Stellar energy. Radioactive disintegration series.

UNIT - IV

Acids and Bases - Arrehenius concept, proton transfer theory – concept of Lowry and Bronsted – Luxflood concept – the solvent system concept – Lewis concept – relative strength of acids and bases – effect of solvent – leveling effect – effect of polarity and dielectric constant – effect of substituent's – factors influencing relative strengths of acids and bases. Applications and Limitations of HSAB concept.

UNIT - V

The solvent - solubility's of compounds - effect of temperature on solubility - Chemical structure and solubility of solvents. Classification of solvents - general behavior - properties of ionizing solvents. Types of reaction in solvents. Aqueous and non aqueous solvents –Protonic solvents-Ammonia. Non-protonic solvents - SO₂.

TEXT BOOKS:

- 1. C.V.Shekar, 2005. A text book of nuclear chemistry. First Edition, Dominant publishers and Distributros, New Delhi.
- 2. Puri, B.R. and L.R.Sharma, 2013. Principles of Inorganic Chemistry, Shoban lal & Co.,
- 3. Wahid Malik, R.D.Madan and G.D.Tuli, 2013. Selected topics in Inorganic Chemistry, S,Chand & Co., New Delhi.

REFERENCE BOOKS :

- 1. Arnikar H.J, 2003. Essentials of Nuclear Chemistry. IV Edition, New Age International Publishers Pvt. Ltd., New Delhi.
- 2. James E Huheey, Elien A Keiter and Richard L Keiter, 2003. Inorganic Chemistry Principles of Structure and Reactivity, 4th Edition, Pearson Education Ltd., Delhi.
- 3. Madan, R.D., 2005. Modern Inorganic Chemistry, S.Chand & Co., New Delhi.
- 4. Puri, B.R. and L.R.Sharma, 2002. Principles of Inorganic Chemistry, Shoban lal & Co.,

- 5. Skoog, D.A. and D.M.West, 2004. Fundamentals of Analytical Chemistry, 8th Edition Thomson Book store, Singapore.
- 6. Soni, P.L., 2004. Inorganic Chemistry, Sultan Chand & Sons.
- 7. Wiley and A.K.De, 1998. A text book of Inorganic Chemistry, New age international publishers, New Delhi.



(Deemed to be University) (Under Section 3 of UGC Act 1956)

KARPAGAM ACADEMY OF HIGHER EDUCATION (Deemed University Established Under Section 3 of UGC Act 1956) **COIMBATORE-21 DEPARTMENT OF CHEMISTRY B.Sc Chemistry**

LECTURE PLAN

INORGANIC CHEMISTRY

Name of the Fac	culty: M. DINESH KUMAR	Department
Semester	: V	Year
Course Code	: 15CHU502	
Unit I	Structure of Metal	s and Allovs Tot

Structure of Metals and Alloys

Total no. of hours: 15

: III

: CHEMISTRY

S.No	Duration	Торіс	Reference
	Hour(period)		
1	1	Structure of metals and alloys,	T1: 167
2	1	Substitutional and interstitial solid solutions	T1: 169
3	1	Hume –Rothery ratios	T1: 169
4	1	Metallic bonding theory –VBT	T2: 456
5	1	Free electron theory,	T1: 169-170
6	1	Electrical, optical and mechanical properties of	T1: 170-172
		metals	
7	1	Metallic bonding based on MO theory	T1:171
8	1	Semi conductors : Introduction and types	T1: 172-173
9	1	Semiconductors: intrinsic and extrinsic & uses	T1: 172-173
10	1	Crystal defects- Introduction and classification	T1: 176-178;
11	1	Stochiometric defects	T2: 615, T1: 177
12	1	Non-stochiometric defects	T2: 615, T1: 177
13	1	Schokty and Frenkel defects	T2: 615, T1: 177
14	1	Metal Deficient Defects, Dislocations.	T1: 178
15	1	Revision & Discussion of possible questions	

Textbooks

1. Puri, Sharma & Pathania, 2013. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.

Unit II		Nuclear Chemistry	Total no. of hours: 15	
S.No	Lecture	Торіс	Reference	
	Hour			
1	1	Nuclear Chemistry- Introduction	T1: 922-923; T2: 313-318	
2	1	General properties of Radio activity radiations	T1: 922-923; T2: 313-318	
3	1	Detection and measurement of radio activity.	T1: 923-925; T2: 320-321	
4	1	Natural radio activity & artificial radioactivity:	T1: 948- 951; T2: 319	
5	1	Artificial transmutation of new elements,	T1: 928; T2:319, 356-358	
6	1	Artificial transmutation of new elements,	T1: 928; T2:319, 356-358	
7	1	Synthesis of radio isotopes of elements.	T2: 378-381	
8	1	Nuclear fission	T1: 953-955; T2: 369-370	
9	1	Nuclear fusion	T1:958 –960; T2: 375-376	
10	1	Nuclear reactors - principles of working -	T1: 956 – 958	
11	1	Production of electrical energy.	T1: 956 – 958	
12	1	Applications of radioactivity	T1: 931-932	
13	1	Atomic energy projects in Industries - Safety measures,	T1: 956	
14	1	Pollution, disposal of reactor wastes.	T1: 957	
15	1	Revision & Discussion of possible questions		

Textbooks

1. Puri, Sharma & Pathania, 2013. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.

Reference Book

UNIT-3		Nuclear Chemistry	Total no. of hours: 15
S.No	Lecture	Торіс	Reference
	Hour		
1	1	Nature of isotopes and isobars	T1: 932; T2: 336-337,
2	1	Detection of isotopes- various methods	T1: 933-934; T2: 346-348
3	1	Isolation of isotopes	T1: 933-934; T2: 346-348
4	1	Separation of isotopes	T2: 346-348
5		Importance of discovery of isotopes	T2: 382-384, T1: 931-932
6	1	Uses of isotopes in various fields.	T1: 929-930
7	1	Nuclear stability: n/p ratio,	T2: 330-321, T2: 363-364
8	1	magic numbers, nuclear binding energies	T2: 365-366
9	1	C-14 dating	T1: 931; T2: 385-388
10	1	Nuclear reactions and types	T2:359-362
11	1	Nuclear reaction mechanism, Stellar energy.	T2: 371-373,
12	1	Stellar Energy	T2: 375-377
13	1	Radioactive disintegration series.	T1: 930-931; T2: 332-333
14	1	Radioactive disintegration series.	T1: 930-931; T2: 332-333
15	1	Revision & Important question discussion	

Textbooks

1. Puri, Sharma & Pathania, 2013. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.

Reference Book

Unit IV		Acids and Bases Tot	al no. of hours: 15
S.No	Lecture	Торіс	Reference
	Hour		
1	1	Acids and bases – Introduction, Definitions	T2: 686
2	1	Different approaches to protonic acid - base systems	T2: 695-696
3	1	Arrhenius theory of acids and bases	T2: 686
4	1	Lowry and Bronsted theory of acids and bases, Luxflood concept,	T2: 686-692
5	1	Luxflood concept,	T2: 686-692
6	1	Lewis concept, the solvent system concept	T2: 698-699
7	1	relative strength of acids and bases	T2: 699
8	1	Effect of solvent, leveling effect	T2: 700-701
9	1	effect of polarity and dielectric constant	T2: 700-701
10	1	effect of substituents	T2: 700-701
11	1	Factors influencing relative strengths of acids	T2: 709
12	1	Factors influencing relative strengths of bases.	T2: 709
13	1	Interactions between Hard and soft acids and bases,	T3: 215-217
14	1	Applications and limitations of HSAB concept	T3: 215-217
15	1	Revision & Discussion of important questions	

Textbooks

- 1. T2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.
- 2. T3. Wahid U.Malik, G.D.Tuli, R.D.Madan; 2010. Selected topics in inorganic chemistry, S.Chand & Company Pvt. Ltd., New Delhi.

Reference Book

Unit V		Solvent To	tal no. of hours: 15
S.No	Lecture	Торіс	Reference
	Hour		
1	1	The solvent – Introduction,	T2: 712-713
2	1	Solubility's of compounds	T2: 712-713
3	1	Effect of temperature on solubility	R1: 219-221
4	1	Chemical structure and solubility	R1: 221-225
5	1	Classification of solvents	R1:219-220
6		General behavior & Properties of ionizing solvents.	R1: 219-223
7	1	Types of reaction in solvents	T4: 2.60-2.67
8	1	Aqueous solvents	T2:713-717, T3: 242
9	1	Non-aqueous solvents	T2:713-717, T3: 242
10	1	Protonic Solvents- NH ₃	T2 :717-720
11	1	Non – Protonic solvents- Sulphur dioxide	R1: 219-220
12	1	Revision and discussion of important questions	
13	1	Discussion of Previous year question	
14	1	Discussion of Previous year question	
15	1	Discussion of Previous year question	

Textbooks

- T2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.
- T3. Wahid U.Malik, G.D.Tuli, R.D.Madan; 2010. Selected topics in inorganic chemistry, S.Chand & Company Pvt. Ltd., New Delhi.
- 3. T4. Soni, P.L., 2014. Text book of Inorganic Chemistry, S.Chand & Sons, New Delhi.

Reference Book

- R1. F.A.Cotton, G.Wilkinson, P.L.Gaus, 2013, 3rd Edition. Basic Inorganic Chemistry; Wiley & Sons INC., Print India Press, Sahibabad.
- 2. R2. Weller, Overtone, Rourke and Armstrong, "Inorganic Chemistry", 6th Edition, 2014.

UNIT- I

Metals and Alloys

Structure of metals and alloys - substitutional and interstitial solid solutions - Hume – Rotheryratios - metallic bonding –theories-VBT, MOT and free electron theory- electrical, optical and mechanical properties of metals -semi conductors, intrinsic and extrinsic – uses, Crystal defects.

METALS:

A **metal** is a material (an element, compound, or alloy) that is typically hard, opaque, shiny, and features good electrical and thermal conductivity. Metals are generally malleable that is, they can be hammered or pressed permanently out of shape without breaking or cracking as well as fusible (able to be fused or melted) and ductile (able to be drawn out into a thin wire). About 91 of the 118 elements in the periodic table are metals (some elements appear in both metallic and non-metallic forms).

The atoms of metallic substances are closely positioned to neighboring atoms in one of two common arrangements. The first arrangement is known as body-centered cubic. In this arrangement, each atom is positioned at the center of eight others. The other is known as facecentered cubic. In this arrangement, each atom is positioned in the center of six others. The ongoing arrangement of atoms in these structures forms a crystal. Some metals adopt both structures depending on the temperature.

Atoms of metals readily lose their outer shell electrons, resulting in a free flowing cloud of electrons within their otherwise solid arrangement. This provides the ability of metallic substances to easily transmit heat and electricity. While this flow of electrons occurs, the solid characteristic of the metal is produced by electrostatic interactions between each atom and the electron cloud. This type of bond is called a metallic bond.

<u>ALLOYS</u>

An alloy is a mixture of two or more elements in which the main component is a metal. Most pure metals are either too soft, brittle or chemically reactive for practical use. Combining different ratios of metals as alloys modifies the properties of pure metals to produce desirable characteristics. The aim of making alloys is generally to make them less brittle, harder, resistant to corrosion, or have a more desirable color and luster. Of all the metallic alloys in use today, the alloys of iron (steel, stainless steel, cast iron, tool steel, alloy steel) make up the largest proportion both by quantity and commercial value. Iron alloyed with various proportions of carbon gives low, mid and high carbon steels, with increasing carbon levels reducing ductility and toughness. The addition of silicon will produce cast irons, while the addition of chromium, nickel and molybdenum to carbon steels (more than 10%) results in stainless steels.

Other significant metallic alloys are those of aluminium, titanium, copper and magnesium. Copper alloys have been known since prehistory—bronze gave the Bronze Age its name—and have many applications today, most importantly in electrical wiring. The alloys of the other three metals have been developed relatively recently; due to their chemical reactivity they require electrolytic extraction processes. The alloys of aluminium, titanium and magnesium are valued for their high strength-to-weight ratios; magnesium can also provide electromagnetic shielding. These materials are ideal for situations where high strength-to-weight ratio is more important than material cost, such as in aerospace and some automotive applications.



SOLID SOLUTION

A solid solution is formed when two metals are completely soluble in liquid state and also completely soluble in solid state. In other words, when homogeneous mixtures of two or more kinds of atoms (of metals) occur in the solid state, they are known as solid solutions. The more abundant atomic form is referred as solvent and the less abundant atomic form is referred as solvent and the less abundant atomic form is referred as solute. For example sterling silver (92.5 percent silver and the remainder copper) is a solid solution of silver and copper. In this case silver atoms are solvent atoms whereas copper atoms are solute atoms. Another example is brass. Brass is a solid solution of copper (64 percent) and

zinc (36 percent). In this case copper atoms are solvent atoms whereas zinc atoms are solute atoms.

% difference =
$$\left(\frac{r_{solute} - r_{solvent}}{r_{solvent}}\right) \times 100 \le 15\%.$$

Types of solid solutions

Solid solutions are of two types. They are

(a)Substitutional solid solutions.

(b)Interstitial solid solutions.

a. Substitutional Solid Solutions

If the atoms of the solvent or parent metal are replaced in the crystal lattice by atoms of the solute metal then the solid solution is known as substitutional solid solution. For example, copper atoms may substitute for nickel atoms without disturbing the F.C.C. structure of nickel. In the substitutional solid solutions, the substitution can be either disordered or ordered. Here the solute atoms have substituted disorderly for the solvent atoms on their lattice site. Here the solute atoms have substituted in an orderly manner for the solvent atoms on their lattice site.

b Interstitial solid solutions.

When the solute atom is equal to or slightly smaller and can fill the interstices of the solvent atoms, an **interstitial solid solution** forms. The atoms crowd into the interstitial sites, causing the bonds of the solvent atoms to compress and thus deform. Elements commonly used to form interstitial solid solutions include H, Li, Na, N, C, and O. Carbon in iron (steel) is one example of interstitial solid solution.



HUME-ROTHERY RULES:

The **Hume-Rothery rules**, named after William Hume-Rothery, are a set of basic rules describing the conditions under which an element could dissolve in a metal, forming a solid solution. There are two sets of rules, one which refers to substitutional solid solutions, and another which refers to interstitial solid solutions.

For substitutional solid solutions, the Hume-Rothery rules are:

1. The atomic diameter of the solute and solvent atoms must differ by no more than 15%:

2. The crystal structures of solute and solvent must match.

3.Complete solubility occurs when the solvent and solute have the same valency.[1] A metal will dissolve into a metal of higher valency to a greater extent than one of lower valency.

4. The solute and solvent should have similar electronegativity. If the electronegativity difference is too great, the metals will tend to form intermetallic compounds instead of solid solutions.

For interstitial solid solutions, the Hume-Rothery rules are:

1. Solute atoms must be smaller than the interstitial sites in the solvent lattice.

2. The solute and solvent should have similar electro-negativity.

<u>Models of Metallic Bonding</u>: Looking at metals in general and transition metals in particular, there is little difference in electronegativity from element to element. So metals and alloys are not likely to undergo ionic bonding. They are also a long way from having filled subshells, so they would require a tremendous number of covalent bonds to achieve complete octets. The experience we've gained so far suggests that individual metal atoms are not likely to form such large numbers of covalent bonds. If neither ionic nor covalent bonding can be expected for a metal, which models can account for the fact that metal atoms do bind to one another?

The first and simplest explanation of metallic bonding is often referred to as the sea of electrons model.

<u>Valence Bond Theory</u> suggests that overlap between two valence orbitals with an unpaired electron forms a covalent bond between two atoms.

Valence bond and molecular orbital theories are used to explain chemical bonding in chemistry. Two dissociated atoms that have unpaired electron in their orbitals can combine to give individual chemical bonds, forming a molecule. When two atomic orbitals overlap head-to-head, a sigma bond is formed. Pi bonds occur when orbitals overlap parallel to each other. Single bonds have one sigma bond, double bonds consist of one sigma bond and one pi bond, and triple bonds contain one sigma bond and two pi bonds. Often, the bonding atomic orbitals have a character of several possible types of orbitals, which are called hybrid orbitals. Hybridization is the method to get an atomic orbital with the proper character for the bonding.

Electron Sea model

Any theory of metallic bonding must account for the key properties of metals, the most important feature of which is the high electrical conductivity. Furthermore, any model should account for the high thermal conductivity and the high reflectivity (metallic luster) of metals. The simplest metallic bonding model is the electron-sea (or electron gas) model. In this model, the valence electrons are free to move through the bulk metal structure (hence the term *electron sea*) and



even leave the metal, thereby producing positive ions. It is valence electrons, then, that convey electric current, and it is the motion of the valence electrons that transfers heat through a metal. However, this model is more qualitative than quantitative. Metals are good conductors of electricity because the electrons in the electron sea are free to flow and carry electric current. Metals are ductile and malleable because local bonds can be easily broken and reformed. Metals are shiny because light cannot penetrate their surface; the photons simply reflect off the electrons. However, there is an upper limit to the frequency at which the photons are reflected, although this frequency is generally too high to be visually perceived.

Metallic bonds can occur between different elements, forming an alloy. Aluminum foil and copper wire are examples of metallic bonding in action

Metallic bonds are mediated by strong attractive forces. This property contributes to the low volatility, high melting and boiling points, and high density of most metals. The group-XIImetals zinc, cadmium, and mercury are exceptions to this rule.

Molecular orbital theory

Molecular orbital theory provides a more comprehensive model of metallic bonding. This extension of molecular orbital theory is sometimes called *band theory*, which we will illustrate by looking at the orbitals of lithium.



If the pair of 2s orbitals interacts in phase with one another, the interference will be constructive. The resulting wave, which will have increased amplitude (or electron density) between the nuclei, is referred to as a **bonding molecular orbital**. On the other hand, if the pair of 2s orbitals interacts out of phase with one another, the resulting wave will have a node between the nuclei. This is known as an **antibonding molecular orbital**. The term —antibonding **l** is used because electrons in this orbital will actually weaken the bond between the atoms.

Two lithium atoms combine in the gas phase to form the dilithium molecule. The molecular orbital diagram showing the mixing of two 2*s* atomic orbitals is given in Figure 4.1. (Both sets of atomic orbitals are shown on the left.). Now suppose that the atomic orbitals of four lithium atoms are mixed. Again, there must be the same number of $\sigma 2s$ molecular orbitals as 2*s* atomic orbitals, half of which are bonding and the other half antibonding. To avoid violating the

quantum rules, the energies of the orbitals cannot be degenerate. That is, one $\sigma 2s$ cannot have exactly the same energy as the other $\sigma 2s$ orbital. Figure 4.2 shows the resulting orbital arrangement.



In a large metal crystal, the orbitals of *n* atoms, where *n* is some enormous number, are mixed. These orbitals interact throughout the three dimensions of the metal crystal, yet the same principles of bonding apply. There will be $1/2n \ 2s$ (bonding) molecular orbitals and 1/2n(antibonding) molecular orbitals. With such a large number of energy levels, the spacing of levels becomes so close that they essentially constitute a continuum. This continuum is referred to as a band. For lithium, the band derived from the 2*s* atomic orbitals will be half filled. That is, the $\sigma 2s$ part of the band will be filled and the other part will be empty (Figure 4.3).

We can visualize electrical conductivity simplistically as the gain by an electron of the infinitesimally small quantity of energy needed to raise it into the empty antibonding orbitals. It can then move freely through the metal structure as electric current.

Similarly, the high thermal conductivity of metals can be visualized as —free electrons transporting translational energy throughout the metal structure.

Light is absorbed and emitted when electrons move from one energy level to another. The light emissions are observed as a line spectrum. With the multitudinous energy levels in a metal, there is an almost infinite number of possible energy level transitions. As a result, the atoms on a metal surface can absorb any wavelength and then re-emit light at that same wavelength as the electrons release that same energy when returning to the ground state. Hence, band theory accounts for the luster of metals. We can use band theory to explain why some substances are electrical conductors, some are not, and some are semiconductors. In the metals, bands overlap and allow a free movement of electrons. In nonmetals, bands are widely separated, so no electron movement can occur (Figure 4.5a). These elements are called insulators. In a few elements, the bands are close enough to allow only a small amount of electron excitation in an upper unoccupied band (Figure 4.5b).



These elements are known as intrinsic *semiconductors*. Our modern technology depends on the use of semiconducting materials, and it has become necessary to synthesize semiconductors with very specific properties. This can be done by taking an element with a wide band gap and —doping it with some other element, that is, adding a trace impurity. The added element has an energy level between that of the filled and empty energy levels of the main component (Figure 4.5c). This impurity band can be accessed by the electrons in the filled band, enabling some conductivity to occur. By this means, the electrical properties of semiconductors can be adjusted to meet any requirements.

Semiconductors

A **semiconductor** is a pure crystaline material which has electrical conductivity between that of a conductor such as copper and that of an insulator such as glass. Semiconductors are the foundation for modern electronics, including transistors, solar cells, lightemitting diodes(LEDs), quantum dots and digital and analog integrated circuits. The modern understanding of the properties of a semiconductor relies on quantum physics to explain the movement ofelectrons and holes inside a lattice. An increased knowledge of semiconductor materials and sophisticated fabrication processes has made increase in the complexity and speed of integrated semiconductor devices possible, an effect known as Moore's Law.

The electrical conductivity of a semiconductor material increases with increasing temperature, behaviour which is opposite to that of a metal conductor. Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by controlled addition of impurities (and by the application of electrical fields or light), 'devices' made from

semiconductors can be used for amplification of electrical signals, logic switching in computers, and energy control and conversion.

Current conduction in a semiconductor occurs through the movement of free electrons and "holes", collectively known as charge carriers. Adding impurity atoms to a semiconducting material, known as "doping", greatly increases the number of charge carriers within it. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type". The semiconductor materials used in electronic devices are doped under precise conditions to control the location and concentration of p- and n-type dopants. A single semiconductor crystal can have many p- and n-type regions; the p- njunctionsbetween these regions are responsible for the useful electronic behaviour.

Although some pure elements and many compounds display semiconductor properties, silicon, germanium, and compounds of gallium are the most widely used in electronic devices.

Properties

Variable conductivity

A pure semiconductor is a poor electrical conductor as a consequence of having just the right number of electrons to completely fill its valence bonds. Through various techniques (e.g.,doping or gating), the semiconductor can be modified to have an excess of electrons (becoming an *n*-type semiconductor) or a deficiency of electrons (becoming a *p*-type semiconductor). In both cases, the semiconductor becomes much more conductive (the conductivity can be increased by one million fold or more). Semiconductor devices exploit this effect to shape electrical current.

Depletion

When doped semiconductors are joined to metals, to different semiconductors, and to the same semiconductor with different doping, the resulting junction often strips the electron excess or deficiency out from the semiconductor near the junction. This depletion region is rectifying (only allowing current to flow in one direction), and used to further shape electrical currents in semiconductor devices.

Energetic electrons travel far

Electrons can be excited across the energy band gap (see *Physics* below) of a semiconductor by various means. These electrons can carry their excess energy over distance scales of micrometersbefore dissipating their energy into heat – a significantly longer distance than is possible in metals. This property is essential to the operation of, e. g., bipolar junction transistors and solar cells.

Light emission

In certain semiconductors, excited electrons can relax by emitting light instead of producing heat. These semiconductors are used in the construction of light emitting diodes and fluorescentquantum dots.

Thermal energy conversion

Semiconductors have large thermoelectric power factors making them useful in thermoelectric generators, as well as high thermoelectric figures of merit making them useful in thermoelectric coolers.

CRYSTAL DEFECTS

Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by **crystallographic point defects.**

Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension. These defects involve at most a few extra or missing atoms. Larger defects in an ordered structure are usually considered dislocation loops.

There are different types of imperfections or **defects** in the ideal arrangement of atoms in a crystal. We will see that the presence of a relatively small number of **defects have a profound**

impact on the macroscopic properties of materials, and the control (and intentional introduction) of defects is important in many kinds of material processing.

Examples

When/if you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size.

Production of advanced semiconductor devices require not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample. The three basic classes of defects in crystals:

•**Point defects** - atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).

•Linear defects - groups of atoms in irregular positions (e.g. screw and edge dislocations).

•**Planar defects** – the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).



Point Defects: Vacancies

A perfect crystal with regular arrangement of atoms cannot exist. There are always defects, and the most common defects are point defects. This is especially true at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites, called **vacancies**. In most cases diffusion (mass transport by atomic motion) - can only occur because of vacancies.

How many vacancies are there? The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, Nv, increases exponentially with the absolute temperature, T, and can be estimated using the equation (Boltzmann Distribution):

Where, Ns is the number of regular lattice sites, k is the Boltzmann constant, and

Ev is the energy needed to form a vacant lattice site in a perfect crystal.

Using this simple equation we can estimate that at room temperature in copper there is one vacancy per 1015 lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms. These are the lower end estimations, a large numbers of additional vacancies can be introduced in a growth process or as a result of further treatment.

More on Point Defects

Interstitials – atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called **self-interstitial**. Creation of a self-interstitialcauses a substantial distortions in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy (Ei > EV) and, under equilibrium conditions, self- interstitials are present in lower concentrations than vacancies.

Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called **interstitial impurities.** They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom replaces or substitutes for a matrix atom, it is called a **substitutional impurity**.

All point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects that we will consider next can give a directionality to an otherwise random jumps of atoms. In particular, a pressure gradient result in a flux of vacancies in the direction towards a compressed region of the sample.

In ionic crystals (e.g. table salt - Na+Cl-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Coulombic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created.

A **Frenkel defect** is a pair of cation (positive ion) vacancy and a cation interstitial. Or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form.

A **Schottky defect** is a pair of anion and cation vacancies. In both Frenkel and Schottky defects, the pair of point defects stay near each other because of strong coulombic attraction of their opposite charges.



vacancies) in an ionic crystal.

defects in a crystal. (1) vacancy; (2) selfinterstitial; (3) interstitial impurity; (4), (5) substitutional impurities. The arrows show the local stresses introduced by the point defects.

Vacancy defects are lattice sites which would be occupied in a perfect crystal, but are vacant. If a neighboring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighboring atoms will not simply collapse around the vacancy. In some materials, neighboring atoms actually move away from a vacancy, because they experience attraction from atoms in the surroundings. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a Schottky defect.

Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms in some crystals can occupy interstices without high energy, such as hydrogen in palladium.

A nearby pair of a vacancy and an interstitial is often called a Frenkel defect or Frenkel pair. This is caused when an ion moves into an interstitial site and creates a vacancy.

Impurities occur because materials are never 100% pure. In the case of an impurity, the atom is often incorporated at a regular atomic site in the crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a *substitutional* defect. The atom is not supposed to be anywhere in the crystal, and is thus an impurity. In some cases where the radius of the substitutional atom (ion) is substantially smaller than that of the atom (ion) it is replacing, its equilibrium position can be shifted away from the lattice site. These types of substitutional defects are often referred to asoff-center ions. There are two different types of substitutional defects: Isovalent substitution and aliovalent substitution. Isovalent substitution is where the ion that is substitution state as the ion it is replacing. Aliovalent substitution schange the overall charge within the ionic compound, but the ionic compound must be neutral. Therefore a charge compensation mechanism is required. Hence either one of the metals is partially or fully oxidised or reduced, or ion vacancies are created.



The fact that the metallic elements are found on the left side of the periodic table offers an important clue to the nature of how they bond together to form solids.

These elements all possess *low electronegativities* and readily form positive ions Mn+. Because they show no tendency to form negative ions, the kind of bonding present in ionic solids can immediately be ruled out.

The metallic elements have empty or nearly-empty outer *p*-orbitals, so there are never enoughouter-shell electrons to place an octet around an atom

These points lead us to the simplest picture of metals, which regards them as a lattice of positive ions immersed in a —sea of electrons^{II} which can freely migrate throughout the solid. In effect the electropositive nature of the metallic atoms allows their valence electrons to exist as a mobile fluid which can be displaced by an applied electric field, hence giving rise to their high *electrical conductivities*. Because each ion is surrounded by the electron fluid in all directions, the bonding has no directional properties; this high *malleability* and *ductility* of metals. This view is an oversimplification that fails to explain metals in a quantitative way, nor can it account for the differences in the properties of individual metals. A more detailed treatment, known as the bond theory of metals, applies the idea of resonance hybrids to metallic lattices. In the case of an alkali metal, for example, this would involve a large number of hybrid structures in which a given Na atom shares its electron with its various neighbors.



Molecular orbitals in metals

The most useful treatment of metallic solids is based on the*molecular orbital* approach It is best understood by considering first a succession of molecules based on lithium (or any other alkali metal having a singles electron in its valence shell). The figure below shows how the MO wave functions for Li2, Li3 and Li4 will look. These are all constructed by combining the individual atomic s functions just as is done in simple MO theory. The only thing new here is that the new molecular orbitals extend over all the atoms of the metal, and that the orbitals of intermediate energy possess both bonding and antibonding character in different regions. Every time we add another atom, we get two new MO's, but since each atom contributes only a single valence electron, the MO's are never more than half filled. If we extrapolate this to a giant —moleculel LiNcontaining a very large number of atoms, we get 2N MO's that are so closely spaced in energy that they form what is known as a *band* of allowed energies. In metallic lithium only the lower half of this band is occupied.

Origin of metallic properties

Metallic solids possess special properties that set them apart from other classes of solids and make them easy to identify and familiar to everyone. All of these properties derive from the liberation of the valence electrons from the control of individual atoms, allowing them to behave as a highly mobile fluid that fills the entire crystal lattice. What were previously valence-shellorbitals of individual atoms become split into huge numbers of closely-spaced levels known as bands that extend throughout the crystal.

Melting point and strength

The strength of a metal derives from the electrostatic attraction between the lattice of positive ions and the fluid of valence electrons in which they are immersed. The larger the nuclear charge (atomic number) of the atomic kernel and the smaller its size, the greater this attraction. As with many other periodic properties, these work in opposite ways, as is seen by comparing the melting points of some of the Group 1-3 metals (right). Other factors, particularly the lattice geometry are also important, so exceptions such as is seen in Mg are not surprising.

In general, the transition metals with their valence-level *d* electrons are stronger and have higher melting points: Fe, 1539°C; Re 3180, Os 2727; W 3380°C. (W is tungsten, the highest-meltingmetal of all; do you know what principal use derives this very high melting point?)

Malleability and ductility

These terms refer respectively to how readily a solid can be shaped by pressure (forging, hammering, rolling into a sheet) and by being drawn out into a wire. Metallic solids are known and valued for these qualities, which derive from the non-directional nature of the attractions between the kernel atoms and the electron fluid. The bonding within ionic or covalent solids may be stronger, but it is also directional, making these solids subject to fracture (brittle) when struck with a hammer, for example. A metal, by contrast, is more likely to be simply deformed or dented.

Electrical conductivity: Why are metals good conductors

In order for a substance to conduct electricity, it must contain charged particles (*charge carriers*) that are sufficiently mobile to move in response to an applied electric field. In the case of ionic solutions and melts, the ions themselves serve this function. (Ionic solids contain the same charge carriers, but because they are fixed in place, these solids are insulators.) In metals the charge carriers are the electrons, and because they move freely through the lattice, metals are



highly conductive. The very low mass and inertia of the electrons allows them to conduct highfrequency alternating currents, something that electrolytic solutions are incapable of. In terms of

the band structure, application of an external field simply raises some of the electrons to previously unoccupied levels which possess greater momentum.

The conductivity of an electrolytic solution decreases as the temperature falls due to the decrease in viscosity which inhibits ionic mobility. The mobility of the electron fluid in metals is practically unaffected by temperature, but metals do suffer a slight conductivity decrease (opposite to ionic solutions) as the temperature rises; this happens because the more vigorous thermal motions of the kernel ions disrupts the uniform lattice structure that is required for free motion of the electrons within the crystal. Silver is the most conductive metal, followed by copper, gold, and aluminum.

Metals conduct electricity readily because of the essentially infinite supply of higherenergyempty MOs that electrons can populate as they acquire higher kinetic energies. This diagram illustrates the overlapping band structure (explained farther on) in beryllium. The MO levels are so closely spaced that even thermal energies can provide excitation and cause heat to rapidly spread through the solid.

Electrical conductivities of the metallic elements vary over a wide range. Notice that those of silver and copper (the highest of any metal) are in classes by themselves. Gold and aluminum follow close behind.

Thermal conductivity: Why do metals conduct heat

Everyone knows that touching a metallic surface at room temperature produces a colder sensation than touching a piece of wood or plastic at the same temperature. The very high thermal conductivity of metals allows them to draw heat out of our bodies very efficiently if they are below body temperature. In the same way, a metallic surface that is above body temperature will feel much warmer than one made of some other material. The high thermal conductivity of metals is attributed to vibrational excitations of the fluid-like electrons; this excitation spreads through the crystal far more rapidly than it does in non-metallic solids which depend on vibrational motions of atoms which are much heavier and possess greater inertia.

Appearance: Why are metals shiny

We usually recognize a metal by its —metallic lustrel, which refers to its ability of reflect light. When light falls on a metal, its rapidly changing electromagnetic field induces similar motions in

when light fails on a metal, its rapidly changing electromagnetic field induces similar motions in the more loosely-bound electrons near the surface (this could not happen if the electrons were confined to the atomic valence shells.) A vibrating charge is itself an emitter of electromagnetic radiation, so the effect is to cause the metal to re-emit, or *reflect*, the incident light, producing the shiny appearance. What color is a metal? With the two exceptions of copper and gold, the closely-spaced levels in the bands allow metals to absorb all wavelengths equally well, so most metals are basically black, but this is ordinarily evident only when the metallic particles are so small that the band structure is not established.

The distinctive color of **gold** is a consequence of Einstein's theory of special relativity acting on the extremely high momentum of the inner-shell electrons, increasing their mass and causing the orbitals to contract. The outer (5d) electrons are less affected, and this gives rise to increasedblue-light absorption, resulting in enhanced reflection of yellow and red light.

Thermionic effect

The electrons within the electron fluid have a distribution of velocities very much like that of molecules in a gas. When a metal is heated sufficiently, a fraction of these electrons will acquire sufficient kinetic energy to escape the metal altogether; some of the electrons are essentially —boiled outl of the metal. This *thermionic effect*, which was first observed by Thomas Edison, was utilized in vacuum tubes which served as the basis of electronics from its beginning around1910 until semiconductors became dominant in the 1960's.

Textbooks

1. Puri, Sharma & Pathania, 2013. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.

Reference

POSSIBLE QUESTIONS

<u>PART A: MULTIPLE CHOICE QUESTIONS</u> (Each question carry one mark)

- 1. In the substitutional solid solutions, the substitution can be
 - a. disordered b. ordered c. either disordered or ordered d. in random
- 2. When the solute atom is equal to or slightly smaller and can fill the interstices of the solvent atoms, it forms
 - a. substitutional solid solution **b. Interstitial solid solution** c. crystal defect
 - b. d. P-type semi conductor
- 3. Elements commonly used to form interstitial solid solutions include
 - a. H, Li, Na, N, C, and O
 - b. halogens substitutions in metal atoms
 - c. chalcogensFe, Co & Ni
 - d. nonmetals with metal atoms
- 4. For substitutional solid solutions, the Hume-Rothery rules are
 - a. The atomic diameter of the solute and solvent atoms must differ by no more than 15%
 - b. Solute atoms must be smaller than the interstitial sites in the solvent lattice
 - c. The solute and solvent should have disimilar electronegativity.
 - d. The solute and solvent should have similar ionisation energy.
- 5. For interstitial solid solutions solid solutions, the Hume-Rothery rules are:
 - a. The atomic diameter of the solute and solvent atoms must differ by no more than 15%:
 - b. The crystal structures of solute and solvent must match.
 - c. Complete solubility occurs when the solvent and solute have the same valency.
 - d. Solute atoms must be smaller than the interstitial sites in the solvent lattice.
- 6. For interstitial solid solutions solid solutions, the Hume-Rothery rules are:
 - a. The atomic diameter of the solute and solvent atoms must differ by no more than 15%:
 - b. The crystal structures of solute and solvent must match.

c. Complete solubility occurs when the solvent and solute have the same valency.

d. The solute and solvent should have similar electronegativity

- According to Valence Bond Theory of metals in crystalline lithium, every atom is connected with
 - a. **8 or 12 lithium atoms** b. two lithium atoms c. It is monoatomic d. 6 lithium atoms
- 8. Which bonding model says 'the valence electrons are free to move through the bulk metal structure and even leave the metal, thereby producing positive ions'
 - a. Electron sea model
 - b. Valence bond model
 - c. Molecular orbital method
 - d. crystal field model
- 9. Which model is called band theory
 - a. Electron sea model
 - b. Valence bond model

c. Molecular orbital method

d. crystal field model

10. In bonding molecular orbitals the two waves interact in

a. Phase	b. Out of phase	c. infinity	d. the area outside the orbital
11. In anti-bondi	ng molecular orbitals	the two waves in	teract in

a. Phase **b. Out of phase** c. infinity d. the area outside the

a. Phase **b. Out of phase** c. infinity d. the area outside the orbital
12. The pair of orbitals interacts in phase with one another, the interference will be constructive. The resulting wave, which will have increased amplitude (or electron density) between the nuclei, is referred to as a

a. bonding molecular orbital

- b. antibonding molecular orbital
- c. nodal plane
- d. Pi-bond
- 13. The pair of orbitals interacts out of phase with one another, the resulting wave will have a node between the nuclei resulting in a
 - a. bonding molecular orbital

b. antibonding molecular orbital

- c. nodal plane
- d. Pi-bond
- 14. In the formation of bonding molecular orbital, the pair of orbitals interacts in phase with one another, the interference will be
 - a. **Constructive** b. destructive c. Creative d. neutralised
- 15. In the formation of anti-bonding molecular orbital, the pair of orbitals interacts out of phase with one another, the interference will be
 - a. Constructive **b. destructive** c. Creative d. neutralised
- 16. The charge carrier in an N-type semiconductors is
- a. Holes **b. electrons** c. positively charged ions d. empty vaccant orbitals
 17. The charge carrier in an P-type semiconductors is
- a. **Holes** b. electrons c. positively charged ions d. negatively charged ions
- 18. Materials which display the property of semiconductors and used in electronic circuits are
 - a. Silicon b. copper c. Iron d. Nichrome
- 19. Materials which display the property of semiconductors and used in electronic circuits are
 - a. Germanium b. copper c. Iridium d. Nickel
- 20. The defect formed by the presence of silver ions in the interstitial spaces of the silver bromide crystal is
 - a. Metal excess defect
 - b. metal deficiency defect
 - c. Frenkel defect
 - d. Schottky defect

PART B (Each question carries 8 marks)

- 1. What are semi conductors, Explain different types of the semiconductors with Examples?
- 2. Explain the different types of crystal defects?.
- 3. a. Use energy level diagrams and the band theory to explain the difference between conductors, insulators and semiconductors.

b. Explain why the electrical conductivity of a metal decreases as the temperature is raised, but the opposite occurs with semiconductors.

- 4. Explain the physical and chemical properties associated with metals?
- 5. Explain Metallic bonding using Molecular Orbital theory?
- 6. Explain the theories which explain the metallic bonding?
- 7. How semi conductors are classified. Write it's uses?
- 8. Explain the theories which explain the metallic bonding.
- 9. Explain (i) Frenkel defect (ii) Substitutional solid solutions (iii) Hume –Rothery Ratios?
- 10. What is solid solution and explain it's types?

[15CHU502] KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER

INORGANIC CHEMISTRY

UNIT 1- OBJECTIVE TYPE QUESTIONS FOR ONLINE EXAMINATION(Each carry 1 Mark)

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answer
A solid solution is formed when two metals are					
completely soluble in	Liquid state	solid state	solid and liquid state	gaseous state.	gaseous state.
If the atoms of the solvent or parent metal are					
replaced in the crystal lattice by atoms of the solute	substitutional solid				
metal then the solid solution is known as	solution.	Interstitial solid solution	crystal defect	P-type semi conductor	crystal defect
In the substitutional solid solutions, the substitution	l		either disordered or		
can be	disordered	ordered	ordered	in random	either disordered or ordered
When the solute atom is equal to or slightly smaller					
and can fill the interstices of the solvent atoms, it	substitutional solid				
forms	solution	Interstitial solid solution	crystal defect	P-type semi conductor	Interstitial solid solution
	substitutional solid				
Carbon in iron (steel) is one example of	solution	Interstitial solid solution	crystal defect	P-type semi conductor	Interstitial solid solution
Elements commonly used to form interstitial solid		halogens substitutions in	chalcogensFe, Co &		
solutions include	H, Li, Na, N, C, and O	metal atoms	Ni	nonmetals with metal atoms	H, Li, Na, N, C, and O
	The atomic diameter of				
	the solute		The solute and		
	and solvent atoms must	Solute atoms must be	solvent should have	The solute and solvent	The atomic diameter of the solute
For substitutional solid solutions, the Hume-	differ by no more than	smaller than the interstitial	disimilar electroneg	should have similar	and solvent atoms must differ by
Rothery rules are	15%	sites in the solvent lattice	ativity.	ionisation energy.	no more than 15%
			The solute and		
	The crystal	Solute atoms must be	solvent should have	The solute and solvent	
For substitutional solid solutions, the Hume-	structures of solute and	smaller than the interstitial	disimilar electroneg	should have	The crystal structures of solute and
Rothery rules are	solvent must match.	sites in the solvent lattice.	ativity	similar ionisation energy	solvent must match.
			The solute and		
	The crystal	Solute atoms must be	solvent should have	The solute and solvent	
For substitutional solid solutions, the Hume-	structures of solute and	smaller than the interstitial	disimilar electroneg	should have	The crystal structures of solute and
Rothery rules are:	solvent must match.	sites in the solvent lattice	ativity	similar ionisation energy	solvent must match.
	Complete solubility occ		The solute and		
	urs when the solvent	Solute atoms must be	solvent should have	The solute and solvent	Complete solubility occurs when
For substitutional solid solutions, the Hume-	and solute have the	smaller than the interstitial	disimilar electroneg	should have	the solvent and solute have the
Rothery rules are:	same valency	sites in the solvent lattice	ativity	similar ionisation energy	same valency
	The solute and solvent		The solute and		
	should have	Solute atoms must be	solvent should have	The solute and solvent	
For substitutional solid solutions, the Hume-	similar electronegativit	smaller than the interstitial	disimilar electroneg	should have	The solute and solvent should have
Rothery rules are	y.	sites in the solvent lattice.	ativity.	similar ionisation energy.	similar electronegativity.

	The atomic diameter of		Complete solubility		
	the solute		occurs when the		
	and solvent atoms must	The crystal structures of	solvent and solute	Solute atoms must be smaller	Solute atoms must be smaller than
For interstitial solid solutions solid solutions, the	differ by no more than	solute and solvent must	have the	than the interstitial sites in	the interstitial sites in the solvent
Hume-Rothery rules are:	15%:	match.	same valency.	the solvent lattice.	lattice.
	The atomic diameter of		Complete solubility		
	the solute		occurs when the		
	and solvent atoms must	The crystal structures of	solvent and solute	The solute and solvent	
For interstitial solid solutions solid solutions, the	differ by no more than	solute and solvent must	have the same	should have	The solute and solvent should have
Hume-Rothery rules are:	15%:	match.	valency.	similar electronegativity	similar electronegativity
According to Valence Bond Theory of metals in					
crystalline lithium, every atom is connected with	8 or 12 lithium atoms	two lithium atoms	It is monoatomic	6 lithium atoms	8 or 12 lithium atoms
Which bonding model says 'the valence electrons		Valence bond model			
are free to move through the bulk metal structure					
and even leave the metal, thereby producing			Molecular orbital		
positive ions'	Electron sea model		method	crystal field model	Electron sea model
Which model is called band theory	Electron sea model	Valence bond model	Molecular orbital method	crystal field model	Molecular orbital method
In bonding molecular orbitals the two waves	Phase	Out of phase	infinity	the area outside the orbital	Phase
interact in		-			
In anti-bonding molecular orbitals the two waves	Phase	Out of phase	infinity	the area outside the orbital	Out of phase
interact in		-			-
The pair of orbitals interacts in phase with one	bonding molecular	antibonding molecular	nodal plane	Pi-bond	bonding molecular orbital
another, the interference will be constructive. The	orbital	orbital			
resulting wave, which will have increased					
amplitude (or electron density) between the nuclei,					
is referred to as a					
The pair of orbitals interacts out of phase with one	bonding molecular	antibonding molecular	nodal plane	Pi-bond	antibonding molecular orbital
another, the resulting wave will have a node	orbital	orbital			
between the nuclei resulting in a					
In the formation of bonding molecular orbital, the	Constructive	destructive	Creative	neutralised	Constructive
pair of orbitals interacts in phase with one another,					
the interference will be					
In the formation of anti-bonding molecular orbital,	Constructive	destructive	Creative	neutralised	destructive
the pair of orbitals interacts out of phase with one					
another, the interference will be					
According to band theory metals, allow a free	bands overlap	bands are widely separated	bands are close	Bands are completely	bands overlap
movement of electrons because .			enough to allow	occupied	
			only a small amount		
			of electron		
			excitation in an		
			upper unoccupied		
			band		

According to band theory metals, insulators do not	bands overlap	bands are widely separated	bands are close	Bands are completely	bands are widely separated
allow a free movement of electrons because .	-		enough to allow	occupied	
			only a small amount		
			of electron		
			excitation in an		
			upper unoccupied		
			band		
According to band theory metals, semiconductors	bands overlap	bands are widely separated	bands are close	Bands are completely	bands are close enough to allow
allow a free movement of electrons because			enough to allow	occupied	only a small amount of electron
			only a small amount		excitation in an upper unoccupied
			of electron		band
			excitation in an		
			upper unoccupied		
			band		
According to band theory semiconductors allow a	bands overlap	bands are widely separated	bands are close	by taking an element with a	bands overlap
free movement of electrons because			enough to allow	wide band gap and "doping"	
			only a small amount	it with some other element	
			of electron		
			excitation in an		
			upper unoccupied		
			band		
If the temperature of the metal is increased the	Decreases	Increases	do not change	first increases and then	Decreases
electrical conductivity				decreases	
If the temperature of the semiconductor is	Decreases	Increases	do not change	first increases and then	Increases
increased the electrical conductivity				decreases	
One of the useful property of a semiconductor	passing current more	Constant resistance for all	sensitive to light	sensitive to heat	passing current more easily in one
device	easily in one direction	materials			direction than the other
	than the other				
One of the useful property of a semiconductor	passing current equally	showing variable resistance	sensitive to light	sensitive to heat	showing variable resistance
device	on both the direction				
Devices made from semiconductors can be used for	amplification of	welding	soldering	galvanising	amplification of electrical signals
	electrical signals	1.1.			.
Devices made from semiconductors can be used for	logic switching in	welding	soldering	galvanising	logic switching in computers
	computers	1.1.	11 .	1	
Devices made from semiconductors can be used for	energy control and	welding	soldering	galvanising	energy control and conversion
	conversion		1		
Adding impurity atoms to a semiconducting	increases the number of	decreases the number of	does not affect the	Number of holes will	increases the number of charge
material, known as "doping", greatly	charge carriers within it	charge carriers	number of charge	increase but not the	carriers within it
			carriers	electrons.	
when a doped semiconductor contains mostly free balas it is called	р-туре	п-туре	rin junction	ive junction type	р-туре
When a doned semiconductor contains mostly	n trine	N turne	DN junction	NP junction type	N type
electrons it is called	h-ràhe	in-type		in junction type	in-type
The charge carrier in an N-type semiconductors is	Holes	electrons	positively charged	empty vaccant orbitals	electrons
The energy suffer in an it type semiconductors is			ions	inpost fuccult of officials	

The charge carrier in an P-type semiconductors is	Holes	electrons	positively charged ions	negatively charged ions	Holes
Materials which display the property of semiconductors and used in electronic circuits are	Silicon	copper	Iton	Nichrome	Silicon
Materials which display the property of semiconductors and used in electronic circuits are	Germanium	copper	Iton	Nichrome	Germanium
In a solid lattice, cation has left a lattice site and is licated at an interstitial position, the lattice defect is	interstitial defect	vacanct defect	Frenkel defect	Schottky defect	Frenkel defect
In a solid lattice, if some of the lattice points are unoccupied	interstitial defect	vacanct defect	Frenkel defect	Schottky defect	Schottky defect
Crystals in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called	Stoichiometric crystals	Non-stoichiometric crystals	Metal excess defect	metal deficiency defect	Stoichiometric crystals
Crystals in which the number of positive and negative ions are not exactly in the ratios indicated by their chemical formulae are called	Stoichiometric crystals	Non-stoichiometric crystals	Metal excess defect	metal deficiency defect	Non-stoichiometric crystals
Crystals which do not obey the law of constant proportions are called	Stoichiometric crystals	Non-stoichiometric crystals	Metal excess defect	metal deficiency defect	Non-stoichiometric crystals
Crystals which obey the law of constant proportions are called	Stoichiometric crystals	Non-stoichiometric crystals	Metal excess defect	metal deficiency defect	Stoichiometric crystals
The defect in which the negative ion may be missing from its lattice sites leaving a hole which is occupied by an extra electron to maintain the electrical balance	Metal excess defect	metal deficiency defect	Frenkel defect	Schottky defect	Metal excess defect
The defect in which an extra positive ion occupies an interstitial position in the lattice and to maintain electrical neutrality, an electron is also presence in the interstitial space.	Metal excess defect	metal deficiency defect	Frenkel defect	Schottky defect	Metal excess defect
One of the positive ions may be missing from its lattice site. The extra negative charge may be balanced by some nearby metal ion acquiring two charges instead one	Metal excess defect	metal deficiency defect	Frenkel defect	Schottky defect	metal deficiency defect
An extra negative ion may occupy an nterstitial position. The extra negative negative charge is balanced again by means of an extra charge on one of the adjacent metal ions. The defect is	Metal excess defect	metal deficiency defect	Frenkel defect	Schottky defect	metal deficiency defect
Germanium containing traces of arsenic begins to exhibit high electrical conductivity and is called	P-type semiconductor	Intrinsic conduction	Extrinsic conduction	Frenkel conduction	Extrinsic conduction
Germanium containing traces of antimony begins to exhibit high electrical conductivity and is called	P-type semiconductor	Intrinsic conduction	Extrinsic conduction	Frenkel conduction	Extrinsic conduction
In germanium crystal one of the covalent bonds gets broken and electrons are set free for conduction. This is called	N-type semiconductor	Intrinsic conduction	c. Extrinsic conduction	Frenkel conduction	Intrinsic conduction
In silicon crystal one of the covalent bonds gets broken and electrons are set free for conduction. This is called	N-type semiconductor	Intrinsic conduction	Extrinsic conduction	Frenkel conduction	Intrinsic conduction
Germanium containing traces of arsenic begins to	P-type semiconductor	Intrinsic conduction	N-type	Frenkel conduction	N-type semiconduction
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exhibit high electrical conductivity and is called			semiconduction		
Germanium containing traces of antimony begins	P-type semiconductor	b. Intrinsic conduction	N-type semi	Frenkel conduction	N-type semi conduction
to exhibit high electrical conductivity and is called			conduction		
In germanium crystal one of the covalent bonds	N-type semiconductor	P-type semi conduction	Extrinsic conduction	Frenkel conduction	P-type semi conduction
gets broken and electrons are set free for					
conduction. This is called					
In silicon crystal one of the covalent bonds gets	N-type semiconductor	P-type semi conduction	Extrinsic conduction	Frenkel conduction	P-type semi conduction
broken and electrons are set free for conduction.					
This is called					
The defect formed by the presence of silver ions in	Metal excess defect	metal deficiency defect	Frenkel defect	Schottky defect	Frenkel defect
the interstitial spaces of the silver bromide crystal					
is					

UNIT II

Nuclear Chemistry - Radioactivity

Radio activity – General properties of Radio activity radiations, detection and measurement of radio activity. Natural radio activity & artificial radioactivity: Artificial transmutation of new elements, synthesis of radio isotopes of elements. Nuclear fission and fusion. Nuclear reactors - principles of working - production of electrical energy. Atomic energy projects in Industries - Safety measures, pollution, disposal of reactor wastes.

THE DISCOVERY OF RADIOACTIVITY

In 1896, a French physicist named Henri Becquerel discovered that uranium-containing crystals emitted rays that could expose and fog photographic plates. He found that these —raysl originated from changes within the atomic nuclei of the U atoms. He proposed that the uranium atoms were unstable. They emitted particles and/or energy to become more stable. These emissions he called *uranic rays*. One of the first women in France to do graduate work, Marie Sklodowska Curie carried out her doctoral work to determine if other substances emitted uranic rays. She discovered two elements, which she later named polonium (after her native Poland) and radium, which emitted high levels of radioactivity. Maric Curie changed the name of uranic rays to **radioactivity** (or **radioactive decay**). She shared the Nobel prize in physics with Becquerel and her husband, Pierre Curie, for discovering radioactivity.

How do chemical and nuclear reactions compare?					
Chemical Reactions	Nuclear Reactions				
	Occur when nuclei emit particles and/or				
occur when bonds are broken	rays				
atoms remain unchanged, though they may be	atoms often converted into atoms of another				
rearranged.	element.				
involve ONLY valence electrons	may involve protons, neutrons and				
	electrons				
associated with small energy changes	associated with large energy changes				
reaction rate influenced by T, particle size,	Reaction rate is NOT normally influenced				
concentration and catalysts	by T, P and catalysts.				

M. DINESH KUMAR

Discovery of Radioactivity (1895 – 1898)

1.Roentgen found that invisible rays were emitted when electrons bombarded the surface of certain materials.

2.Becquerel accidently discovered that phosphorescent uranium salts produced spontaneous emissions that darkened photographic plates.

3.Marie Curie

a.isolated the components (uranium atoms) emitting the rays

b.*radioactivity* - Process by which particles give off rays

c.*radiation* - the penetrating rays and particles emitted by a radioactive source

d. identified 2 new elements, **Polonium** and **Radium** on the basis of their radioactivity



Discovery contradicted Dalton's theory of indivisible atoms!

Recall that isotopes are atoms of the *same* element that have different numbers of neutrons **Radioisotopes** – isotopes of atoms isotopes of atoms with unstable nuclei (too many or too few neutrons)

Radioactive decay – these unstable nuclei lose energy by emitting radiation to attain more stable atomic configurations, spontaneous process.

PropertyAlpha(α)Beta(β)Gamma(γ)AlphaBetaHighAlphaBetaenergyparticlesparticleselectromagneticComposition(Helium Nucleus)(electrons)radiations

PROPERTIES OF ALPHA, BETA AND GAMMA RADIATIONS.

Symbol	А	β	γ
Charge	2+	1-1	0
Mass	4	1/1837	0
Energy	5 MeV	0.05 to 1 Mev	1 MeV
Penentrating power	low	moderate	Very high
Shielding	Paper, cloth	Metal foil	Lead, concrete



Alpha rays: α

Nature of the radiation: a helium nucleus of 2 protons and 2 neutrons, mass = 4, charge = +2Penetrating power, and what will block it: Low penetration, biggest mass and charge, stopped by a few cm of air or thin sheet of paper.

Ionising power: Very high ionising power, the biggest mass and charge of the three radiation's, the biggest 'punch'!



Beta rays: β

Nature of the radiation: high kinetic energy electrons, mass = 1/1850, charge = -1

Penetrating power, and what will block it: Moderate penetration, 'middle' values of charge and mass, most stopped by a few mm of metals like aluminium

Ionising power: Moderate ionising power, with a smaller mass and charge than the alpha particle **Gamma rays:** γ

Nature of the radiation: very high frequency electromagnetic radiation, mass = 0, charge = 0 Penetrating power, and what will block it: Very highly penetrating, smallest mass and charge, most stopped by a thick layer of steel or concrete, but even a few cm of dense lead doesn't stop all of it!

Ionising power: The lowest ionising power of the three, gamma radiation carries no electric charge and has virtually no mass, so not much of a 'punch' when colliding with an atom.



Alpha particles may be completely stopped by a sheet of paper, beta particles by aluminium shielding. Gamma rayscan only be reduced by much more substantial mass, such as a very thick layer of lead.

NATURAL RADIOACTIVITY

Nuclear reactions which occur spontaneously are said to be an example of natural radioactivity. There are three naturally occurring radioactive series among the elements in the periodic table. These are known as the uranium series, the actinium series and the thorium series, each named after the element at which the series start (except the actinium series which starts with a different uranium isotope). Each series decays through a number of unstable nuclei by means of alpha and beta emission, until each series end on a different stable isotope of lead.

Radioactivity is the random spontaneous disintegration of an atom of an element. The stability of the nucleus depends on the relative numbers of protons and neutrons present. The most stable

nuclides tend to have an even number of protons and an even number of neutrons as each group of two protons and two neutrons, in the nucleus, makes an especially stable combination. A number of elements have atoms or nuclei which are unstable and consequently split up to form smaller atoms. This is due to all elements wanting to achieve equilibrium or stability in the nucleus. A substance is said to be radioactive if it contains unstable nuclei and is able to naturally release energy in the process of shedding high speed charged particles, in an attempt to reach a stable state. With this, a non-radioactive substance will remain intact indefinitely unless acted upon by an external force. In the process of transmutation, known as decay, the radioactive nuclei emits charged particles or electromgnetic rays depending on the nature it's instability. This results in a daughter nuclide being produced which may be radioactive or stable, but if it is radioactive it will in turn decay into a daughter nuclide, continuing to do so until it reaches the point of stability, an isotope of lead. The disintegration of a radioactive nucleus is conveniently



1,4N , ÉHe >[18F] > 1,7O 1H 1870 and 1H

represented in the form of radioactive decay series that consists of a sequence of nuclear reactions that ultimately ends in a stable isotope. Some of these are the uranium series, the thorium series, and the neptunium series. For example, the principle isotope of uranium is 238U that constitutes 99.3% of the natural element and has the half-life of 4.5 x 109 years. It

disintegrates by emitting an alpha-particle forming 234Th. This isotope undergoes a betaemission forming 234Pa, which in turn disintegrates into 234U. Then five successive emissions occur giving 214Pb, which ultimately ends in 206Pb, a stable isotope. This involves fourteen steps. You may consult any standard general chemistry textbook for further information.

NATURAL AND ARTIFICIAL RADIOACTIVITY.

NATURAL RADIOACTIVITY:-

Nuclear reactions which occur spontaneously are said to be an example of natural radioactivity. There are three naturally occurring radioactive series among the elements in the periodic table. These are known as the uranium series, the actinium series and the thorium series, each named after the element at which the series start (except the actinium series which starts with a different uranium isotope). Each series decays through a number of unstable nuclei by means of alpha and beta emmission, until each series end on a different stable isotope of lead.

ARTIFICIAL RADIOACTIVITY:-

Not all nuclear reactions are spontaneous. These reactions occur when stable isotopes are bombarded with particles such as neutrons. This method of inducing a nuclear reaction to proceed is termed artificial radioactivity. This meant new nuclear reactions, which wouldn't have been viewed spontaneously, could now be observed. Since about 1940, a set of new elements with atomic numbers over 92 (the atomic number of the heaviest naturally occurring element, Uranium) have been artificially made. They are called the transuranium elements.

Artificial or Induced radioactivity

- If a substance emits radiations by itself, it is said to possess natural radioactivity.
- If a substance does not possess radioactivity but starts emitting radiations on exposure to rays from a natural radioactive substance, it is said to possess induced or artificial radioactivity.
- The first artificial transmutation was caused out by Rutherford in 1919 who bombarded nitrogen gas with alpha particles and obtained hydrogen and oxygen.

The isotope	are stable and no further disintegration takes place. Nowadays other
bombarding particles	(i.e., projectiles) like protons (1H1), deutrons 1H2 electrons can be

$$\begin{array}{l} {}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}n_{0} \\ \\ {}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}n_{0} \\ \\ {}^{30}_{15}\text{P} \\ \end{array}$$

$$\begin{array}{l} {}^{30}_{15}\text{P} \longrightarrow {}^{31}_{14}\text{Si} + \beta^{+} \\ \\ {}^{12}\text{C}_{6} + {}^{2}_{1}\text{H} \longrightarrow {}^{73}_{14}\text{N} + {}^{1}n_{0} \text{ (D, n reactions)} \\ \\ {}^{16}_{8}\text{O} + {}^{2}_{1}\text{H} \longrightarrow {}^{74}_{7}\text{N} + {}^{4}_{2}\text{He} \text{ (D, }\alpha \text{ reactions)} \\ \\ \\ {}^{7}_{7}\text{N} + {}^{1}_{1}\text{H} \longrightarrow {}^{15}_{7}\text{O} + \gamma \text{ (p, r)reaction} \\ \\ \\ {}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{H} + {}^{4}_{2}\text{He} \text{ (p, }\alpha \text{)reaction} \\ \\ \\ \\ {}^{23}_{11}\text{Na} + {}^{1}n_{0} \longrightarrow {}^{24}_{13}\text{Na} + \gamma \text{ (n, r)reaction} \\ \\ \\ \\ {}^{131}_{2}\text{Te} + {}^{1}n_{0} \longrightarrow {}^{132}_{53}\text{P} + {}_{-1}\text{e}^{0} \text{ (n, }\beta^{-1} \text{)reaction} \\ \\ \\ \\ \\ {}^{14}_{7}\text{N} + {}^{1}n_{0} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H} \text{ (n, p)reaction} \\ \end{array}$$

It accelerated to very high speeds by fluctuating electric and magnetic fields in machines such as cyclotron, synchrotron etc. These high speed particles are more efficient in causing nucleus to disintegrate on impact.

The typical transmutations involving various particles are summarised below:

(i) a particle induced reactions

Since a particle is used and a neutron is produced, the reaction is termed as (a, n) reaction.

The first example of radioactivity produced by artificial means is given below:

The isotope produces is itself radioactive.

undergoes decay by positron (b+) emission.

(ii) Deutron induced reactions

(iii) Proton - induced reactions

(iv) Neutron - induced reactions

Thus this phenomenon in which artificial transmutation of a stable non - radioactive nucleus leads to the formation of radioactive isotope is called artificial radioactivity or induced radioactivity. Some of the isotopes produced as a result of neutron bombardment find applications in different areas.

The features of artificial radioactive isotopes are given below:

- i) Artificial radioactive isotopes exhibit behaviour similar to natural radioactive elements and follow some rate law with regard to their disintegration.
- ii) Natural radioactivity is shown by elements with high atomic numbers (> 83) whereas artificial radioactivity can be induced in elements with low atomic numbers.
- iii) Artificial radioactive isotopes generally have short half-life periods.
- iv) They are very rarely found in nature because they decay off as soon as they are formed due to short half-life periods.

DETECTION AND MEASUREMENT OF RADIATIONS:

The **Geiger–Müller counter**, also called a **Geiger counter**, is an instrument used for measuringionizing radiation.

It detects radiation such as alpha particles, beta particles and gamma rays using the ionization produced in a Geiger–Müller tube, which gives its name to the instrument. In wide and prominent use as a hand-held radiation survey instrument, it is perhaps one of the world's best-known radiation instruments.

The Geiger counter consists of two main elements; the Geiger-Müller tube which detects the radiation, and the processing and display electronics. The Geiger-Müller tube is filled with an inert gas such as helium, neon, or argon at low pressure, which briefly conducts electrical charge when a particle or photon of incident radiation makes the gas conductive by ionization. The ionization current is greatly amplified within the tube by the Townsend avalanche effect to produce an easily measured detection pulse. This makes the G-M counter relatively cheap to manufacture, as the subsequent electronic processing is greatly simplified.

There are fundamentally two types of radiation readout; counts or radiation dose. The counts display is the simplest and is the number of ionizing events displayed either as a count rate, commonly "counts per second", or as a total over a set time period (an integrated total). The

counts readout is normally used when alpha or beta particles are being detected. There is usually an option to produce audible clicks representing the number of ionization events detected. This is the distinctive sound normally associated with hand held or portable Geiger counters. The purpose of this is to allow the user to concentrate on manipulation of the instrument whilst retaining auditory feedback on the radiation rate.

Limitations

There are two main limitations of the Geiger counter. Because the output pulse from a Geiger-Müller tube is always the same magnitude regardless of the energy of the incident radiation, the tube cannot differentiate between radiation types. A further limitation is the inability to measure high radiation rates due to the "dead time" of the tube. This is an insensitive period after each ionization of the gas during which any further incident radiation will not result in a count, and the indicated rate is therefore lower than actual.

Scintillation Counter

A scintillation counter is an instrument for detecting and measuring ionizing radiation. It consists of a scintillator which generates photons of light in response to incident radiation, a sensitive photomultiplier tube which converts the light to an electrical signal, and the necessary electronics to process the photomultiplier tube output. Scintillation counters are widely used because they can be made inexpensively yet with good quantum efficiency and can measure both the intensity and the energy of incident radiation.

When a charged particle strikes the scintillator, its atoms are excited and photons are emitted. These are directed at the photomultiplier tube's photocathode, which emits electrons by thephotoelectric effect. These electrons are electrostatically accelerated and focused by an electrical potential so that they strike the first dynode of the tube. The impact of a single electron on the dynode releases a number of secondary electrons which are in turn accelerated to strike the second dynode. Each subsequent dynode impact releases further electrons, and so there is a current amplifying effect at each dynode stage. Each stage is at a higher potential than the previous to provide the accelerating field. The resultant output signal at the anode is in the form of a measurable pulse for each photon detected at the photocathode, and is passed to the processing electronics. The pulse carries information about the energy of the original incident radiation on the scintillator. Thus both intensity and energy of the radiation can be measured.

The scintillator must be in complete darkness so that visible light photons do not swamp the individual photon events caused by incident ionising radiation. To achieve this a thin opaque foil, such as aluminised mylar, is often used, though it must have a low enough mass to prevent undue attenuation of the incident radiation being measured.

The scintillator consists of a transparent crystal, usually a phosphor, plastic (usually containing anthracene) or organic liquid (see liquid scintillation counting) that fluoresces when struck by ionizing radiation.

Cesium iodide (CsI) in crystalline form is used as the scintillator for the detection of protons and alpha particles. Sodium iodide (NaI) containing a small amount ofthallium is used as a scintillator for the detection of gamma waves and Zinc Sulphide is widely used as a detector of alpha particles. Zinc Sulphide is the material Rutherford used to do his scattering experiment. Lithium iodide (LiI) is used as a neutron detector.

Wilson cloud chamber method:

It is an instrument used for the detection and identification of the path of subatomic particles. In Wilson Cloud Chamber, paths of subatomic particles or ionized particles can be photographed.

Principle

When a particle is passed through the supersaturated vapours, droplets are formed on the line due to ionization along the track and particle is detected.

Construction and working

It is consist of a closed cylinderical chamber with the transparent glass top, a movable piston at the bottom. On the sides near the top, the cylinder is provided with a glass window. inside the cylinder a liquid of low boiling point is placed. The piston can be moved up or down. The whole system is air tight. A strong light source is used to illuminate the chamber while the photograph is taken by the camera.

Some volatile liquid having low boiling point (methanol CH3OH or ethanol C2H5OH) is poured on the inner surface of the chamber. The piston first is moved slowly up so that the air inside the chamber is cleaned and then it is then moved down, so that the internal pressure is dropped and the air get vapours of the liquid and becomes supersaturated and a fog is observed in the chamber. At the right moment particles are allowed to enter into the chamber and a powerful and intense beam of light is used to illuminate the track of the particles and photos are taken by the sensitive camera. If a strong electric or magnetic field is applied to the particles (charged) then their path is altered. By the study of path's length, thickness, continuity or discontuinity and the influence of magnetic field (curve) .i.e. geometry the e/m ratio can be calculated and hence the particle is detected.

Transmutation is the conversion of an atom of one element to an atom of another element (radioactive decay is one way that this occurs)

Type of radioactive	Particle emitted	Change in mass	Change in atomic
decay		number(A)	number(Z)
Alpha decay	4	Decrease by 4	Decrease by 2
	2He		
Beta decay	0e	No change	Increase by 1
	-1		
Gamma emission	γ	No change	No change

Nuclear equations

Some atoms are unstable. Emission of particles or electromagnetic radiation is one way to gain stability.

Alpha radiation

Uranium 238 undergoes alpha decay in attempt to be stable daughter nuclide: the nuclide formed from the decay Parent nuclide: the original nuclide undergoing decay.

 $^{238}U_{92} \longrightarrow ^{234}Th_{90} + ^{2}He_{4}$

Beta radiation

Consists of a stream of beta particles which are high speed electrons. Represented by the symbol 0-1e

Iodine-131 is an example of a radioactive isotope that undergoes Beta emission. (an antineutrino also emitted)

¹³¹ I₅₃ \longrightarrow ¹³¹ Xe ₅₄ -+ ₋₁ e ⁰

Notice the atomic number increases. Beta emission in the conversion of a neutron to a proton

1
 n₀ \longrightarrow $_{1}$ P¹ $+$ $_{-1}e$

The electron comes from the neutron being converted not from the electron cloud.

Gamma radiation

 ${}^{1}\mathbf{p_{1}} \rightarrow {}^{1}n_{0} + {}^{-1}e^{0}$

Electron capture

Capture by the nucleus on an inner shell electron of the electron cloud. Rubidium-81 does this

⁸¹Rb₃₇ + $-_1e^0 \rightarrow {}^{81}Kr_{36}$

Electron capture has the effect of positron emission, converting a proton to a neutron

 ${}^{1}\mathbf{p_{1}} \longrightarrow {}^{1}n_{0} + {}^{-1}\mathbf{e}^{0}$

High energy photons (electromagnetic radiation of a short wavelength), Gamma radiation does not change the mass or atomic number and is represented as 0.

It almost always accompanies other radioactive emission because it represents the energy lost when the remaining nucleons reorganize into more stable arrangements. Generally you do not show gamma rays when writing nuclear equations

Positron emission

A positron is a particle that has the same mass as an electron but opposite charge. The positron is represented as 0

1e. Carbon-11 is an example of a particle that undergoes positron emission.

NUCLEAR FISSION

When a nucleus fissions, splits into several smaller fragments. These fragments, or fission products, are about equal to half the original mass. Two or three neutrons are also emitted.

The sum of the masses of these fragments is less than the original mass. This 'missing' mass (about 0.1 percent of the original mass) has been converted into energy according to Einstein's equation.

Fission can occur when a nucleus of a heavy atom captures a neutron, or it can happen spontaneously.



In nuclear physics and nuclear chemistry, **nuclear fission** is either a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller parts (lighter nuclei). The fission process often produces free neutrons and photons (in the form of gamma rays), and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission is a form of nuclear transmutation because the resulting fragments are not the same element as the original atom. The two nuclei produced are most often of comparable but slightly different sizes, typically with a mass ratio of products of about 3 to 2, for common fissile isotopes.

Fission as encountered in the modern world is usually a deliberately produced man-made nuclear reaction induced by a neutron. It is less commonly encountered as a natural form of spontaneousradioactive decay (not requiring a neutron), occurring especially in very high-mass-number isotopes.

Nuclear fission and nuclear fusion both are nuclear phenomena that release large amounts of energy, but they are different processes which yield different products. Learn what nuclear fission and nuclear fusion are and how you can tell them apart.

This is an exothermic process releasing kinetic energy of the fission products and energy in the form of gamma radiation. Fission may be considered a form of element transmutation since changing the number of protons of an element essentially changes the element from one into another. An example for nuclear fission

 $_{92}U^{235} + _{1}n^0 \rightarrow _{90} Sr {}^{38} + _{54}Xe^{143} + 3_1n^0$

NUCLEAR FUSION

Nuclear fusion is a process in which atomic nuclei are fused together to form heavier nuclei. Extremely high temperatures (on the order of 1.5×10^{7} °C) can force nuclei together. Large amounts of energy are released when fusion occurs.



Nuclear Fusion Examples

The reactions which take place in the sun provide an example of nuclear fusion:

$11H + 21H \rightarrow 32He$	
$32\text{He} + 32\text{He} \rightarrow 42\text{He} + 211\text{H}$	
$11H + 11H \rightarrow 21H + 0+1\beta$	

In nuclear physics, **nuclear fusion** is a nuclear reaction in which two or more atomic nucleicollide at a very high speed and join to form a new type of atomic nucleus. During this process, matter is not conserved because some of the matter of the fusing nuclei is converted to photons(energy). Fusion is the process that powers active or "main sequence" stars.

Fusion reactions of light elements power the stars and produce virtually all elements in a process called nucleosynthesis. The fusion of lighter elements in stars releases energy (and the mass that always accompanies it). For example, in the fusion of two hydrogen nuclei to form helium, 0.7% of the mass is carried away from the system in the form of kinetic energy or other forms of energy (such as electromagnetic radiation).

It takes considerable energy to force nuclei to fuse, even those of the lightest element, hydrogen. This is because all nuclei have a positive charge due to their protons, and as like charges repel, nuclei strongly resist being put close together. Accelerated to high speeds, they can overcome this electrostatic repulsion and be forced close enough for the attractive nuclear force to be sufficiently strong to achieve fusion. The fusion of lighter nuclei, which creates a heavier nucleus and often a free neutron or proton, generally releases more energy than it takes to force the nuclei together; this is an exothermic process that can produce self-sustaining reactions.

Energy released in most nuclear reactions is much larger than in chemical reactions, because thebinding energy that holds a nucleus together is far greater than the energy that holds electrons to a nucleus. For example, the ionization energy gained by adding an electron to

a hydrogen nucleus is 13.6 eV—less than one-millionth of the 17.6 MeV released in the deuterium–tritium (D–T) reaction shown in the diagram to the right (one gram of matter would release 339 GJ of energy).

Fusion reactions have an energy density many times greater than nuclear fission; the reactions produce far greater energy per unit of mass even though *individual* fission reactions are generally much more energetic than *individual* fusion ones, which are themselves millions of times more energetic than chemical reactions. Only direct conversion of mass into energy, such as that caused by the annihilatory collision of matter andantimatter, is more energetic per unit of mass than nuclear fusion.

Distinguishing between Fission and Fusion

Both fission and fusion release enormous amounts of energy. Both fission and fusion reactions can occur in nuclear bombs. So, how can you tell fission and fusion apart?

•Fission breaks atomic nuclei into smaller pieces. The starting elements have a higher atomic number than that of the fission products. For example, uranium can fission to yield strontium and krypton.

•Fusion joins atomic nuclei together. The element formed has more neutrons or more protons than that of the starting material. For example, hydrogen and hydrogen can fuse to form helium.

ATOMIC POWER PROJECTS IN INDIA

Nuclear power is the fourth-largest source of electricity in India after thermal, hydroelectric and renewable sources of electricity. As of 2012, India has 20 nuclear reactors in operation insixnuclear power plants, having an installed capacity of 4780 MW and producing a total of 29,664.75 GWh of electricity while seven other reactors are under construction and are expected to generate an additional 6,100 MW.

In October 2010, India drew up "an ambitious plan to reach a nuclear power capacity of 63,000 MW in 2032", but, after the 2011 Fukushima nuclear disaster in Japan, "populations around proposed Indian NPP sites have launched protests, raising questions about atomic energy as a clean and safe alternative to fossil fuels". There have been mass protests against the Frenchbacked 9900 MW Jaitapur Nuclear Power Project in Maharashtra and the Russian-backed 2000 MW Kudankulam Nuclear Power Plant in Tamil Nadu. The state government of West Bengal state has also refused permission to a proposed 6000 MW facility near the town of Haripur that intended to host six Russian reactors. A Public Interest Litigation (PIL) has also been filed against the government's civil nuclear programme at the Supreme Court.

India has been making advances in the field of thorium-based fuels, working to design and develop a prototype for an atomic reactor using thorium and low-enriched uranium, a key partofIndia's three stage nuclear power programme. India's domestic uranium reserves are small and the country is dependent on uranium imports to fuel its nuclear power industry. Since early 1990s, Russia has been a major supplier of nuclear fuel to India. Due to dwindling domestic uranium reserves, electricity generation from nuclear power in India declined by 12.83% from 2006 to 2008.

Power station	Operator	State	Total capacity (MW)
Kaiga	NPCIL	Karnataka	880
Kakrapar	NPCIL	Gujarat	440
Kalpakkam	NPCIL	Tamil Nadu	440
Narora	NPCIL	Uttar Pradesh	440
Rawatbhata	NPCIL	Kota Rajasthan	1180
Tarapur	NPCIL	Maharashtra	1400
Kudankulam	NPCIL	Tamil Nadu	1000

NUCLEAR REACTOR



A nuclear reactor, formerly known as an atomic pile, is a device used to initiate and control sustained nuclear chain reaction. Nuclear reactors are used at nuclear power а plants for electricity generation and in propulsion of ships. Heat fromnuclear fission is passed to a working fluid (water or gas), which runs through steam turbines. These either drive a ship'spropellers or turn electrical generators. Nuclear generated steam in principle can be used for industrial process heat or fordistrict heating. Some reactors are used to produce isotopes for medical and industrial use, or for production of weapons-gradeplutonium. Some are run only for research. Today there are about 450 nuclear power reactors that are used to generate electricity in about 30 countries around the world

Parts of Nuclear Power Plant

- A Nuclear Reactor mainly consists of
- a) Fuel
- b) Moderators
- c) Control rods
- d) Shielding
- e) Coolant
- f) Turbines
- g) Generator
- h) Cooler Pipes
- i) Water Supply



Fuel: The fissionable material used in the reactor is called as fuel. The commonly used fuels are Uranium, Plutonium or Thorium. It can be U-235, U-238, Pu-236 or Th-232. Uranium is mostly preferred as it has high melting point.

Moderators: Only neutrons of a fairly low speed should be used to have controlled chain reaction. To slow down the speed fast moving neutrons produced during the fission process, moderators are used. Moderator reduces the speed of the neutron by absorbing its energy but not absorb neutron. Graphite, Heavy water and Beryllium are common moderators.

Control Rods: These rods absorb neutrons and stop the chain reaction to proceed further. These are made up of steel containing a high percentage of material like cadmium or boron which can absorb neutrons. When control rods are completely inserted into the moderator block then all the neutrons is absorbed and reaction comes to halt.

Shielding: Shielding prevents radiations to reach outside the reactor. Lead blocks and concrete enclosure that is strong enough of several meters thickness are used for shielding.

Coolant: The coolant substance in a pipe to the steam generator where water is boiled. This is where heat-exchange process occurs. Heat is absorbed by the coolant that is produced in the reactor. Typical coolants are water, carbon dioxide gas or liquid sodium.

Turbines: Steam produced in the boiler is now passes to a turbine. The force of the steam jet causes the turbine to rotate. Heat energy (steam) is converted to mechanical energy (moving turbine).

Generator: The generator consists of coils that change the mechanical energy into electric energy. The turbine moves and the change in magnetic flux cause electricity. This is transmitted to substations for distribution of electric power.

RADIOACTIVE WASTE MANAGEMENT

• Nuclear power is the only large-scale energy-producing technology which takes full responsibility for all its wastes and fully costs this into the product.

• The amount of radioactive wastes is very small relative to wastes produced by fossil fuel electricity generation.

• Used nuclear fuel may be treated as a resource or simply as a waste.

• Nuclear wastes are neither particularly hazardous nor hard to manage relative to other toxic industrial wastes.

• Safe methods for the final disposal of high-level radioactive waste are technically proven; the international consensus is that this should be geological disposal.

All parts of the nuclear fuel cycle produce some radioactive waste (radwaste) and the relatively modest cost of managing and disposing of this is part of the electricity cost, *i.e.* it is internalised and paid for by the electricity consumers.

At each stage of the fuel cycle there are proven technologies to dispose of the radioactive wastes safely. For low- and intermediate-level wastes these are mostly being implemented. For high-level wastes some countries await the accumulation of enough of it to warrant building geological repositories; others, such as the USA, have encountered political delays.

Unlike other industrial wastes, the level of hazard of all nuclear waste - its radioactivity - diminishes with time. Each radionuclide contained in the waste has a half-life – the time taken for half of its atoms to decay and thus for it to lose half of its radioactivity. Radionuclides with long half-lives tend to be alpha and beta emitters – making their handling easier – while those with short half-lives tend to emit the more penetrating gamma rays. Eventually all radioactive wastes decay into non-radioactive elements. The more radioactive an isotope is, the faster it decays.

The main objective in managing and disposing of radioactive (or other) waste is to protect people and the environment. This means isolating or diluting the waste so that the rate or concentration of any radionuclides returned to the biosphere is harmless. To achieve this, practically all wastes are contained and managed – some clearly need deep and permanent burial. From nuclear power generation, none is allowed to cause harmful pollution.

All toxic wastes need to be dealt with safely, not just radioactive wastes. In countries with nuclear power, radioactive wastes comprise less than 1% of total industrial toxic wastes (the balance of which remains hazardous indefinitely).

Storage and disposal of used fuel and other HLW

There are about 270,000 tonnes of used fuel in storage, much of it at reactor sites. About 90% of this is in storage ponds (smaller versions of that illustrated above), the balance in dry storage. Much of the world's used fuel is stored thus, and some of it has been there for decades. Annual arisings of used fuel are about 12,000 tonnes, and 3,000 tonnes of this goes for reprocessing. Final disposal is not urgent in any logistical sense.

Storage ponds at reactors, and those at centralized facilities such as CLAB in Sweden, are 7-12metres deep, to allow several metres of water over the used fuel comprising racked fuel assemblies typically about 4 m long and standing on end. The circulating water both shields and cools the fuel. These pools are robust constructions made of thick reinforced concrete with steel liners. Ponds at reactors are often designed to hold all the used fuel for the life of the reactor.

Some storage of fuel assemblies which have been cooling in ponds for at least five years is in dry casks, or vaults with air circulation inside concrete shielding. One common system is for sealed steel casks or multi-purpose canisters (MPCs) each holding about 80 fuel assemblies with inert gas. Casks/ MPCs may be used also for transporting and eventual disposal of the used fuel. For storage, each is enclosed in a ventilated storage module made of concrete and steel. These are commonly standing on the surface, about 6m high, cooled by air convection, or they may be below grade, with just the tops showing. The modules are robust and provide full shielding. Each cask has up to 45 kW heat load.

A collection of casks or modules comprises an Independent Spent Fuel Storage Installation (ISFSI), which in the USA is licensed separately from any associated power plant, and is for interim storage only. About one quarter of US used fuel is stored thus.

For disposal, to ensure that no significant environmental releases occur over tens of thousands of years, 'multiple barrier' geological disposal is planned. This immobilises the radioactive elements in HLW and some ILW and isolates them from the biosphere. The main barriers are

•Immobilise waste in an insoluble matrix such as borosilicate glass or synthetic rock (fuel pellets are already a very stable ceramic: UO2).

•Seal it inside a corrosion-resistant container, such as stainless steel.

•Locate it deep underground in a stable rock structure.

•Surround containers with an impermeable backfill such as bentonite clay if the repository is wet.

Recycling used fuel

Any used fuel will still contain some of the original U-235 as well as various plutonium isotopes which have been formed inside the reactor core, and the U-238_c. In total these account for some 96% of the original uranium and over half of the original energy content (ignoring U-238).Reprocessing, undertaken in Europe and Russia, separates this uranium and plutonium from the wastes so that they can be recycled for re-use in a nuclear reactor Plutonium arising from reprocessing is recycled through a MOX fuel fabrication plant where it is mixed with depleted uranium oxide to make fresh fuel. European reactors currently use over 5 tonnes of plutonium a year in fresh MOX fuel.

Textbooks

1. Puri, Sharma & Pathania, 2013. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.

Reference

1. Weller, Overtone, Rourke and Armstrong, "Inorganic Chemistry", 6th Edition, 2014.

POSSIBLE QUESTIONS

PART A: MULTIPLE CHOICE QUESTIONS (Each question carry one mark)

- 1. Nuclear reactions involve
 - a. Valence electrons

b. Neutrons and protons

- c. electrons in the inner orbitals
- d. excited electrons
- 2. Nuclear reactions involve
 - a. Small amounts of energy

b. Large amount of energy

- c. affected by temperature affected by concentration.
- d. Small amount of radiation
- 3. Which is high ionising power
 - a. Alpha particles b. beta particles c. gamma rays d. positron
- 4. Nuclear reactions are
 - a. Releasing Small amounts of energy

b. independent of temperature and concentration

- c. affected by temperature
- d. affected by concentration
- 5. Nuclear reactions which occur spontaneously are called

a. Natural radioactivity

- b. Artificial radioactivity
- c. artificial transmutation Chemical reactions
- d. Transuranium elements
- 6. The stability of the nucleus depends on the relative numbers of

a. Protons and neutrons present

- b. protons present
- c. neutrons present
- d. electrons present
- 7. The most stable nuclides tend to have an

	a. even number of protons and an even number of neutrons							
	b. odd number of protons							
	c. odd number of neutrons							
	d. odd number of protons and neutrons.							
8.	. The reactions which occur when stable isotopes are bombarded with particles such as							
	neutrons.							
	a. Natural radioactivity b. Artificial radioactivity							
	c. artificial transmutation d. Chemical reactions							
9.	A set of new elements with atomic numbers over 92 have been artificially made. They are							
	called							
	a. Transuranium elements b. Transition elements							
	c. non-radioactive elements d. Lanthanides							
10.	. Natural radioactivity is shown by elements with							
	a. high atomic numbers b. Low atomic numbers c. Transition elements							
	d. Transuranium elements							
11.	Artificial radioactive isotopes generally have							
	a. short half-life periods. b. Long half-life periods							
	c. high atomic number d. fractional molecular weight							
12.	. The Geiger-Müller counter is an instrument used for measuring							
	a. ionizing radiation b. particle size analyser							
	c. measures the surface morphology d. penentration power of radiations							
13.	. The scintillator for the detection of protons and alpha particles							
	a. Cesium iodide b. sodium iodide c. zinc sulphide d. Lithium iodide							
14.	. Cesium iodide has been used as a scintillator in the scintillation counters for the							
	detection of							
	a. Protons b. gamma rays c. alpha particle d. neutrons							
15.	Sodium iodide has been used as a scintillator in the scintillation counters for the							
	detection of							
	a. Protons b. gamma rays c. alpha particles d. neutrons							
16.	. Which is not connected to nuclear fission							
	a. Exothermic process							

- b. Releases kinetic energy along with fission products
- c. Form of transmutation
- d. Union of two small nucleus
- 17. Which is not connected to nuclear fusion
 - a. Endothermic process
 - b. Releases kinetic energy along with products

c. Form of transmutation

- d. Union of two small nucleus
- 18. For which process extremely high temperatures of the order of 1.5 x 107°C is requireda. Nuclear fission b. Nuclear fusion c. Radioactive decay d. artificial transmutation
- 19. The reaction of two hydrogen nuclei to form helium is an example for
- a. Nuclear fission **b. Nuclear fusion** c. chemical reaction d. artificial radioactivity 20. The percentage of U-235 in naturally occurring uranium is
 - a.93.70% **b. 7%** c. 80% d. 20%

PART B (Each question carries 8 marks)

- 1. Discusses the properties of β and γ rays.
- 2. Explain in detail about nuclear fission and fusion.
- 3. Mention the important uses of radioactive materials
- 4. Describe different methods of detection and measurement of radioactivity
- 5. Explain in detail the applications of radioactive isotopes
- 6. Explain how electricity is generated from a nuclear reactor.
- 7. Write short notes on (i) transuranic elements (ii) Uranium as nuclear fuel.
- 8. Discusses about the artificial disintegration of elements
- 9. What are nuclear reactions? Describe nuclear reactions with deuterons, neutrons and photons with suitable examples.
- 10. Compare the processes of nuclear fission and fusion as sources of energy.

[15CHU502] KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER

INORGANIC CHEMISTRY

UNIT 3- OBJECTIVE TYPE QUESTIONS FOR ONLINE EXAMINATION(Each carry 1 Mark)

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answer
The radioactive decay of $_6$ C 14 to $_7$ N 14 occurs by					
the process of	beta particle emission	alpha particle emission	electron capture	neutron capture	neutron capture
Which of the following elements is utilized as a			<u> </u>		<u>^</u>
shield from sources of radiation?	Pb	Ca	Zn	As	Pb
Which of the following types of elements in the					
periodic table are always radioactive?	Noble gases	Alkali metals	Halogens	Actinides	Actinides
				Nearly five times	
		Nearly four times that of		that of hydrogen	Nearly four times that of
Each a- particle has the mass:	Equal to that of hydrogen	hydrogen atom	Half of the hydrogen atom	atom	hydrogen atom
Which among the following has the highest					
penetrating power?	$\gamma - rays$	β – rays	alpha – rays	cathode rays	$\gamma - rays$
	High momentum and low	Low momentum and high	Low momentum and kinetic	High momentum	Low momentum and kinetic
β rays possess:	kinetic energy	kinetic energy	energy	and kinetic energy.	energy
Atoms of different elements containing the same					
number of neutrons but different number of total					
nucleons is known as:	Isotones	Isodiaphers	Isotopes	Isosterism	Isotones
				Atomic number	
When positron is emitted by a radioactive nucleus	Atomic number remains	Atomic number increases	Atomic number decreases by	increases by 2	Atomic number decreases by
then:	the same	by 1 unit	1 unit	units.	1 unit
The process of conversion of stable isotope of one					
element into isotope of another element is known				Induced	
as:	Artificial radioactivity	Artificial transmutation	Natural radioactivity	radioactivity.	Artificial radioactivity
The temperature level inside a nuclear reactors is					
maintained using	Shielding	Coolants	Moderators	control rods	Coolants
Which radioactive emission have a charge of -1?	Neutrons	protons	gamma rays	beta particles	beta particles
As the temperature of a sample of a radioactive					
element decreases, the half-life will	Decrease	Increase	remains the same	double	remains the same
What kind of radiation will travel through an					
electric field on a pathway that remains unaffected					
by the field?	a proton	a gamma ray		an electron	a gamma ray
Which radioactive emanations have a charge of					
+1?	Neutrons	protons	gamma rays	beta particles	protons
Which radioactive emanations have a charge of					
+2?	Neutrons	alpha particles	gamma rays	beta particles	alpha particles

The number of neutrons inside a nuclear reactors					
is reduced using	Shielding	Coolants	Moderators	control rods	control rods
The speed of the neutrons inside a nuclear					
reactors is reduced by using	Shielding	Coolants	Moderators	control rods	Moderators
Which particle cannot be accelerated in a					
magnetic field	Neutrons	protons	alpha particle	beta particles	Neutrons
In a fusion reaction, reacting nuclei must collide.				oppositely charged	
Collisions between two nuclei are difficult to	both negatively charged	both positively charged	oppositely charged and	and repel each	both positively charged and
achieve because the nuclei are	and repel each other	and repel each other	attract each other	other	repel each other
Which nuclide is a radioisotope used in the study					
of organic reaction mechanisms?	carbon-12	carbon-14	Uranium-235	Uranium-238	carbon-14
To make nuclear fission more efficient, which					
device is used in a nuclear reactor to slow the					
speed of neutrons?	internal shield	external shield	control rod	moderator	control rod
Fissionable uranium-233 are used in nuclear					
reactors as	coolants	control rods	moderators	fuel	fuel
Fissionable uranium 235 are used in nuclear					
reactors as	Coolants	control rods	moderators	fuel	fuel
Fissionable plutonium-239 are used in nuclear					
reactors as	Coolants	control rods	moderators	fuel	fuel
	carbon-14 is very unstable	living tissue will not	the ratio of carbon-14 to	the amount of	the ratio of carbon-14 to
	and is readily lost from the	absorb carbon-14 but will	carbon-12 in the atmosphere	carbon-14 in all	carbon-12 in the atmosphere
The basis for the carbon-14 dating method is that	atmosphere	absorb carbon-12	is a constant	objects is the same.	is a constant
What is required for a nuclear transmutation to		a particle to collide with	gamma emission		a particle to collide with a
occur?	a corrosive environment	a nucleus	spontaneous nuclear decay		nucleus
Which type of radioactive decay results in no					
change in mass number and atomic number for the					
starting nucleus?	Beta	positron emission	alpha	gamma	gamma
		Ê		The mass number	
		The mass number does		does not change	
What happens to the mass number and the atomic	The mass number decreases	not change and the		and the atomic	The mass number does not
number of an element when it undergoes beta	by 4 and the atomic number	atomic number decreases	Neither the mass number nor	number increases	change and the atomic
decay?	decreases by 2	by 2	the atomic number change	by 1.	number increases by 1.
The amount of material necessary to sustain a fissi	-				
on reaction is known as	Radioactivity	tonnage	substantial mass	critical mass	critical mass
The energy which holds the nucleus together is kn	-				
own as the	nuclear binding energy	mass defect	critical mass	fusion energy	nuclear binding energy
				containment for hig	
Which of these is most significant problem in deve				h temperature react	containment for high tempera
loping fusion controlled energy?	limited resources	air pollution	low energy yield	ion	ture reaction
The combination of two atomic nuclei into one,					
accompanied by a release of energy, is called	Fusion	Fission	substitution	radioactive decay	Fusion

				involve the protons	
				and/or neutrons	
Nuclear changes differ from normal chemical				(nucleus) of an	
changes in that all nuclear changes	absorb energy	release energy	produce explosions	atom	release energy
				The mass number	
		The mass number does		does not change	
What happens to the mass number and the atomic	The mass number decreases	not change and the		and the atomic	The mass number decreases
number of an element when it undergoes alpha	by 4 and the atomic number	atomic number decreases	Neither the mass number nor	number increases	by 4 and the atomic number
decay?	decreases by 2	by 2	the atomic number change	by 1	decreases by 2
				The mass number	-
		The mass number does		does not change	
What happens to the mass number and the atomic	The mass number decreases	not change and the		and the atomic	
number of an element when it undergoes gamma	by 4 and the atomic number	atomic number decreases	Neither the mass number nor	number increases	Neither the mass number nor
decay?	decreases by 2	by 2	the atomic number change	by 1	the atomic number change
Example for moderator in nuclear reactor	Water	heavy water	boron	cadmium	heavy water
Example for moderator in nuclear reactor	Water	graphite	boron	cadmium	graphite
The fuel used in most of the thermal reactors in		6 1			
the form of aluminium-plated rods	Uranium-235	uranium-238	thorium-232	Thorium-235	Uranium-235
The fissionable nuclei used in thermal nuclear					
reactors	Uranium-235	uranium-238	thorium-232	Thorium-235	Uranium-235
The fissionable nuclei used in Fast breeder					
nuclear reactors	Uranium-235	uranium-238	thorium-232	Thorium-235	uranium-238
The fissionable nuclei used in Fast breeder					
nuclear reactors	Uranium-235	uranium-236	thorium-232	Thorium-235	thorium-232
The fissionable nuclei used in thermal nuclear					
reactors	Plutonium 239	uranium-238	thorium-232	Thorium-235	Plutonium 239
The heat generated in the reactor is removed by					
circulating a liquid called	Moderator	control rods	coolant	water	coolant
The heat generated in the reactor is removed by					
circulating a liquid called coolant such as	Sodium	lithium		rubidium	Sodium
Elements having the same number of neutrons.	Isotopes	Isotones	Isobars	Isomers	Isotones
Chlorine - 37 and Potassium – 39, both have 20					
neutrons in their nuclei. They are called	Isotopes	Isotone	Isobars	Isomers	Isotone
				small differences in	
				chemical reaction	
				rates produced by	small differences in chemical
	properties related to atomic			different atomic	reaction rates produced by
Isotopes cannot be separated using	weight	Their chemical properties	Nuclear resonances	weights.	different atomic weights.
	-			Centrifuge and	ž
By which method isotopes can be separated	Oxidation	reduction	Hydrolysis	distillation	Centrifuge and distillation
By which method isotopes can be separated	Oxidation	reduction	Hydrolysis	Electrolysis	Electrolysis
By which method isotopes can be separated	Oxidation	reduction	Hydrolysis	Gaseous diffusion	Gaseous diffusion
By which method isotopes can be separated	Oxidation	reduction	Hydrolysis	Thermal diffusion	Thermal diffusion

By which method isotopes cannot be separated	Electromagnetism	distillation	Oxidation	Thermal diffusion	Oxidation
By which method isotopes cannot be separated	Electromagnetism	distillation	Reduction	Thermal diffusion	Reduction
Nuclei above the belt of stability move to the belt					
of stability by emitting	a beta particle	a neutron	proton	alpha particle	a beta particle
Nuclei below the belt of stability move to the belt					
of stability by emitting	a positron	a neutron	proton	alpha particle	a positron
Nuclei with atomic numbers greater than 84					
move to the belt of stability by emitting	a positron	a neutron	proton	alpha particle	alpha particle
Nuclei below the belt of stability move to the belt					
of stability by	an electron capture	a neutron	proton	alpha particle	an electron capture
The energy required to break up a nucleus into its					
components protons and neutrons is called	Binding energy	Enthalpy of fusion	Enthalpy of formation	Nuclear energy	Binding energy
The difference between experimental mass of the					
atom and the sum of the masses of its	mass defect	Mass spectra	metastable defect	mass number	mass defect

UNIT-III

Nuclear Chemistry-Isotopes and Isobars

Nature of isotopes and isobars - Detection and isolation of isotopes - various methodsimportance of discovery of isotopes - uses of isotopes in various fields. Nuclear stability n/p ratio, magic numbers, C-12 and C-14 and nuclear binding energies. Nuclear reactions, mechanism and different types. Stellar energy. Radioactive disintegration series.

ISOTOPES, ISOBARS AND ISOTONES

Isotopes

These are the elements having same atomic number but different mass number. They have the same atomic number because the number of protons inside their nuclei remains the same. The difference in their mass number is due to the difference in their number of neutrons. Since they are neutral isotopes are elements having same number of electrons, which make them to possess identical chemical properties. Let us see some examples $1H^1$, $1H^2$, $1H^3$ are all isotopes of hydrogen. They all have their atomic number to be unity but the number of neutrons are 0, 1, 2 and z respectively. $17Cl_{37}$, $17Cl_{35}$ are isotopes of chlorine. They have 17 protons in the nucleus but have number of neutrons equal to 20 and 18 respectively. Practically every element consists of a mixture of several isotopes. The relative abundance of different isotopes differs from element to element. For example chlorine is composed of two isotopes of masses 34.98U and 36.98U, which are nearly integral multiples of the mass of hydrogen atom. Their relative abundances are 75.4 and 24.6 percent respectively. Mass of natural chlorine atom can be found as = 35.47. The isotope can occur either naturally or can be produced artificially in the laboratory.

Isobars

Isotopes are chemically same and physically different. But the converse is true in isobars. That is isobars are elements, which are chemically different but physically same. So, isobars are atoms of different elements having the same atomic mass but different atomic number. Since their number of electrons is different, their chemical properties are different. The light nuclei have unstable isobars. Heavy nuclei have stable isobars and these occur in pairs. Suppose the

3 number of protons of one isobar matches with that of another they are called as mirror-nuclides of each other.

Examples of isobars are

Since isobars are different elements they appear in different places in the periodic table.

Isotones

Isotones are elements having the same number of neutrons. Examples of isotones are Chlorine - 37 and Potassium - 39. Both have 20 neutrons in their nuclei.

Isotope separation is the process of concentrating specific isotopes of a chemical element by removing other isotopes. This process is a crucial one in the manufacture of uranium fuel for nuclear power stations, and is also required for the creation of uranium based nuclear weapons.

There are three types of isotope separation techniques:

•Those based directly on the atomic weight of the isotope.

•Those based on the small differences in chemical reaction rates produced by different atomic weights.

•Those based on properties not directly connected to atomic weight, such as nuclear resonances.

SEPARATION

The separation of isotopes of the same element from each other is difficult. Full separation in one step by chemical methods is impossible, because isotopes of the same elements have the same chemical properties; physical methods are generally based on the extremely small differences in physical properties caused by the differences in mass of the isotopes. Electrolytic separation and various exchange procedures for isotope separation, however, depend on chemical rate or equilibrium differences that are based primarily on the difference in energy of chemical bonds, which are a function of isotope mass. The isotopes of hydrogen, deuterium (hydrogen-2) and ordinary hydrogen (hydrogen-1) were the first to be separated in appreciable quantities. This accomplishment is credited to the American chemist Harold Urey, who discovered deuterium in 1932.

Before 1940 many methods were used for the separation of small amounts of isotopes for research purposes. Some of the most successful were the centrifuge method, fractional distillation, thermal diffusion, electrolysis, gaseous diffusion, and electromagnetic separation. Each of these methods depends on the small difference in weight of the isotopes to be separated, and is most effective with the hydrogen isotopes, where the difference in mass between the two substances amounts to 100%; by contrast, the difference in mass between the carbon isotopescarbon-12 and carbon-13 or between the neon isotopes neon-20 and neon-22 amounts to only about 10%, and between the uranium isotopes uranium-235 and uranium-238 to only a little over 1%. This factor of 10 to 1 or 100 to 1 makes the separation far more than 10 or 100 times as difficult. In all processes except the electromagnetic, which is the sole one-stage procedure, isotope separation involves a series of production stages. The net result of any single stage is the separation of the original material into two fractions, one of which contains a slightly higher percentage of the heavy isotope than the original mixture and the other contains slightly more of the light isotope.

To obtain an appreciable concentration, or enrichment, in the desired isotope, it is necessary to separate further the enriched fraction. This process is usually carried out by means of a cascade, comprising a large number of stages. The enriched fraction from any stage becomes the raw material for the next stage, and the depleted fraction, which still contains a considerable percentage of the desired isotope, is mixed with the raw material for the preceding stage. Even the depleted material from the original stage is stripped in additional stages when the raw material (for example, uranium) is scarce. Suitable apparatus is designed to make the flow from stage to stage automatic and continuous such a cascade is extremely flexible, and units can be shifted from one stage of the separation to another as desired. For example, in the separation of uranium, a large amount of material must be handled at the beginning, where the desired uranium-235 is mixed with about 140 times as much uranium-238; at the end of the process theuranium-235 is almost pure, and the volume of material is much smaller. Furthermore, by merely changing the piping, it is possible to shift stages to compensate for addition at an intermediate stage of material that results from preliminary enrichment by a different process.

Centrifuge and distillation

In the centrifuge method the apparatus is so arranged that vapor flows downward in the outer part of the rotating cylinder and upward in the central region of the cylinder. The centrifugal force acts more strongly on the heavy molecules than on the light ones, increasing the concentration of the heavy isotopes in the outer region. In separation by fractional distillation a mixture containing various isotopes is distilled. The molecules of the fraction having the lower boiling point (the lighter isotopes) tend to concentrate in the vapor stream and are collected.

Thermal diffusion

This method utilizes the tendency of lighter molecules of a liquid or gas to concentrate in a hot region and for heavier molecules to concentrate in a cold region. A simple form of thermaldiffusion apparatus consists of a tall vertical tube with a wire electrically heated to about 500°C (932° F) running down its center, producing a temperature gradient between the center and wall of the tube. The heavier isotopes tend to concentrate in the outer portions of the tube, and the lighter isotopes, to concentrate toward the center. At the same time, because of thermal convection, the gas or liquid near the wire tends to rise, and the cooler outer gas or liquid tends to fall. The overall effect is that the heavier isotopes collect at the bottom of the tube and the lighter at the top

Electrolysis

The electrolytic method of separation is of historical as well as current interest, because it was the first method used to separate practically pure deuterium. This method depends on the fact that when water undergoes electrolysis, the lighter hydrogen isotope tends to come off first, leaving behind a residue of water that is enriched in the heavier isotope.

Gaseous diffusion

This and the electromagnetic method of separating isotopes of uranium afforded the firstlarge-scale separation ever achieved. The problem of separating uranium-235 from uranium-238 arose in 1940 after the demonstration of the susceptibility of the 235 isotope to fission by neutrons. Uranium-235 exists in naturally occurring uranium to the extent of 7 parts to 1000 of uranium-238. Under the auspices of the atomic bomb project, the various methods for separating isotopes were considered, and the gaseous-diffusion and electromagnetic methods

were put into large-scale operation for the production of about 1 kg (2.2 lb) per day of uranium-235 to be used in atomic bombs.

The gaseous-diffusion method exploits the different rate of diffusion of gases of different molecular weight. The rate of diffusion of a gas is inversely proportional to the square root of the mass; light atoms diffuse through a porous barrier faster than heavier atoms. In the separation of uranium isotopes, the only gaseous compound of uranium, the fluoride of uranium, UF6, is used. The uranium hexafluoride is pumped continuously through porous barriers. The difference in weight between uranium-235 and uranium-238 is slightly greater than 1%, but the difference in weight between the fluorides is slightly less than 1%. The enrichment factor, which depends on the square root of the above difference, is theoretically 0.43% for an instantaneous process or 0.30% for a continuous process, but in practice an enrichment factor of only about 0.14% per stage has been achieved. To produce 99% uranium-235 from natural uranium, which contains about 0.7% uranium-235, 4000 such stages are required. The process requires the use of thousands of miles of pipe, thousands of pumps and motors, and intricate control mechanisms.

Electromagnetism

Although the gaseous-diffusion method yields large amounts of uranium-235, the first comparatively large amounts of the isotope were produced by electromagnetic means at Oak Ridge, Tenn. A series of separator units was built in which an ionic beam obtained from a uranium compound was passed through a magnetic field. Because the radius of the curvature of the path of the ions deflected by the beam depends on the mass of the ion, ions of different mass complete their path at different positions, and the uranium isotopes are appreciably separated.

Only a small amount of material, however, can be treated in one operation. Because of this limitation on production, the use of the electromagnetic process for large-scale isotope separation was abandoned after the war in favor of the gaseous-diffusion Process.

Laser beam

The concept of <u>laser</u> separation and enrichment of isotopes arose soon after the invention of the laser in 1960. It gained further incentive six years later with the development of the tunable dye laser, which provides photon beams in a selectably narrow range of infrared to ultraviolet wavelengths. According to this concept, if an element is first vaporized its atoms can then be selectively excited and ionized by an accurately tuned laser beam to separate out the desired isotope. Isotopes can also be separated in molecular form by selective laserbeamdissociation of those molecules of the compound that contain the desired isotope. Since 1972 such processes have been under development, particularly for uranium and plutoniumenrichment-for nuclear power and nuclear weapons, respectively. Much of the work in the U.S. is classified, but a pilot plant may be operational by the later 1980s. The method is costly and technically difficult, but only a few stages are required for production of highly enriched material.

Why are Isotopes Important ?

While discovered less than 100 years ago, Isotopes are now used in a wide variety of scientific applications that touch the lives of almost every citizen. These include:

Radiopharmaceuticals used for medical imaging in the diagnosis of a wide range of ailments, from pneumonia to heart problems to cancer;

Radiopharmaceuticals for cancer treatment and other therapeutic applications; Smoke detectors used in our home and offices;

Batteries that power NASA satellites in the far reaches of our solar system;

Control rods that preventnuclear power reactors from melting down;

As a "fingerprint" used in forensic analysis of food preparation sites and techniques;

To calibrate detectors used to keep our shipping ports safe from nuclear terrorism;

To enable new sources of energy such as nuclear fusion;

and many other applications in energy production, industrial diagnostic methods, archeology, geology, ecology, astronomy, and physics.

There are 90 naturally occurring elements with roughly 250 stable isotopes, and over 3200 unstable or radioactive isotopes. Different isotopes of the same element often have completely different properties -- making some of them invaluable for mankind, and others worthless.

The production of separated isotopic samples -- whereby the purity of one isotope is greatly enhanced over its natural abundance -- can be very time consuming and expensive, and supplying the amounts needed for the growing demand in the above applications is a tremendous challenge.

Radioactive Disintegration Series

In nuclear science, the **decay chain** refers to a series of radioactive decays of different radioactive decay products as a sequential series of transformations. It is also known as a "radioactive cascade". Most radioisotopes do not decay directly to a stable state, but rather undergo a series of decays until eventually a stable isotope is reached.

Decay stages are referred to by their relationship to previous or subsequent stages. A *parent isotope* is one that undergoes decay to form a *daughter isotope*. One example of this is uranium (atomic number 92) decaying into thorium (atomic number 90). The daughter isotope may be stable or it may decay to form a daughter isotope of its own. The daughter of a daughter isotope is sometimes called a *granddaughter isotope*.

The time it takes for a single parent atom to decay to an atom of its daughter isotope can vary widely, not only between different parent-daughter pairs, but also randomly between identical pairings of parent and daughter isotopes. The decay of each single atom occurs spontaneously, and the decay of an initial population of identical atoms over time *t*, follows a decaying exponential distribution, $e^{-\lambda t}$, where λ is called a decay constant. One of the properties of an isotope is its half-life, the time by which half of an initial number of identical parent radioisotopes have decayed to their daughters, which is inversely related to λ . Half-lives have been determined in laboratories for many radioisotopes (or radionuclides). These can range from nearly instantaneous to as much as 10^{19} years or more.

238 U 92 4.5 Gy	234 U 922 245.5 ky	Uranium
	a	Protactinium
234 Th 24.1 d	230 Th 75.38 ky	Thorium
	226 Ra 1 602 y	Radium
	222 Rn 86 Rn 3.82 d	Radon
Astatine	$\alpha \beta^{-}$	SAt
Polonium	218 PO 84 PO 3.1 min	β - 184.3 μ5 β - 184.3 μ5 β - 138 σ
Bismuth	α β- 13	$\begin{array}{c} \mathbf{Bi} \\ 9 \text{ min} \\ \end{array} \alpha \qquad \qquad$
Lead	214 Pb 26.8 min	$\beta = 22.2 \text{ y} \qquad \alpha \qquad \beta = 282 \text{ Pb} \text{ stable}$
Thallium	21	
Mercury		280 Hg 8.32 mm

Actinide alpha decay chains

Thorium series

The 4n chain of Th-232 is commonly called the "thorium series" or "thorium cascade". Beginning with naturally occurring thorium-232, this series includes the following elements: actinium, bismuth, lead, polonium, radium, radon and thallium. All are present, at least transiently, in any natural thorium-containing sample, whether metal, compound, or mineral. The series terminates with lead-208.

The total energy released from thorium-232 to lead-208, including the energy lost to neutrinos, is 42.6 MeV



Neptunium series (Artificial disintegration)

The 4n + 1 chain of Np-237 is commonly called the "neptunium series" or "neptunium cascade". In this series, only two of the isotopes involved are found naturally, namely the final two: bismuth-209 and thallium-205. A smoke detector containing an americium-241 ionization chamber accumulates a significant amount of neptunium-237 as its americium decays; the following elements are also present in it. at least transiently, as decav products of the neptunium: actinium, astatine, bismuth, francium, lead, polonium, protactinium, radium, thallium, thorium, and uranium. Since this series was only studied more recently, its nuclides do not have historic names. One unique trait of this decay chain is that it does not include the noble-gas radon, and thus does not migrate through rock nearly as much as the other three decay chains.

The total energy released from californium-249 to thallium-205, including the energy lost to neutrinos, is 66.8 MeV



Uranium series

The 4n+2 chain of U-238 is called the "uranium series" or "radium series". Beginning with naturally occurring uranium-238, this series includes the following elements: astatine, bismuth, lead, polonium, protactinium, radium, radon, thallium, and thorium. All are present, at least transiently, in any natural uranium-containing sample, whether metal, compound, or mineral. The series terminates with lead-206.

The total energy released from uranium-238 to lead-206, including the energy lost to neutrinos, is 51.7 MeV.


NUCLEAR STABILITY

What makes a nucleus stable?

It depends on a variety of factors and no single rule allows us to predict whether a nucleus is radioactive and might decay unless we observe it. There are some observations that have been made to help us make predictions.

Neutron to proton ratio

Strong nuclear force exists between nucleons. The more protons packed together the more neutrons are needed to bind the nucleus together. Atomic nucleus with an atomic number up to twenty has almost equal number of protons and neutrons. Nuclei with higher atomic numbers have more neutrons to protons.



The number of neutrons needed to create a stable nucleus increase more than the number of protons.

MAGIC NUMBERS

In nuclear physics, a **magic number** is a number of nucleons such that they are arranged into complete shells within the atomic nucleus. The seven most widely recognized magic numbers as of 2007 are **2**, **8**, **20**, **28**, **50**, **82**, **and 126**. Atomic nuclei consisting of such a magic number of nucleons have a higher average binding energy per nucleon than one would expect based upon predictions such as the semi-empirical mass formula and are hence more stable against nuclear decay.

The unusual stability of isotopes having magic numbers means that transuranium elements can be created with extremely large nuclei and yet not be subject to the extremely rapid radioactive decay normally associated with high atomic numbers (as of 2007, the longest- lived known isotope among all of the elements between 110 and 118 lasts only 8.9 min and the next 3.7 min). Large isotopes with magic numbers of nucleons are said to exist in an island of stability. Unlike the magic numbers 2–126, which are realized in spherical nuclei, theoretical calculations predict that nuclei in the island of stability are deformed. Before this was realized, higher magic numbers, such as 184 and 258, were predicted based on simple calculations that assumed spherical shapes. It is now believed that the sequence of spherical magic numbers cannot be extended in this way.

N/P ratio

The neutron–proton ratio (N/Z ratio or nuclear ratio) of an atomic nucleus is the ratio of its number of neutrons to its number protons. The ratio generally increases with increasing atomic numbers due to increasing nuclear charge due to repulsive forces of protons. Light elements, up to calcium (Z =20), have stable isotopes with N/Z ratio of one except for beryllium (N/Z ratio = 1.25), and every element with odd proton numbers from fluorine to potassium. Hydrogen-1 (N/Z ratio = 0) and helium-3 (N/Z ratio = 0.5) are the only stable isotopes with neutron-proton ratio under one. Uranium-238and plutonium-244 have the highest N/Z ratios of any primordial nuclide at 1.587 and 1.596, respectively, while lead-208 has the highest N/Z ratio of any known stable isotope at 1.537.

$$=\frac{(75.4\times34.98)+(24.6\times36.98)U}{100}$$

All nuclei with 84 or more protons are radioactive

1. Nuclei above the belt of stability. These neutron rich isotopes can lower their ratio and move to the belt of stability by emitting a beta particle. This increases number of protons and decreases neutrons

```
_{92}^{\circ}U \rightarrow \alpha
                                                                                     \downarrow 4.51 x 10<sup>9</sup> yr
                                                                                ^{234}_{90}Th \rightarrow \beta
                                                                                      ↓ 24.1 days
                                                                                  ^{34}_{01}Pa \rightarrow \beta
                                                                                     ↓ 1.17 min
                                                                                ^{234}_{02}U \rightarrow \alpha
                                                                                     \downarrow 2.47 x 10<sup>5</sup> yr
                                                                              ^{230}_{00}Th \rightarrow \alpha
                                                                                    \downarrow 7.5 x 10<sup>4</sup> yr
                                                                                  etc ...
                                                                                     1
                                                                                <sup>206</sup>
82P
^{1}_{0}n \rightarrow ^{1}_{1}p + ^{0}_{-1}e
                                                           <sup>1</sup><sub>1</sub>p→ <sup>1</sup><sub>0</sub>n + <sup>0</sup><sub>1</sub>e
                                              238<sub>92</sub>U → 234<sub>90</sub>Th + 4<sub>2</sub>He
```

2. Nuclei below the belt of stability These proton rich nuclei increase their neutrons and decrease protons by positron emission (more common in lighter nuclei) and electron capture (more common in heavier nuclei)

3. Nuclei with atomic numbers greater than 84 These tend to undergo alpha emission. This emission decreases the number of neutrons and protons by 2 moving the nucleus diagonally toward the belt of stability

RADIOACTIVE SERIES

Some nuclei will not gain stability by one emission and may undergo many until they reach stability. For example, U-238 decays to Th-234 which decays to Pa-234 which decays...eventually, lead-206 is obtained.

```
^{14}<sub>7</sub>N +^{4}<sub>2</sub>He → ^{17}<sub>8</sub>O + ^{1}<sub>1</sub>H
```

Three series occur in nature. The other two is Uraniunm-235 to lead-207 and thorium-232 and ends with lead-208

Other observations for prediction

Nuclei with 2, 8, 20, 28, 50 or 82 protons or 2, 8, 20, 28, 50, 82 or 126 neutrons are generally more stable magic numbers.

Nuclei with even number of protons or neutrons are more stable than odd number.

These stability factors can be liken to the stability of 2, 8, 18, 32 in electron shells

NUCLEAR TRANSMUTATIONS

Nuclear reactions that are induced are called nuclear transmutations.

The first conversion was performed by Rutherford in 1919.

Converted nitrogen-14 into oxygen-17 by bombarding with alpha particles from radium

The particles must be moving fast to overcome the electrostatic repulsion between the charged particle and the charged nucleus.

Particle accelerators (atom smashers)

Fermi National accelerator laboratory in Batavia, Ill has a particle accelerator 6.3 km in circumference

Using neutrons

Neutrons can be used to bombard nuclei and do not need to be accelerated since they have no charge. All transuranium elements (elements after uranium that are synthetic) are produced by this method.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U \rightarrow ^{239}_{92}Np + ^{0}_{-1}e$$

 $g_t = g_0 (^{1}/_2)^n$
 $\ln (N_t/N_o) = -kt$

Some are made by bombardment of one atom type with another

Bismuth bombarded with nickel for several days produced element 111.

Rates of Radioactive Decay

Example: The half-life of cobalt-60 is 5.3 years. How much of a 1.000 mg sample will remain

after 15.9 years?

Dating

Because the half-life of any nuclide is constant, the amount of substance remaining in an artifact can serve as a nuclear clock to determine ages of objects. When an animal is alive it maintains a caron-14 to carbon-12 ratio identical to that in the atmosphere. When it dies, this ratio decreases. By measuring this ratio and contrast it to the atmosphere, we can get an approximate age. Radioactive decay is a first order process. Remember, half-life of a first order process is T1/2 = 0.693/k where k is the decay constant. We can determine the k constant by using the rate equation of a first order reaction

Example: If we start with 1.000 grams of Sr-90, 0.953 grams will remain after 2.0 years. (a) what is the half-life of strontium-90? (b) How much strontium-90 will remain after 5.00 years? (28.8 yr, 0.887g)

Energy Changes in Nuclear Reactions

 $E = mc^2$

A very familiar equation that shows mass and energy change are proportional. If a system loses mass, it loses energy (exothermic) and if it gains mass, it gains energy (endothermic). The

The nuclei in this reaction have the following masses:

²³⁸₉₂U = 238.0003 amu, ²³⁴₉₀Th = 233.9942 amu and ⁴₂He = 4.0015 amu

The)m is products minus reactants is 233.9942 + 4.0015 - 238.0003 = -0.0046g

Change in energy would be

 $E = (-0.0046 \text{ g})(1\text{kg}/1000\text{g})(3.00 \text{ x} 10^8 \text{ m/s})^2$

$$= -4.1 \times 10^{11} \text{kg-m}^2/\text{s}^2 = -4.1 \times 10^{11} \text{ J}$$

C2 shows a small mass loss can cause a large energy loss. This is why conservation of mass seems to hold in reactions. For example, combustion of one mole methane loses 9.9 x 10-9grams.

In nuclear reactions, these mass changes are much greater, 50,000 times greater than methane combustion.

NUCLEAR BINDING ENERGIES

Scientists discovered in the 1930'2 that the masses of nuclei combined are always less than these nucleons individually.

Mass of 2 protons 2x (1.00728 amu)

Mass of 2 neutrons 2x (1.00867 amu)

Total = 4.03190 amu

The mass of a Helium-4 nucleus is 4.00150 causing a mass defect of 0.0304 amu.

Protons	Neutrons	Number of Stable Nuclides	Stability
Odd	Odd	4	least stable
Odd	Even	50	1
Even	Odd	57	1
Even	Even	168	most stable

The origin of this mass defect is some of the mass is converted to binding energy which binds the nucleons together in the nucleus. Energy then needs to be added to separate these nucleons to overcome this binding energy. This energy added to break the nucleons apart is called nuclear binding energy.

Nuclear Stability

What is the nuclear stability?

Nuclear stability means that nucleus is stable meaning that it does not spontaneously emit any kind of radioactivity (radiation). On the other hand, if the nucleus is unstable (not stable), it has the tendency of emitting some kind of radiation, i.e., it is radioactive. Therefore the radioactivity is associated with unstable nucleus:

Stable nucleus – non-radioactive
Unstable nucleus – radioactive
That less stable means more radioactive and more stable means less radioactive.

We want to know why there is a radioactivity. What makes the nucleus a stable one? There are no concrete theories to explain this, but there are only general observations based on the available stable isotopes. It appears that neutron to proton (n/p) ratio is the dominant factor in nuclear stability. This ratio is close to 1 for atoms of elements with low atomic number and increases as the atomic number increases. Then how do we predict the nuclear stability? One of the simplest ways of predicting the nuclear stability is based on whether nucleus contains odd/even number of protons and neutrons:

(a)	¹⁶ ₈ O and ¹⁷ ₈ O
(b)	³⁵ 17Cl and ³⁶ 17Cl
(c)	$^{20}{}_{10}\rm{Ne}$ and $^{17}{}_{10}\rm{Ne}$
(d)	$^{40}{}_{20}\rm{Ca}$ and $^{45}{}_{20}\rm{Ca}$
(e)	¹⁹⁵ 80Hg and ¹⁹⁶ 80 Hg

Nuclides containing odd numbers of both protons and neutrons are the least stable means more radioactive.

• Nuclides containing even numbers of both protons and neutrons are most stable means less radioactive.

• Nuclides contain odd numbers of protons and even numbers of neutrons are less stable than nuclides containing even numbers of protons and odd numbers of neutrons.

In general, nuclear stability is greater for nuclides containing even numbers of protons and neutrons or both.

Example

Based on the even-odd rule presented above, predict which one would you expect to be radioactive in each pair?

(a) The 8O₁₆ contains 8 protons and 8 neutrons (even-even) and the 8O₁₇ contains 8 protons and 9 neutrons (even-odd). Therefore, 178O is radioactive.

(b)The 17Cl 35 has 17 protons and 18 neutrons (odd-even) and the 17Cl36 has 17 protons and 19 neutrons (odd-odd). Hence, 3617Cl is radioactive.

(c)The 10Ne₂₀ contains 10 protons and 10 neutrons (even-even) and the 10Ne₁₇ contains 10 protons and 7 neutrons (even-odd). Therefore, 10Ne₁₇ is radioactive.

(d)The 20Ca40 has even-even situation and 20Ca45 has even-odd situation. Thus, 20Ca45 is radioactive.

(d) The 80Hg195 has even number of protons and odd number of neutrons and the 80 Hg 196 has even number of protons and even number of neutrons. Therefore, 80Hg195 is radioactive.

Nuclear Binding Energy

The nuclear binding energy is an energy required to break up a nucleus into its components protons and neutrons. In essence, it is a quantitative measure of the nuclear stability. The concept of nuclear binding energy is based on Einstein's famous equation, E = mc2, where E is the energy, m is the mass and c is the velocity of light, and according to which the energy and mass are inter-convertible.

Nucleus contains mainly two particles – protons and neutrons- in addition to many other elementary particles. Thus, the mass of the nucleus is primarily comes from the masses of protons and neutrons. But the experiments have shown that the sum of the masses of protons and neutrons is always greater than experimentally determined nuclear mass. Why is it so? The answer to this question lies in the way the nature creates nucleus. When nature creates nucleus, it takes protons and neutrons and binds them together and puts them in a tiny space called nucleus. In order to bind protons and neutrons together, some energy is needed, which is taken out of the masses of protons and neutrons. It means that nature is very smart, it does not spend any of its own energy rather it converts some of the masses of protons and neutrons into an energy and utilizes that energy to bind the protons and neutrons within the nucleus. If we know how much mass (known as mass defect) is utilized, we can convert it into binding energy using the

Einstein's equation. Let us see how this is done.

Consider 26Fe 56 that has an atomic mass of 55.934942 amu (experimental) that is created using 26 protons and 30 neutrons:



We can calculate the total mass of the nucleus, i.e., total mass of 26 protons and 30 neutrons. The mass of proton $(1H_i)$ is 1.007825 amu and that of neutron is 1.008665 amu. Thus 10n

Mass of 26 protons = 26 x 1.007825 = 26.20345 amu

Mass of 30 neutrons = $30 \times 1.008665 = 30.25995$ amu

Total mass of 26 protons and 30 neutrons is

26.20345 amu + 30.25995 amu = 56.46340 amu

This mass is larger than 55.934942 amu (the experimentally determined mass) by 0.52846 amu. The difference between experimental mass of the atom and the sum of the masses of its protons, neutrons, and electrons is known as **mass defect** (Δm), which is calculated as

 $\Delta m = mass of products - mass of reactants$

=experimental mass of an atom - calculated mass of an atom

=55.934942 amu -56.46340 = -0.52846 amu

Note that Δm is a negative quantity. As a consequence, the calculated energy will also be negative because the formation of 56Fe from 26 protons and 30 neutrons is an exothermic reaction meaning that the energy is released to the surrounding. Also note that Δm does proton or neutron and hence it can safely be omitted.

Let $\Delta m = 1 \text{ amu}$. Then $\Delta E = \Delta m \times c^2 = 1 \text{ amu} \times (3.0 \times 10^8 \text{ m/s})^2$ $= 9 \times 10^{16} \text{ amu} \text{ m}^2/\text{s}^2$ We further utilize the following relations to convert amu m²/s² into joules. 1 kg = 6.022 \times 10^{26} \text{ amu}
and 1 J = 1 kg m²/s² Then $\Delta E = 9 \times 10^{16} \text{ amu} \text{ m}^2/\text{s}^2 \times (1 \text{ kg} / 5.022 \times 10^{26} \text{ amu}) \times (1 \text{ J} / 1 \text{ kg} \text{ m}^2/\text{s}^2)$ $= 1.4945 \times 10^{-10} \text{ J}$ That is, 1 amu = 1.4945 × 10⁻¹⁰ J

Therefore,

 $\Delta E = \Delta m \ge 1.4945 \ge 10^{-10} \text{ J/amu} = -0.528458 \text{ amu} \ge 1.4945 \ge 10^{-10} \text{ J/amu}$

7.8978 x 10⁻¹¹ J/ nucleus

This mass defect can be further transformed into energy using Einstein's equation in the following form:

 $\Delta E = \Delta m \mathbf{x} \mathbf{c}^2$

In this equation, ΔE is the change in energy in joule, Δm is the mass defect in amu, and c is the velocity of light that is equal to 3.0 x 108 m/s. Substituting these values into above equation and converting all the units to joules gives the energy in proper units (J), which is of course little bit tedious. To make things simpler, one can directly convert the mass defect into energy using the following conversation factor (if you are interested, see the following box for derivation of this relationship).

1amu = 1.4945 x 10-10 J

This is the amount of energy released when one iron-56 nucleus is created from 26 protons and 30 neutrons. Therefore, the nuclear binding energy for this nucleus is 7.8978 x 10-11 J, which is also the amount of energy required to decompose this nucleus into 26 protons and 30 neutrons. The above calculated energy is per nucleus. The energy released for the formation of 1

mole of iron nuclei is calculated by multiplying the above energy with Avogadro's number.

nuclear binding energy per nucleon = $\frac{7.8978 \times 10^{-11} j}{56} = 1.4070 \times 10^{-12} j / nucleon$

 $\Delta E = -7.8978 \text{ x } 10_{-11} \text{ J x } 6.022 \text{ x } 10_{23} \text{ /mol} = -4.7560 \text{ x } 10_{13} \text{ J /mol} = -4.7560 \text{ x } 10_{10} \text{ kJ /mol}$

Therefore, the nuclear binding energy for 1 mole of iron-56 is 4.7560 x 1010 kJ (this is about 48 billion), which is a tremendous amount of energy, considering the energy of ordinary chemical reactions that are usually in the order of 200 kJ. How tremendous this energy is? Well, it will heat up about 40 million gallons of water from room temperature to boiling point. Can you imagine just about 56 g of iron-56 has the ability to heat up about 40 million gallons of water? Pretty impressive, is it not? Binding energies are usually reported per nucleon to facilitate the comparison between various binding energies, which is calculated using the following formula.

Nuclear binding energy pernucleon = nuclear binding energy /number of nucleons

For the iron-56 nucleus, we have <u>MECHANISMS</u>

FISSION

The liquid drop model

The mechanism by which nuclei fission is best represented is the liquid drop model. Considering the nucleus to be a special drop of liquid can approximate the collective behavior of all the nucleons. The liquid drop is held together by surface tension (nuclear forces). When the drop is deformed, the surface tension forces may be insufficient to restore the drop to its original shape. Splitting may occur. Figure below illustrates this model in the case of a nucleus.

Normally, the nucleus is at its minimum energy level (ground state), i.e., spherical form

(I). If the nucleus receives excitation energy (incident neutron binding energy + kinetic energy), it will start to oscillate, first going into an ellipsoidal shape (II), and then a "dumbbell" form (III). If the excitation energy is not sufficient, it will oscillate between these two shapes until the excess energy is given off, probably in the form of a gamma ray. Then it will return to special



form (ground state). However, if the excitation energy is in excess of the critical energy, the dumbbell will neck down until the width is zero (IV). At that point, two positively charged nuclei are formed and they repel each other with great force (V).

The Liquid Drop Model of Fission

Neutron interactions

Reactions, which are initiated by neutrons, are of primary concern in the study of nuclear reactors. When charged particles approach the nucleus, they must overcome the repulsive

electrostatic force before getting close enough for the strong nuclear force to act. This requires that the incident particle possess a significant amount of energy in order for the reaction to occur. Neutrons have no charge and therefore are not subject to overcoming electrostatic repulsion in order to penetrate the nucleus. This means that neutrons need not possess large amounts of kinetic energy to initiate nuclear reactions. In fact, low energy neutrons initiate the reactions, which are of prime importance to power production (fission reactions).

In nuclear work, there are several terms, which are commonly used to classify neutron energies. Neutrons with energies below approximately 1 eV are referred to as "slow" neutrons. Neutrons with energies in the range of approximately 1 eV to 10,000 eV are called "intermediate" neutrons. Finally, neutrons with energies above approximately 10,000 eV or 0.01 Mev are called "fast" neutrons. There is no upper limit on the fast region, but from a practicality point of view, neutrons in the reactor rarely exceed 10 Mev.



A low energy neutron (Kinetic energy less than about .65 eV) which is in temperature equilibrium with its surroundings is called a thermal neutron.

Elastic scattering

The elastic scatter (or elastic collision) is one of the simplest interactions a neutron can undergo. This type of reaction can be compared to two billiard balls colliding. There is no energy transferred into excitation of the target or neutron. The only energy transfer involves changes in the kinetic energy of the neutron and target. Physically, the neutron may touch the target and bounce off; it may only come close to the target and be deflected; or it may directly collide with the target and bounce off. The criterion is that no energy be transferred into nuclear excitation; as long as this holds, the collision may be considered elastic. Figure illustrates an elastic scattering reaction

Remember, in elastic scattering reactions the only energy transfer is a change in the kinetic energy of the neutron and target nucleus. The target nucleus is normally considered to be at rest (no kinetic energy) prior to the reaction

Inelastic scattering

Inelastic scattering differs from elastic scattering in that the target nucleus is raised to an excited state as a result of the collision. Physically, the neutron may only touch the nucleus, or it may enter the nucleus and exit at a reduced energy. The energy transformations are then a change in the kinetic energy of the neutron, a change in the nuclear energy level of the target nucleus, and possible a change in the kinetic energy of the target. When the excited target

nucleus returns to the ground state, excess energy is released by the emission of a gamma ray. Figure illustrates an inelastic scattering reaction.

Inelastic Scatter

Remember, inelastic scattering results in nuclear excitation of the target nucleus, followed by gamma emission when the excited nucleus returns to the ground state. The neutron leaves the collision site at reduced kinetic energy.

Radiative capture

In a radiative capture reaction, the incident neutron enters the target nucleus and remains. This results in a "new" nucleus with a mass number increased by one. The new nucleus contains excess energy in the form of nuclear excitation. This excess energy is released by the emission of a gamma ray and the nucleus returns to the ground state.



Figure illustrates a radiative capture reaction. Remember, in radiative capture reactions, the neutron is absorbed by the target nucleus resulting in an excited nucleus resulting in an excited nucleus with a mass number increased by one. The excited nucleus returns to the ground state by emitting a gamma ray.



Particle ejection

In some cases, the incident neutron is absorbed by the target nucleus and the newly formed nucleus is raised to a sufficient energy level to immediately eject another particle. This is a particle ejection reaction. The ejected particle can be a proton, neutron, or in some cases an alpha. Even after the particle is ejected, the nucleus normally is still in the excited state and releases a gamma ray to return to the ground state. Figure illustrates particle ejection upon bombardment with a neutron.

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Reference

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POSSIBLE QUESTIONS

<u>PART A: MULTIPLE CHOICE QUESTIONS</u> (Each question carry one mark)

- 1. The radioactive decay of $_6$ C 14 to $_7$ N 14 occurs by the process of
- a. beta particle emission
- b. alpha particle emission
- c. electron capture
- d. neutron capture
- 2. Which of the following elements is utilized as a shield from sources of radiation?
- a. **Pb** b. Ca c. Zn d. As
- 3. Which of the following types of elements in the periodic table are always radioactive?
- a. Noble gases b. Alkali metals c. Halogens d. Actinides
- 4. Each a- particle has the mass:
- a. Equal to that of hydrogen
- b. Nearly four times that of hydrogen atom
- c. Half of the hydrogen atom
- d. Nearly five times that of hydrogen atom
- 5. Which among the following has the highest penetrating power?
- a. $\gamma rays$ b. $\beta rays$ c. alpha rays d. cathode rays
- 6. β rays possess:
- a. High momentum and low kinetic energy
- b. Low momentum and high kinetic energy
- c. Low momentum and kinetic energy
- d. High momentum and kinetic energy.
- 7. Atoms of different elements containing the same number of neutrons but different number of total nucleons is known as:
- a. **Isotones** b. Isodiaphers c. Isotopes d. Isomers
- 8. When positron is emitted by a radioactive nucleus then:
- a. Atomic number remains the same
- b. Atomic number increases by 1 unit
- c. Atomic number decreases by 1 unit
- d. Atomic number increases by 2 units.
- 9. The process of conversion of stable isotope of one element into isotope of another element is known as:

a. Artificial radioactivity

- b. Artificial transmutation
- c. Natural radioactivity
- d. Induced radioactivity.
- 10. The temperature level inside a nuclear reactors is maintained using
- a. Shielding **b. Coolants** c. Moderators d. control rods

11. What kind of radiation will travel through an electric field on a pathway that remains unaffected by the field?

- a. a proton **b. a gamma ray** c. an electron d. a neutron
- 12. Which radioactive emanations have a charge of +1?
- a. Neutrons **b. protons** c. gamma rays d. beta particles
- 13. The speed of the neutrons inside a nuclear reactors is reduced by using
- a. Shielding b. Coolants **c. Moderators** d. Control rods
- 14. Which nuclide is a radioisotope used in the study of organic reaction mechanisms?
- a. carbon-12 **b. carbon-14** c. Uranium-235 d. Uranium-238

15. To make nuclear fission more efficient, which device is used in a nuclear reactor to slow the speed of neutrons?

- a. internal shield b. external shield c. control rod d. moderator
- 16. What is required for a nuclear transmutation to occur?
- a. a corrosive environment

b. a particle to collide with a nucleus

- c. gamma emission spontaneous nuclear decay
- d. a beta emission

17. Which type of radioactive decay results in no change in mass number and atomic number for the starting nucleus?

- a. Beta b. positron emission c. alpha d. gamma
- 18. Example for moderator in nuclear reactor
- a. Water **b. graphite** c. boron d. cadmium
- 19. The fuel used in most of the thermal reactors in the form of aluminium-plated rods
- a. **Uranium-235** b. uranium-238 c. thorium-232 d. Thorium-235
- 20. Nuclei above the belt of stability move to the belt of stability by emitting
- a. **a beta particle** b. a neutron c. proton d. alpha particle

<u>PART B</u> (Each question carries 8 marks)

- 1. Discuss the stability of nucleus on the basis of n/p ratio (ii) odd even rule.
- 2. What are magic numbers? How is the stability of nuclei related with magic numbers?
- 3. Draw a diagram to illustrate how the binding energy per nucleon varies with the mass number. Comment on the shape of the curve.
- 4. Describe different methods of separation of isotopes.
- How would you work out the binding energy per nucleon for a given atomic nucleus. What is the significance of this value.
- 6. Work out the binding energy per nucleon Iin MeV per nucleon) for the isotope

 $_{26}$ Fe 56 given the masses 56 Fe 55.93494 amu, neutron 1.008665 amu, proton

1.00783 amu, electron 0.00054859 amu.

- 7. Explain nuclear binding energy in detail and how it contributes to the nuclear Stability
- 8. Explain the principle and working of Astons mess spectrograph for the detection of isotopes
- 9. Discusses the uses of isotopes as tracers.
- How would you work out the binding energy per nucleon for a given atomic nucleus.
 What is the significance of this value.
- 11. Solve the following equations

i) $_{24}Cr^{50} + _1H^1 \longrightarrow \cdots + \gamma$
ii) $_9F^{19} + _1H^1 \longrightarrow \dots + \alpha$
iii) $_7N^{14} + _2He^4 \longrightarrow _8O^{17} + \cdots$
iv) (n, α) reaction
3Li ⁶ + → +
v) (T,p) reaction
27Co ⁵⁹ + ++

[15CHU502] KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER

INORGANIC CHEMISTRY

UNIT 2- OBJECTIVE TYPE QUESTIONS FOR ONLINE EXAMINATION(Each carry 1 Mark)

QUESTION	OPTION A	OPTION B	OPTION C	OPTION D	ANSWER
Nuclear reactions occur when	Bonds are broken	Bonds are broken	nucleus emits particles	atoms looses valence	nucleus emits particles and
	and atoms remain	and atoms	and gamma rays	electrons	gamma rays
	unchanged	rearranged			
Nuclear reactions involve	Valence electrons	Neutrons and	electrons in the inner	excited electrons	Neutrons and protons
		protons	orbitals		
Nuclear reactions involve	Small amounts of	Large amount of	affected by		Large amount of energy
	energy	energy	temperature affected		
			by concentration		
Which is high ionising power	Alpha particles	beta particles		gamma rays	Alpha particles
Nuclear reactions are	Releasing Small	independent of	affected by	affected by concentration	independent of temperature
	amounts of energy	temperature and	temperature		and concentration
		concentration			
Nuclear reactions which occur spontaneously are called	Natural radioactivity	Artificial	artificial	Transuranium elements	Natural radioactivity
		radioactivity	transmutation		
The stability of the nucleus depends on the relative numbers of	protons and neutrons	protons present	neutrons present	electrons present	protons and neutrons
	present				present
The most stable nuclides tend to have an	even number of	odd number of	odd number of	odd number of protons	even number of protons
	protons and an even	protons	neutrons	and neutrons	and an even number of
	number of neutrons	_			neutrons
The reactions which occur when stable isotopes are bombarded with	Natural radioactivity	Artificial	artificial	Chemical reactions	Artificial radioactivity
particles such as neutrons.		radioactivity	transmutation		
A set of new elements with atomic numbers over 92 have been	Transuranium	Transition	non-radioactive	Lanthanides	Transuranium elements
artificially made. They are called	elements	elements	elements		
Natural radioactivity is shown by elements with	high atomic numbers	Low atomic	Transition elements	Transuranium elements	high atomic numbers
		numbers			
Artificial radioactive isotopes generally have	short half-life	Long half-life	high atomic number	fractional molecular	short half-life periods.
	periods.	periods		weight	
Artificial radioactive isotopes generally have	short half-life	Long half-life	high atomic number	fractional molecular	very rarely found in nature
	periods.	periods		weight	
The Geiger–Müller counter is an instrument used for measuring	ionizing radiation	particle size	measures the surface	penentration power of	ionizing radiation
		analyser	morphology	radiations	
The scintillator for the detection of protons and alpha particles	Cesium iodide	sodium iodide	zinc sulphide	Lithium iodide	Cesium iodide
The scintillator for the detection of gamma rays	Cesium iodide	sodium iodide	zinc sulphide	Lithium iodide	sodium iodide
The scintillator for the detection of only alpha particles	Cesium iodide	sodium iodide	zinc sulphide	Lithium iodide	zinc sulphide
The scintillator for the detection of neutrons	Cesium iodide	sodium iodide	zinc sulphide	Lithium iodide	Lithium iodide

Cesium iodide has been used as a scintillator in the scintillation counters for the detection of	Protons	gamma rays	alpha particle	neutrons	Protons
Sodium jodide has been used as a scintillator in the scintillation	Protons	gamma rays	alnha narticles	neutrons	gamma ravs
counters for the detection of	1100015	gamma rays	aipila particles	licutions	gamma rays
Zinc sulphide has been used as a scintillator in the scintillation	Protons	gamma rays	alpha particles	neutrons	alpha particles
counters for the detection of					
Lithium iodide has been used as a scintillator in the scintillation	Protons	gamma rays	alpha particles	neutrons	neutrons
counters for the detection of		0 ,			
Which is not connected to nuclear fission	Exothermic process	releases kinetic	form of transmutation	Union of two small	Exothermic process
	1	energy along with		nucleus	
		fission products			
Which is not connected to nuclear fusion	Endothermic process	releases kinetic	form of transmutation	Union of two small	form of transmutation
		energy along with		nucleus	
		products			
Which is connected to nuclear fusion	Exothermic process	releases kinetic	form of transmutation	Union of two small	Union of two small
	Litetite protects	energy along with		nucleus	nucleus
		fission products			
Which is connected to nuclear fission	Endothermic process	releases kinetic	form of transmutation	Union of two small	releases kinetic energy
	Endouiennie process	energy along with	form of transmutation	nucleus	along with products
		products		nucleus	along with products
A process in which atomic nuclei are fused together to form heavier.	Nuclear fission	Nuclear fusion	Radioactive decay	artificial transmutation	releases kinetic energy
nuclei	i vuotoai hission	Tuelear Tuston	Rudiouetive deedy	artificial transmutation	along with products
For which process extremely high temperatures of the order of 1.5 x	Nuclear fission	Nuclear fusion	Radioactive decay	artificial transmutation	Nuclear fusion
10^{7} °C is required	ruelear hoston	ruciour rubion	itualouetive accuy	a thiolar transmatation	i vuotour ruston
A reaction which is usually a deliberately produced man	Nuclear fission	Nuclear fusion	Padiaastiva daaw	artificial radioactivity	Nuclear fission
A feaction which is usually a denoted they produced man-	Nuclear fission	Nuclear fusion	Radioactive decay		Nuclear fission
Inde nuclear reaction induced by a neutron.	Nuclear figgion	Nuclear fusion	ahomical reaction	artificial radioactivity	Nuclear fission
It is a form of nuclear transmutation because the resulting fragments	Nuclear fission	Inuclear fusion	chemical reaction	artificial radioactivity	Nuclear fission
are not the same element as the original atom.	N. 1		Dell'accellant	and Chair and the state of the	NI - Los Costo
into smaller parts	Nuclear fission	Nuclear Jusion	Radioactive decay	artificial radioactivity	Nuclear fission
When a neutron is hombarded on uranium it results in strontium and	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fission
xenon nuclei along with three neutrons. The process is called	i vuotoai hission	Tuelear Tuston	enemieur reaction	artificial factoactivity	
The reaction taking place in the sun is	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fusion
The reaction taking place in the atomic bomb is	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fusion
The reaction taking place in the nuclear reactors is	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fission
The reactions of light elements power the stars and produce	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fusion
virtually all elements in a process called nucleo synthesis	i tuoiour mosion			and in radio activity	
The reaction of two hydrogen nuclei to form helium is an example	Nuclear fission	Nuclear fusion	chemical reaction	artificial radioactivity	Nuclear fusion
for	i (deredi ilosion	r autoritar rabion		and in radio activity	
The percentage of U-235 in naturally occurring uranium is	93,70%	7%	80%	20%	7%
Among the following which is used as a control rod in nuclear	Iron rods	copper rods	uranium rods	cadmium rods	cadmium rods
reactors		TL			
Among the following which is used as a control rod in nuclear	Iron rods	copper rods	cadmium rods	heavy water	boron rods
reactors				-	

Which substance is used to capture neutrons and control the number	Iron rods	copper rods	cadmium rods	heavy water	boron rods
of neutrons in a nuclear reactor		11		5	
Which substance is used to capture neutrons and control the number	Iron rods	copper rods	cadmium rods	heavy water	cadmium rods
of neutrons in a nuclear reactor		**			
The number of nucleons (either protons or neutrons) such that they	Atomic number	Mass number	Magic number	Avagadro number	Magic number
are arranged into complete shells within the atomic nucleus is called			_	-	-
Atomic nuclei consisting of a magic number of nucleons have a	higher average binding energy per nucleon	lower average binding energy per nucleo n	low stability	spontaneous radioactivity.	higher average binding energy per nucleon
Atomic nuclei consisting of 2, 8, 20, 28, 50, 82, and 126 number	higher	lower	low stability	spontaneous radioactivity.	higher average binding
of nucleons have a	average binding energy per nucleon	average binding energy per nucleo n			energy per nucleon
Atomic nuclei consisting of 2, 8, 20, 28, 50, 82, and 126 number of nucleons have a	high stability	lower average binding energy per nucleo n	low stability	spontaneous radioactivity.	high stability
Magic number of nucleons is	2, 8, 20, 28, 50, 82, and 126	2,8,25,56, 82 and 126	2,8,18, 36, 82 and 126	2,8,18,54,84 and 126	2, 8, 20, 28, 50, 82, and 126
The ratio of its number of neutrons to its number protons	N/P ratio	magic number	binding energy	binding energy per nucleon	N/P ratio
For hydrogen N/P ratio is	One	zero	two	1.5	zero
For elements with atomic number below 20, the N/P ratio is	One	zero	two	1.5	One
The only stable isotopes with neutron-proton ratio under one.	Helium-3	Helium-4	chlorine -35	calcium -20	Helium-3
The isotopes with neutron-proton ratio under one.	Helium-3	Helium-4	chlorine -35	calcium -20	Helium-3
The element with highest N/P ratio	lead-208	calcium-40	potassium-39	iron-58	lead-208
The elements having same atomic number but different mass number.	Isotopes	Isotones	Isobars	Isomers	Isotopes
The difference in their mass number of isotopes is due to the difference in their number of	neutrons	protons	electrons	nucleons	neutrons
The elements which are chemically same and physically different are called	Isotopes	Isotones	Isobars	Isomers	Isotopes
Elements which are chemically different but physically same	Isotopes	Isotones	Isobars	Isomers	Isobars
Atoms of different elements having the same atomic mass but	Isotopes	Isotones	Isobars	Isomers	Isobars
different atomic number.	-				
The type of nuclei with unstable isobars.	Light nuclei	Heavy nuclei	even numbered nuclei	odd numbered nuclei	Light nuclei
The type of nuclei with stable isobars.	Light nuclei	Heavy nuclei	even numbered nuclei	odd numbered nuclei	Heavy nuclei

UNIT-IV

Acids and Bases

Acids and Bases - Arrehenius concept, proton transfer theory – concept of Lowry and Bronsted –Luxflood concept – the solvent system concept – Lewis concept – relative strength of acids and bases – effect of solvent – leveling effect – effect of polarity and dielectric constant – effect of substituents – factors influencing relative strengths of acids and bases. Applications and Limitations of HSAB concept.

ACIDS AND BASES

There are several ways to define acids and bases. Perhaps the easiest way to start is to list some of the properties of acids and bases.

i. Acids are substances which donate hydrogen and form lots of H3O+ (hydronium) ions when dissolved in water

ii.Bases are substances which accept hydrogen and form lots of OH- (hydroxide) ions in solution.

What are Acids and Bases?

a. Taste & feel

b. Are acids necessarily dangerous? And are bases therefore necessarily safe?

c. Litmus as an indicator

d. Phenolphthalein as an indicator

e. In chemistry, an **indicator** is a substance that changes color when the pH of its environment is changed. If you dissolve an indicator in a solution, it will change colors when the solution's pH changes. At what pH value will the indicator change its color? Answer: it depends on the indicator. This is called the **pH range** of the indicator.

ARRHENIUS DEFINITION OF ACIDS AND BASES

- i. Suggested that acids produced H⁺ ions in solution, and that bases produced OH- ions in solution
- ii. H^+ ion is called a hydrogen ion. OH^- is called a hydroxide ion.



iii. Explained for the first time many behaviors of acids and bases, especially their ability to neutralize one another in aqueous solution:

ACID:
$$HCl(aq) \rightarrow \Box H+(aq) + Cl-(aq)$$

NaOH(aq) $\rightarrow \Box Na+(aq) + OH-$
BASE: (aq)

BRØNSTED-LOWRY DEFINITION OF ACIDS AND BASES

i.Danish and English man – developed theories independently

ii. This is the most useful and important theory of acids and bases

iii.First, let's define what we mean by "proton" when we speak of donating and

accepting protons.

The Brønsted-Lowry definition of acids:

ACIDS are proton (H+) donors. HCl donates H+ (a proton) to water. HCl is an example of a Brønsted -Lowry acid.



The Brønsted-Lowry definition of bases:

BASES are proton (H+) acceptors.Ammonia (NH3) accepts a proton from water to make the ammonium ion. NH3 is an example of a Brønsted-Lowry base.

Conjugate acids and bases

1. Substances on opposite sides of the equation that are one proton (H+) different from each other are called **conjugate acid-base pairs**.

2. In the reaction between HCl and water, HCl and Cl- are a conjugate acid-base pair. The other conjugate acid-base pair is H2O/H3O+.

a. HCl is the conjugate acid of Cl-, and Cl- is the conjugate base of HCl.

b. H3O⁺ is the conjugate acid of H2O, and H2O is the conjugate base of H3O+

3. In the reaction between NH3 and water, ammonia/ammonium ion are a conjugate acid-basepair, and H2O/OH- are the other conjugate acid-base par.

a. NH3 is the conjugate base of NH4+, and NH4+ is the conjugate acid of NH3.

b. H2O is the conjugate acid of OH-, and OH- is the conjugate base of H3O+.



Lewis definition of acids and bases

i. This is the best and most current theory. However, for our chemistry course, this is the least important theory of acids and bases. The Lewis theory will be very useful in Biology class and most college chemistry classes, though.

- ii. ACIDS are electron pair acceptors
- iii. BASES are electron pair donors

The Self-Ionization of Water and the Ion Product Constant for water, Kw

WATER CAN ACT AS AN ACID OR AS A BASE.

a. As you can see from the reactions above, water can act as either an acid or a base depending on the situation. Such a substance is said to be "**amphoteric**" or "**ambiprotic**", since it can either accept or donate a proton under various conditions.

b. Pure water is not pure H2O! Can you believe it?!?! Water reacts with itself to make theOH-

ion (hydroxide ion) and the H3O+ ion (hydronium ion).

c. The concentrations of these ions in pure water at 25oC is always

[OH-]=[H3O+]=1.00X10-7 M

*Neutral solutions and pure water ONLY!

It is important to make two points here:

•NO hydrogen ion need be involved.

•NO solvent need be involved.

The Arrhenius model required an acidic or basic species to posses ionizable H+ or OH– ions. Br¢nsted-Lowry theory requires only the transfer of a proton from an acid to a base, which broadens the available bases to include ammonia and other species that not have hydroxide groups. Thus pyridine, alkyl amines and of course all the "bases" of living cells, e.g. the acid/base pairs of DNA can be understood under this theory. But consider now the Lewis definition:

A Lewis acid is any species possessing a vacant orbital capable of accepting an electron pair.

Examples of Lewis acids:

•positive ions

•having less than a full octet in the valence shell

•polar double bonds (one end)

•expandable valence shells

•one of more unshared pairs in the valence shell

•polar double bonds (the other end)

the presence of a double bond

A Lewis base is any species capable of donating an electron pair into a vacant orbital in a Lewis acid. Lewis thus extends the theory to include acids other than proton sources, breaking the second barrier to a broader definition of acidic and basic compounds. However, in doing so Lewis ignored the true uniqueness of the proton, which is the **only cation which is a bare nucleus**.

Although Lewis' concept is genuinely useful, it has not completely replaced the Br¢nsted- Lowry interpretation. Thus typically when chemists refer to "acid" and "base" in ordinary parlance, they mean those species which fit the Br¢nsted-Lowry definition. When the Lewis definition is meant, we must specifically call the species "a Lewis acid" or "a Lewis base". Note that *most* Lewis bases are also Br¢nsted-Lowry bases, though a good Lewis base can be a very poor Br¢nsted-Lowry base, and vice versa. However *only* the H+ ion is both a Lewis and aBr¢nsted-Lowry acid.

Examples:

a) Electron-deficient compounds

Some compounds are defined to be electron-deficient by Lewis theory, i.e. those for which the central atom cannot achieve a stable octet structure. It is found in practice that such species readily react with Lewis bases (lone-pair sources) to give quite stable adducts. One common example of such electronically unsaturated molecules are the boron halides. Thus for example consider the reaction of BF3 with ammonia, a common undergraduate experiment using a vacuum line to safely combine the two gaseous reagents. The product is a stable white powder which may be handled in air. In this reaction, shown below, the donor orbital is a lone pair on the N and the acceptor is the empty p orbital left over in BF3 from the sp2 hybridization at boron. Generally you will not be identifying the nature of the acceptor orbitals, but in this case it is a well known bonding situation. Notice that the result is an ethane-like covalent bond between the N and the B, and the bond has a reasonably high bond energy.

Coordinatively-unsaturated species

Many inorganic molecules of the elements of the 3rd period onward have large central atoms that can achieve high coordination numbers such as five, six and sometimes even seven. These are said to be **coordinatively unsaturated** when the coordination number is not the maximum possible. Consider the following three reactions which may be classified as reactions of the coordinatively-unsaturated acids PF5, AlCl3, and SbCl5. The bases are thus F–, Cl– and S4N4. Note that the latter, S4N4, has lone pairs on all the sulfur and nitrogen atoms. Only a single lone pair from a N atom is used in the interaction with the Lewis acid. Also note that the second example is different in that the base is transferred from the acid TeCl3 + to the acid AlCl3.

Metal cations: alkali or alkaline-earth elements

Metal ions are extremely electron deficient, often having lost all their valence electrons when they ionize. Not surprisingly, they are the largest single class of Lewis acids. Much of the chemistry of metal ions involves their reaction with a wide variety of Lewis bases. Organic chemists perform reactions involving active metals such as Li or Na, e.g. BuLi or KtBuO, ether or THF. Why? Because these coordinating ether solvents can stabilize the metal ion in non-protic solvents.

Metal cations: transition metal elements

```
Consider the following reaction: Cu2+(aq) + NH3 ?
What explains the initial blue ppt? What about the purple solution?
1. Cu 2+(aq) + OH- Cu(OH)2 (where the hydroxide comes from: H2O + NH3
4+ -
NH + OH )
```

2. Cu(OH)2 + excess NH3 [Cu(NH3)4]2+

We call this last species, [Cu(NH3)4]2+, a complex ion. It is a well-defined molecule built up from a Lewis acid cation and multiple Lewis base donor atoms, which are normally called **ligands**.

Summary of basic concepts

Lewis base, donor or ligand means much the same thing. When transition metal adducts are considered, the term ligand is used most commonly. The organic chemist would call most of these nucleophiles.

Lewis acid, acceptor or electrophile means much the same thing.

The resulting bonds are called **coordinate covalent bonds**, or **dative bonds**, in which both electrons are contributed by the Lewis base. Many coordinate bonds are easily reversible, a measure NOT of the weakness of these bonds, which can be quite strong, but of the excellentleaving-group character of most Lewis bases. Hence there are many displacement reactions to consider. The resulting compound is called a Lewis acid/base adduct, a coordination complex, a coordination compound, or a complex ion (if it is ionic).

Some reaction classifications

It is important to be able to recognize different types of reactions using Lewis acids and bases, and one approach to this is to classify them by some common reaction types. You have most likely already encountered some of these.

a) Adduct or Complex formation reactions

The most fundamental reaction type, and one which occurs also in (b) and (c) is complex formation. Consider again the first reaction we considered between ammonia and boron trifluoride:

F3B + :NH3 **F3B**-NH3

b) Displacement reactions

These are reactions which involve the displacement of one Lewis base by another, such the reaction:

Et2O–BF3 + :N(C2H5)3 Et2O + F3B–N(C2H5)3

9. In this case, the base trimethylamine displaces the base diethyl ether from the acid boron trifluoride. It is therefore a **base displacement** reaction. It is also possible for one acid to

displace another acid from a common base, and these are called **acid displacement** reactions. In both types of reaction, a previously formed adduct is broken down and replaced by a new adduct.

c) Metathesis or "double displacement" reactions

When two Lewis acid/base adducts react and "switch partners", the reaction is called a metathesis reaction. There are many examples of such reactions. The following is easily recognized as a metathesis reaction:

Cl5Sb:O2(CH2)2 + Me3In:NC5H5 - Cl5Sb:NC5H5 + Me3In:O2(CH2)2

The acids and bases involved, antimony pentachloride, dioxane, trimethyl indium and pyridine.

HARD/SOFT ACID-BASE THEORY

There are several reasons that the Lewis theory has not displaced the Br¢nsted-Lowry model for protic acids. One of these is certainly that no acceptable way has been found to make the strength of a general Lewis acid quantitative. It remains a largely qualitative theory. Even when we try to qualitatively classify the strength of Lewis acids by comparing their reactions with a common base, we find that it is impossible to come up with a single scale that encompasses all possible Lewis acids. Some Lewis acids (e.g. Al3+, BF3) act very much like H+ when reacted with a base. Thus for example we could use reactions with Al3+ to set up a scale of pKa's very similar to that using H+. But other Lewis acids, e.g. Hg2+, give an entirely different series of base strengths if the same procedure is followed for them. The origin of this phenomenon is believed to lie in the fact that the origin of protic acid strength is primarily electrostatic. But when all Lewis acids are considered, a pure electrostatic model cannot be used. Many species react with bases using a significant amount of covalent bonding, and these cannot be directly related to the others which are compatible with an electrostatic model. In response to this discovery a simple, but extremely useful, qualitative scheme which divides Lewis acids and bases into two groups (along with a less-well-defined "borderline" category) has been developed. This is called the **Pearson hard-soft acid base**, or HSAB, theory. This model has found extensive application in the categorization of the chemical properties of the elements relative to their place in the periodic table, and is perhaps the single most important organizational scheme in use.

The origin of the HSAB scheme came from a consideration of the thermodynamic strength of the interaction of acids with halides. The halide ions, F-, Cl-, Br-, I- form adducts with most of the elements in the periodic table, and they are relatively simple monatomic ions. They vary extensively in chemical properties, with F– being a small, dense ion with a highly focused negative charge, and I– being a large diffuse ion, with a charge that is readily polarized. This difference in polarizability is seen in terms of the relative order of reactivity of the Lewis acids with the halides. Indeed, one finds two classes:

"Class A" - Hard acids - bond in the order I- > Br- > Cl- >> F- "Class B" - Soft acids - bond in the order F- >> Cl- > Br- > I.

I. The hard acids include H+ and those acids that behave like H+: Al3+, BF3, Cr3+ etc. This type of acid is found to prefer a whole range of bases as follows (stronger interaction):

F- >> Cl- > Br- > IR2O >> R2S R3N >> R3P

Soft acids include Hg2+, Au+, Pt2+, Cd2+, Pb2+. This type of metal ion prefers to bind to bases as follows (stronger interaction):

I-> Br-> Cl- >> FR2S >> R2O R3P >> R3N

The HSAB classification can be extended using the two groups of acids to group the bases into hard and soft categories as well, using the principle that **hard acids tend to bind hard bases; soft acids tend to bind soft bases**.

Thus F-, R2O: an R3N: are harder bases; Cl-, Br-, I-, R2S and R3P are softer bases. The bonding between hard acids and bases is dominated by electrostatic interactions. This is shown by the fact that a strong interaction correlates with (1) small size and (2) high electronegativity of the base. These are purely electrostatic parameters, and this implies that the bonding is essentially ionic.

The bonding between soft acids and bases seems to be primarily covalent in nature. Thus a strong interaction occurs between large metal ions with high electronegativity (for example, Pt, Au and Pb, which have -values similar to that of boron and carbon) and the most polarizable bases. The HSAB classification scheme is presented on the periodic table shown here. Note that for some of the metals, different oxidation states belong to different groups. The softest acids have the highest electronegativity of all the metals, while the softest bases have the lowest electronegativity of the non-metals. Compare this table to the one featuring electronegativities of the elements that is given earlier in the notes.

Periodic table



Summary of the HSAB classification

We can summarize the HSAB scheme by considering the properties of the hard and soft acids and base. This is done in the following table.

Property	Hard Acid	Soft Acid	Soft Base	Hard Base
χ	0.7-1.6	1.9-2.5	2.1-3.0	3.4-4.0
ionic radius	small	large	large	small
Charge	high	low	N/A	N/A

Using HSAB theory to predict the course of reactions

Consider the following chemical equilibria. For each reaction, we can compare the HSAB character of the donor and acceptor atoms, and thus predict which adducts will have greater stability, using the principle that hard acids tend to bind hard bases; soft acids tend to bind soft bases. This will usually allow us to predict whether the products or the reactants will be favored in each reaction. See that you can rationalize each prediction (i.e. by identifying the correct donor and acceptor atoms:

 Nb2S5 + 5HgO
 Nb2O5 + 5 HgS (right)

 La2(CO)3 + Tl2S3
 La2S3 + Tl2(CO3)3 (left)

 2 CH3MgF + HgF2
 (CH3)2Hg + 3MgF2 (right)

Interpretation of the qualitative analysis scheme

The Chemistry 2810 laboratory contains a small scale version of the qualitative analysis scheme for some representative cations from the periodic table. This experiment is part of a classical analysis scheme developed by chemists of past generations to identify unknowns. In commercial practice the qual-scheme, as it is affectionately known, has large been surpassed by automated analysis instrumentation. But the scheme retains real value in teaching many of the chemical attributes of the elements, and for this reason we have retained it in the 2810 laboratory. For background references on the qual scheme, you may consult the books by Wisner, *Qualitative analysis and ionic equilibria*, and Hogness, *Qualitative analysis and chemical equilibrium*. A flow chart is provided to indicate the separation scheme, and a rationale using HSAB and other principles is given for each separation. The full qualitative analysis scheme for the element is presented in periodic table format below.

Group 1 The silver group

Ag+, Hg22+, Tl+, Pb2+

These ions precipitate (as the chlorides) from 0.3 M HCl solution. Rationale: *Softest* acids react strongly enough with a borderline base to precipitate in acid solution.

Group 2 The copper group

Hg2+, Bi3+, Cu2+, Sn2+, Sn4+

These ions precipitate as the sulfides from 0.3 M HCl containing H2S. Rationale: Soft acids react with a very soft base.

Group 3 Zinc-aluminum group

Zn2+, Fe2+, Fe3+, Ni2+, Cr3+, Al3+

These ions precipitate from an alkaline solution of H2S. Some tend to form sulfides, some the hydroxides. Further discrimination is possible, because FeS, Cr(OH)3 and Al(OH)3 will redissolve if the precipitate is layered with 10-2 M acid, but NiS and ZnS will not.

Rationale (1): ZnS, NiS, FeS as sulfides, i.e. borderline acids bind to a very soft base, when the pH is adjusted so as to weaken the M(OH2)n m+ hydrated cation.

Group 4 Alkaline earths

Ca2+, Sr2+, Ba2+

Precipitate from basic solution on the addition of CO32- in the form of sodium carbonate. The carbonates are the insoluble products formed. Rationale: These are weakly acidic (Br¢nsted definition) cations. The carbonates are insoluble because of the favorable lattice energy when the weakly basic carbonate ion reacts with these cations, since the cation and anion are both doubly charged and similar in size.



Group 5 Alkali elements

Na+, K+ and NH4+

These have soluble hydroxides and carbonates. They do not precipitate from the qualitative analysis scheme. Rationale: Lattice energy for carbonates is unfavorable, since the cations are small, and bear a 1+ charge. The hydroxides are soluble because the cations are non-basic, while hydroxide is strongly basic. They are therefore likely to be soluble by the "cross-terms" rule.

Goldschmidt classification of minerals

As a final example of the use of HSAB theory we will briefly consider its application to Geology. Goldschmidt independently developed his own scheme for the mineralogical classification of the elements. Note however how closely his categories match the predictedHard-soft acid-base properties discussed above. The common minerals of the elements as found on earth have been classified by Goldschmidt as follows:

Siderophiles: elements which are alloyed with the molten iron in the core, including Ni, Co, Pd, Pt, Rh and Ir. complex SiOx

Chalcophiles: found predominantly in sulfide ores.

Lithophiles: found in nature as parts of alumino-silicate minerals (i.e. as cations towardsy - and AlOz anions). Most rocks are minerals of this type.

Atmophiles: found in nature as gases.

HSAB concept

HSAB theory rationalizes the middle two categories: the soft acid metals preferentially form sulfide minerals; the hard acid metals prefer the oxygen donors in aluminosilicates.

The **HSAB concept** is an initialism for "hard and soft (Lewis) acids and bases". HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable. The concept is a way of applying the notion of orbital overlap to specific chemical cases.

The theory is used in contexts where a qualitative, rather than quantitative, description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

Hard acids and hard bases tend to have the following characteristics:

- •small atomic/ionic radius
- •high oxidation state
- •low polarizability
- •high electronegativity (bases)

• hard bases have highest-occupied molecular orbitals (HOMO) of low energy, and hard acids have lowest-unoccupied molecular orbitals (LUMO) of high energy.

Examples of hard acids are: H+, light alkali ions (Li through K all have small ionic radius), Ti4+, Cr3+, Cr6+, BF3. Examples of hard bases are: OH–, F–, Cl–, NH3, CH3COO–, CO32–. The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and soft bases tend to have the following characteristics:

 $\bullet \square$ large atomic/ionic radius

 $\bullet \Box$ low or zero oxidation state bonding

● □ high polarizability

 $\bullet \Box$ low electronegativity

• soft bases have HOMO of higher energy than hard bases, and soft acids have LUMO of lower energy than hard acids. (However the soft-base HOMO energies are still lower than the soft-acid LUMO energies.)

Examples of soft acids are: CH3Hg+, Pt2+, Pd2+, Ag+, Au+, Hg2+, Hg22+, Cd2+, BH3. Examples of soft bases are: H–, R3P, SCN–, I–. The affinity of soft acids and bases for each other is mainly covalent in nature.

Borderline cases are also identified: **borderline acids** are trimethylborane, sulfur dioxide and ferrous Fe2+, cobalt Co2+ caesium Cs+ and lead Pb2+ cations. **Borderline bases** are: aniline, pyridine, nitrogen N2 and the azide, bromide, nitrate and sulfate anions.

Generally speaking, acids and bases interact and the most stable interactions are hardhard (ionogenic character) and soft-soft (covalent character).

An attempt to quantify the 'softness' of a base consists in determining the equilibrium constant for the following equilibrium:

 $BH + CH3Hg + \leftrightarrow H + CH3HgB$

Where CH3Hg+ (methylmercury ion) is a very soft acid and H+ (proton) is a hard acid, which compete for B (the base to be classified).

Some examples illustrating the effectiveness of the theory:

• Bulk metals are soft acids and are poisoned by soft bases such as phosphines and sulfides.

• Hard solvents such as hydrogen fluoride, water and the protic solvents tend

to solvate strong solute bases such as the fluorine anion and the oxygen anions. On the other hand dipolar aprotic solvents such as dimethyl sulfoxide and acetone are soft solvents with a preference for solvating large anions and soft bases.

• In coordination chemistry soft-soft and hard-hard interactions exist between ligands and metal centers.

An application of HSAB theory is the so-called **Kornblum's rule** which states that in reactions with ambident nucleophiles (nucleophiles that can attack from two or more places), the more electronegative atom reacts when the reaction mechanism is SN1 and the less electronegative one in a SN2 reaction. This rule (established in 1954) actually predates HSAB theory but in HSAB terms its explanation is that in a SN1 reaction the carbocation (a hard acid) reacts with a hard base (high electronegativity) and that in a SN2 reaction tetravalent carbon (a soft acid) reacts with soft bases.

According to recent findings electrophilic alkylations at free CN– occur preferentially at carbon, regardless of whether the SN1 or SN2 mechanism is involved and whether hard or soft electrophiles are employed. Preferred N attack, as postulated for hard electrophiles by the HSAB principle, could not be observed with any alkylating agent. Isocyano compounds are only formed with highly reactive electrophiles that react without an activation barrier because the diffusion limit is approached. It is claimed that the knowledge of absolute rate constants and not of the hardness of the reaction partners is needed to predict the outcome of alkylations of the cyanide ion

APPLICATIONS OF HSAB PRINCIPLE

In hydrogen bonding: The strong hydrogen bond is possible in cases of H2O, NH3 and HF, since the donor atoms (F, O & N) are hard Lewis bases and their interactions with partially positively charged H, which is a hard acid, are stronger.

Linkage of ambidentate ligands to metal atoms: The ambidentate ligand, SCN- can bind either by S end or N end. The bonding mode can be determined by using HSAB principle. It bonds through sulfur atom (soft base) when bonded to Pt2+, a soft acid.

However it bonds through nitrogen atom (a hard base) when linked to Cr3+, a hard acid.

Site preference in organic reactions: RCOX is a hard acid and reacts with the nitrogen end of SCN- ion to form an acyl isothiocyanate. Whereas the softer methyl group bonds to the Sulfur atom and forms methyl thiocyanate.

Inorganic reactions: HSAB principle is used to predict the outcome of some of the reactions.

1) The following reaction is possible because As is softer than P and I- is softer than F-. Remember that both As and P are soft but relatively As is softer.

2) The following reaction is possible since Mg2+ is harder acid than Ba2+ and O2- is harder base than S2-.

Precipitation reactions: The softer acids like Ag+, Hg+, Hg2+ etc., and border line acids like Fe2+, Ni2+, Cu2+, Zn2+, Pb2+ etc., can be precipitated as sulfides from their aqueous solutions since S2- ion is a softer base.

Limitations of HSAB Principle:

Hardness and softness has to do with competition and says nothing about the strength of a donor or acceptor.

The HSAB Principle is descriptive, not explanatory.

Generally it is assumed that hard-hard interactions are more electrostatic in nature (involving smaller, more highly charged ions, and/or more polar molecules) and that HOMO/LUMO overlap is more important in soft-soft interactions. Thus soft donors should have a relatively high HOMO and soft acceptors a relatively low LUMO, so that efficient mixing can occur. However, other factors may be involved. Soft-soft interactions may have a significant contribution from dispersion forces between polarisable atoms. In some cases, π -back bonding may also be important.

Type of acid	Characteristics	Examples
/base		
	* Atomic centres of small ionic radii	H+, Li+, Na+, K+, Be2+, Mg2+,
		Ca2+,
	(<90 pm).	
		Sr2+, Sn2+
	* High positive charge.	
	* Empty orbitals in their valence	
Hard acids	shells.	Al3+, Ga3+, In3+, Cr3+, Co3+, Fe3+,
	* Low electronegativity $(0.7-1.6)$ and	Ir3+, La3+, Si4+, Ti4+, Zr4+, Th4+,

Characteristics of hard, soft & borderline acids & bases

	low electron affinity. * Likely to be strongly solvated. * High energy LUMO.	VO2+ , UO22+ BeMe2, BF3, BC13, B(OR)3, AlMe3
Coft poids	 * Large radii (>90 pm). * Low or partial positive charge. * Completely filled orbitals in their valence shells. 	Cu+, Ag+, Au+, Hg+ , Cs+ , Tl+ , Hg2+ , Pd2+, Cd2+ , Pt2+
Soft acids	 * Intermediate electronegativities (1.9- 2.5) * Low energy LUMO's with large magnitude of LUMO coefficients. 	Metal atoms in zero oxidation states
Border line Acids		Fe2+ , Co2+ , Ni2+ , Cu2+ , Zn2+ , Pb2+ , B(CH3)3, SO2, NO+
Hard bases	 * Small radii (around 120pm) & highly solvated . * electronegative atomic centres (3.0-4.0). * Weakly polarizable. * Difficult to be oxidized. * High energy HOMO. 	H2O, OH-, F-, Cl-, CH3CO2-, PO43-, SO42-, CO32-, NO3-, ClO4-, ROH, RO-, R2O, NH3, RNH2, N2H4
Soft bases	* Large atoms (>170 pm) with	RSH, RS-, R2S, I-, CN-, SCN-, S2O3-
	intermediate electronegativity (2.5-	R3P, R3As (RO)3P, RNC, CO, C2H4,
-------------	--------------------------------------	------------------------------------
	3.0).	C6H6, R-, H-
	* High polarizability	
	* Easily undergo oxidation.	
	* Low energy HOMO's but large	
	magnitude HOMO coefficients.	
Border line		Aniline, pyridine, N3-, Br-, NO2-,
Bases		SO32-, N2

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases CI^- , Br^- , and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-} , and the amide ion, NH-2NH2-, are such strong bases that they react completely with water:

 $O2-(aq)+H2O(l) \rightarrow OH-(aq)+OH-(aq)$

 $NH-2(aq)+H2O(l) \rightarrow NH3(aq)+OH-(aq)$

Thus, O^{2-} and NH-2NH2- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic

table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 14.3.614.3.6).



Figure 1 As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH , perchloric acid, O_3CIOH , aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is

characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic -OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4 , or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3 , or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO₃, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO₂, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 14.3.714.3.7).





Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate

 $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]-[Al(H_2O)_2(OH)_4]-$, by reaction with hydroxide ion:

 $[Al(H2O)3(OH)3(aq)+OH-(aq) \rightleftharpoons H2O(l)+[Al(H2O)2(OH)4]-(aq)$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)6]3+[Al(H_2O)6]3+$ by reaction with hydronium ion:

 $3H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_3 + 6 (aq) + 3H_2O (l)$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Leveling effect



Leveling effect or **solvent leveling** refers to the effect of solvent on the properties of acids and bases. The strength of a strong acid is limited ("leveled") by the basicity of the solvent. Similarly the strength of a strong base is leveled by the acidity of the solvent. When a strong acid is dissolved in water, it reacts with it to form hydronium ion (H_3O^+) . An example of this would be the following reaction, where "HA" is the strong acid:

 $HA + H_2O \rightarrow A^- + H_3O^+$

Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+ . Therefore, no acid stronger than H_3O^+ exists in H_2O . Similarly, when ammonia is the solvent, the strongest acid is ammonium (NH_4^+), thus HCl and a super acid exert the same acidifying effect.

The same argument applies to bases. In water, OH^- is the strongest base. Thus, even though sodium amide (NaNH₂) is an exceptional base (pK_a of NH₃ ~ 33), in water it is only as good as sodium hydroxide. On the other hand, NaNH₂ is a far more basic reagent in ammonia than is NaOH.

The pH range allowed by a particular solvent is called the acid-base discrimination window.

Leveling and differentiating solvents

In a differentiating solvent, various acids dissociate to different degrees and thus have different strengths. In a leveling solvent, several acids are completely dissociated and are thus of the same strength. A weakly basic solvent has less tendency than a strongly basic one to accept a proton. Similarly a weak acid has less tendency to donate protons than a strong acid. As a result, a strong acid such as perchloric acid exhibits more strongly acidic properties than a weak acid such as acetic acid when dissolved in a weakly basic solvent. On the other hand, all acids tend to become indistinguishable in strength when dissolved in strongly basic solvents owing to the greater affinity of strong bases for protons. This is called the leveling effect. Strong bases are leveling solvents for acids, weak bases are differentiating solvents for acids. Because of the leveling effect of common solvents, studies on super acids are conducted in solvents that are very weakly basic such as sulfur dioxide (liquefied) and SO₂CIF.

Types of solvent on the basis of proton interaction On the basis of proton interaction, solvents are of four types,

(i) Protophilic solvents: Solvents which have greater tendency to accept protons, i.e., water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, i.e., water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, e.g., water, ammonia, ethyl alcohol, etc.

(iv) Aprotic solvents: Solvents which neither donate nor accept protons, e.g., benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as an acid in H₂O, a stronger acid in NH₃, a weak acid in CH₃COOH, neutral in C_6H_6 and a weak base in HF.

Factors that Control the Relative Strengths of Acids and Bases

The Polarity of the X - H Bond

When all other factors are kept constant, acids become stronger as the X – H bond becomes more polar. The second-row nonmetal hydrides, for example, become more acidic as the difference between the electronegativity of the X and H atoms increases. HF is the strongest of these four acids, and CH₄ is one of the weakest Brnsted acids known.

HF	$K_a = 7.2 \ge 10^{-4}$	$\Delta EN = 1.8$
H ₂ O	$K_a = 1.8 \ge 10^{-16}$	$\Delta EN = 1.2$
NH ₃	$K_a = 1 \ge 10^{-33}$	$\Delta EN = 0.8$
CH ₄	$K_a = 1 \ge 10^{-49}$	$\Delta EN = 0.4$

When these compounds act as an acid, an H-X bond is broken to form H⁺ and X⁻ ions. The more polar this bond, the easier it is to form these ions. Thus, the more polar the bond, the stronger the acid.

An 0.1 M HF solution is moderately acidic. Water is much less acidic, and the acidity of ammonia is so small that the chemistry of aqueous solutions of this compound is dominated by its ability to act as a base.

HF	pH = 2.1
H ₂ O	pH = 7
NH ₃	pH = 11.1

The Size of the X Atom

At first glance, we might expect that HF, HCl, HBr, and HI would become weaker acids as we go down this column of the periodic table because the *X*-H bond becomes less polar. Experimentally, we find the opposite trend. These acids actually become stronger as we go down this column.

This occurs because the size of the X atom influences the acidity of the X-H bond. Acids become stronger as the X-H bond becomes weaker, and bonds generally become weaker as the atoms get larger as shown in the figure below.



The K_a data for HF, HCl, HBr, and HI reflect the fact that the X-H bond-dissociation enthalpy (*BDE*) becomes smaller as the X atom becomes larger.

HF	$K_a = 7.2 \times 10^{-4}$	BDE = 569 kJ/mol
HCl	$K_a = 1 \ge 10^6$	BDE = 431 kJ/mol
HBr	$K_a = 1 \ge 10^9$	BDE = 370 kJ/mol
HI	$K_a = 3 \ge 10^9$	BDE = 300 kJ/mol

The Charge on the Acid or Base

The charge on a molecule or ion can influence its ability to act as an acid or a base. This is clearly shown when the pH of 0.1 *M* solutions of H_3PO_4 and the $H_2PO_4^{-}$, HPO_4^{2-} , and PO_4^{3-} ions are compared.

H ₃ PO ₄	pH = 1.5
H ₂ PO ₄ ⁻	pH = 4.4
HPO ₄ ²⁻	pH = 9.3
PO4 ³⁻	pH = 12.0

Compounds become less acidic and more basic as the negative charge increases. Acidity: $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$ Basicity: $H_2PO_4^- < HPO_4^{2-} < PO_4^{3-}$

The Oxidation State of the Central Atom

There is no difference in the polarity, size, or charge when we compare oxyacids of the same element, such as H_2SO_4 and H_2SO_3 or HNO_3 and HNO_2 , yet there is a significant difference in the strengths of these acids. Consider the following K_a data, for example.

H₂SO₄:
$$K_a = 1 \ge 10^3$$
 HNO₃: $K_a = 28$
H₂SO₃: $K_a = 1.7 \ge 10^{-2}$ HNO₂: $K_a = 5.1 \ge 10^{-4}$

The acidity of these oxyacids increases significantly as the oxidation state of the central atom becomes larger. H_2SO_4 is a much stronger acid than H_2SO_3 , and HNO_3 is a much stronger acid than HNO_2 . This trend is easiest to see in the four oxyacids of chlorine.

Oxyacid	Ka	Oxidation
		Number of
		the Chlorine
HOCl	2.9 x 10 ⁻⁸	+1
HOCIO	1.1 x 10 ⁻²	+3
HOClO ₂	$5.0 \ge 10^2$	+5
HOClO ₃	$1 \ge 10^3$	+7

This factor of 10^{11} difference in the value of K_a for hypochlorous acid (HOCl) and perchloric acid (HOClO₃) can be traced to the fact that there is only one value for the electronegativity of an element, but the tendency of an atom to draw electrons toward itself increases as the oxidation number of the atom increases.

As the oxidation number of the chlorine atom increases, the atom becomes more electronegative. This tends to draw electrons away from the oxygen atoms that surround the chlorine, thereby making the oxygen atoms more electronegative as well, as shown in the figure below. As a result, the O-H bond becomes more polar and the compound becomes more acidic.

Textbooks

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POSSIBLE QUESTIONS

<u>PART A: MULTIPLE CHOICE QUESTIONS</u> (Each question carry one mark)

- 1. A buffer solution is formed by adding which of the following to water?
 - (a) HCl and KOH (b) HCN and RbCN (c) NaBr and NaOH (d) HNO3 and LiNO₃
- 2. An Arrhenius acid is defined as a chemical species that
 - (a) is a proton donor(b) is a proton acceptor(c) produces hydrogen ions in solution
 - (d)produces hydroxide ions in solution
- 3. According to the HSAB concept, among the following which is a borderline base
 (a) Nitrate ion (b) OH⁻ (c) F⁻ (d) ferrous Fe2+
- 4. The affinity of hard acids and hard bases for each other is mainly

(a) ionic in nature. (b) Covalent in nature (c) Coordinate in nature

- (d) Metallic in nature
- 5. An Arrhenius base is defined as a substance that

(a) basic solution (b) acidic solution (c) standard solution (d) indicating solution.

- 6. In acid-base titrations, the solution of known concentration is called a(n)
 - (a) basic solution (b) acidic solution (c) standard solution (d) indicating solution.
- 7. Benzene is an example for

(a) Polar solvents (b) nonpolar solvent (c) organic solvents (d) non aqueous solvents

- 8. In an aqueous solution of NaCl, the pH is
 - (a) standard point (b) transition point (c) equivalence point (d) stoichiometric point.
- 9. Sodium chloride is highly soluble in

(a) Water (b) alcohol (c) benzene (d) carbon di sulphide

10. Which of the following are general properties of bases in aqueous solution?

(a) feel slippery and increase [OH⁻]

- (b) turn litmus red and accept a proton
- (c) Conduct electricity and turn litmus blue

- (d) feel slippery and react with Au to produce H_2
- 11. According to the HSAB concept Pick out the hard acid

(a) Cr^{3+} (b) OH^{-} (c) F^{-} (d) Cl^{-}

12. A Bronsted-Lowry base is defined as:

(a) Proton donor (b) **Proton acceptor** (c) a hydroxide donor (d) a hydroxide acceptor

13. Which one of the following salts would produce a basic solution when dissolved in water?

(a) Ammonium chloride(b) Potassium nitrate(c) Sodium cyanide(d) Sodium(d) Sodium

14. Which of the following are general properties of acids in aqueous solution?

(a) feel slippery and increase [H⁺]
(b) turn litmus blue and accept a proton
© conduct electricity and turn litmus red
(d) feel slippery and not react with Au

15. The conjugate acid of $C_6H_5NH_2$ is

(a) $C_6H_5NH^-$ (b) $C_6H_5NH_3$ (c) $C_6H_5NH_2^+$ (d) $C_6H_5NH_3^+$

- 16. Which one of the following gave the cationic charcterstic to the solvents(a) metalloids (b) acid (c) base (d) H₂O
- 17. The pH at which an indicator changes colour is known as its
 - (a) releases $H^+(aq)$ (b) releases OH-(aq) (c) accepts a proton (d) donates a proton
- 18. All metal cations are
 - (a) Arrhenius acid (b) Lewis acid (c) Lewis base (d) Bronsted base
- 19. A solvent other than water, that is not an organic compound
 - (a) Aprotic (b) protic (c) nonpolar (d) Nonaqueous
- 20. HSAB is widely used in chemistry for explaining
 - (a) **reaction Pathways** (b) Reactivity of compounds
 - (c) Common ion effect (d) Solubility product of the compounds

PART B (Each question carries 8 marks)

- 1. Apply HSAB principle in : (i) occurrence of metal minerals and (ii) predicting the stability of halogen acids.
- 2. (i) Explain Bronsted-Lowry concept of acids and bases with suitable examples.(ii) BCl₃ is stronger acid than BF₃. Explain
- 3. (i) Apply HSAB principle in : (a) occurrence of metal minerals

(b) predicting the stability of halogen acids.

(ii) Classify the following as hard and soft acids: Ca^{2+} and Hg^{2+} .

- 4. Discuss the different concepts of acids and bases.
- 5. (i) What are Lewis acids and bases? How are they classified.
 (ii) Which is a Lewis acid in the following? (i) NaCl (ii) BaCl₂ (iii) AlCl₃
- 6. (i) What are Lewis acids and bases? How are they classified.
 - (ii) Which is the stronger acid of each following pair
 - (a) H_3O^+ or H_2O ,
 - (b) NH_4^+ or H_2S or HS^- .
 - \bigcirc H₂O or OH⁻. Suggest reasons
- What are the limitations of HSAB concept. What are characteristics of hard acids. Which one is hard base F⁻ or I⁻?
- 8. Write a note on factors influencing the relative strength of acids and bases?
- 9. Write a note on Effects of temperature, dielectric constant and temperature on acids and bases?
- 10. Discuss about the relative strength of acids and bases?

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UNIT 4- OBJECTIVE TYPE QUESTIONS FOR ONLINE EXAMINATION(Each carry 1 Mark)

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answer
Consider the following acid-base equilibrium: $HCO^{3-} + H_2O \leftrightarrow H_2CO_3^{-2} + OH^{-1}$	H ₂ O and OH	HCO ₃ ⁻ and OH ⁻	H ₂ O and H ₂ CO ₃	HCO ₃ ²⁻ and H ₂ CO ₃	H ₂ O and H ₂ CO ₃
As the $[H_3O^+]$ in a solution decreases, the $[OH^-]$	increases and the pH increases	increases and the pH decreases	decreases and the pH increases	decreases and the pH decreases	increases and the pH increases
A buffer solution is formed by adding which of the following to water?	HCl and KOH	HCN and RbCN	NaBr and NaOH	HNO ₃ and LiNO ₃	HCN and RbCN
An Arrhenius acid is defined as a chemical species that	is a proton donor	is a proton acceptor	produces hydrogen ions in solution	produces hydroxide ions in solution.	produces hydrogen ions in solution
Which of the following are general properties of bases in aqueous solution?	feel slippery and increase [OH]	turn litmus red and accept a proton	conduct electricity and turn litmus blue	feel slippery and react with Au to produce $H_2(g)$	feel slippery and increase [OH]
The conjugate acid of C ₆ H ₅ NH ₂ is	C ₆ H ₅ NH ⁻	C ₆ H ₅ NH ₃	C ₆ H ₅ NH ₂ ⁺	$C_{6}H_{5}NH_{3}^{+}$	$C_{6}H_{5}NH_{3}^{+}$
Which of the following is a property of 1.0M HCl but not a property of 1.0M CH ₃ COOH ?	less than 7 and the solution is acidi	equal to 7 and the solution is neutral	greater than 7 and the solution is basi	greater than 7 and the solution is acidi	equal to 7 and the solution is neutral
In an aqueous solution of NaCl, the pH is	standard point	transition point	equivalence point	stoichiometric point.	equivalence point
The pH at which an indicator changes colour is known as its	releases $H^{+}_{(aq)}$	releases OH _(aq)	accepts a proton	donates a proton	releases OH ⁻ _(aq)
An Arrhenius base is defined as a substance that	basic solution	acidic solution	standard solution	indicating solution.	standard solution
In acid-base titrations, the solution of known concentration is called a(n)	basic solution	acidic solution	standard solution	indicating solution.	standard solution
A substance which produces hydroxide ions in solution is a definition of which of the following?	an Arrhenius acid	an Arrhenius base	a Bronsted-Lowry acid	a Bronsted-Lowry base	an Arrhenius base
HSAB is widely used in chemistry for explaining	Stability of compounds	Reactivity of compounds	Common ion effect	solubility product of the compounds	Stability of compounds
HSAB is widely used in chemistry for explaining	reaction mechanisms	Reactivity of compounds	Common ion effect	solubility product of the compounds	reaction mechanisms
HSAB is widely used in chemistry for explaining	reaction Pathways	Reactivity of compounds	Common ion effect	solubility product of the compounds	reaction Pathways
In HSAB concept "Hard" applies to	big species	have high charge states have low charge states	are strongly polarizable species	are weak polarizable species	have high charge states have low charge states
In HSAB concept "Hard" applies to	big species	Small species	have low charge states	are strongly polarizable species	Small species
In HSAB concept "Hard" applies to	big species	weakly polarisable	have low charge states	are strongly polarizable species	weakly polarisable
In HSAB concept "Soft " applies to	Small species	weakly polarisable	have low charge states	highly charged species	have low charge states
In HSAB concept "Soft" applies to	Small species	weakly polarisable	Big species	highly charged species	Big species
In HSAB concept "Soft" applies to	Small species	weakly polarisable	Strongly polarisable	highly charged species	Strongly polarisable
Hard acids tend to have the following characteristic property	high electro positivity	high electronegativity	high molecular weight	high velocity	High electronegativity
Hard acids tend to have the following characteristic property	large atomic/ionic radius	low or zero oxidation state bonding	high polarizability	low polarizability	low polarizability
Hard acids tend to have the following characteristic property	large atomic/ionic radius	low or zero oxidation state bonding	high polarizability	high oxidation state	high oxidation state
Hard acids tend to have the following characteristic property	large atomic/ionic radius	low or zero oxidation state bonding	high polarizability	Small atomic/ionic radius	Small atomic/ionic radius
According to the HSAB concept, example for a hard acid	BF ₃	OH	F	СГ	BF ₃
According to the HSAB concept Pick out the hard acid	Cr ³⁺	OH	F	СГ	Cr ³⁺

According to the HSAB concept, among the following which is a hard acid	H^+	OH	F ⁻	СГ	H^+
According to the HSAB concept example for a hard base	Cr ³⁺	OH	light alkali ions	BF ₃	OH_
According to the HSAB concept Pick out the hard base	Cr ³⁺	CH ₃ COO ⁻	light alkali ions	BF ₃	CH₃COO⁻
According to the HSAB concept among the following which is a hard base	Cr ³⁺	NH ₃	light alkali ions	BF ₃	NH ₃
According to the HSAB concept example for a soft acid	Pt ²⁺	OH	F ⁻	CΓ	Pt^{2+}
According to the HSAB concept Pick out the soft acid	Pd^{2+}	OH	F	Cl	Pd ²⁺
According to the HSAB concept, among the following which is a soft acid	Ag^+	OH	F	СГ	Ag^+
According to the HSAB concept example for a soft base	Cr ³⁺	H	light alkali ions	BF ₃	H
According to the HSAB concept Pick out the soft base	Cr ³⁺	SCN [−]	light alkali ions	BF ₃	SCN
According to the HSAB concept among the following which is a soft base	Cr ³⁺	I	light alkali ions	BF ₃	Γ
According to the HSAB concept example for a borderline acid	BF ₃	OH	F	trimethylborane,	BF ₃
According to the HSAB concept Pick out the borderline acid	Cr ³⁺	OH	F	sulfur dioxide	Cr ³⁺
According to the HSAB concept, among the following which is a borderline acid	H^+	OH	F	ferrous Fe2+	H^+
According to the HSAB concept example for a borderline base	Aniline	OH	F ⁻	trimethylborane	Aniline
According to the HSAB concept Pick out the borderline base	Pyridine	OH	F	sulfur dioxide	Pyridine
According to the HSAB concept, among the following which is a borderline base	Nitrate ion	OH	F ⁻	ferrous Fe2+	Nitrate ion
The affinity of hard acids and hard bases for each other is mainly	ionic in nature.	Covalent in nature	Coordinate in nature	Metallic in nature	ionic in nature.
The affinity of soft acids and soft bases for each other is mainly	ionic in nature.	Covalent in nature	Coordinate in nature	Metallic in nature	Covalent in nature
According to HSAB theory bulk metals are	Soft acids	Soft bases	Hard acids	Hard bases	Soft acids
According to HSAB theory bulk metals are soft acids and are poisoned by	Soft acids	Soft bases	Hard acids	Hard bases	Soft bases
The conjugate base of acetic acid is	CH ₃ COO ⁻	Sodium acetate	acetic anhydride	Ethyl aceto acetate	CH ₃ COO ⁻
The conjugate base of hydrochloric acid is	Chloride ion	Hydrogen ion	Hydronium ion	chlorine	Chloride ion
The conjugate acid of ammonia	ammonium ion	ammonium acetate	Ammonium chloride	Hydroxyl ion	ammonium ion
Aluminium trichloride is a	Arrhenius acid	Lewis acid	Lewis base	Bronsted acid	Lewis acid
Boron trifluoride is a	Arrhenius acid	Lewis acid	Lewis base	Bronsted acid	Lewis acid
Ammonia is a	Arrhenius base	Lewis acid	Lewis base	Bronsted acid	Lewis base
All metal cations are	Arrhenius acid	Lewis acid	Lewis base	Bronsted base	Lewis acid

UNIT V

Solvents

The solvent - solubility's of compounds - effect of temperature on solubility - Chemical structure and solubility of solvents. Classification of solvents - general behavior - properties of ionizing solvents. Types of reaction in solvents. Aqueous and non aqueous solvents – Protonic solvents - Ammonia. Non-protonic solvents - SO₂.

SOLVENT

The solubility of a substance is the amount of that substance that will dissolve in a given amount of solvent. Solubility is a quantitative term. The terms *soluble* and *insoluble* are relative. A substance is said to be soluble if more than 0.1 g of that substance dissolves in 100 mL solvent. If less than 0.1 g dissolves in 100 mL solvent, the substance is said to be insoluble or, more exactly, sparingly soluble. The terms miscible and immiscible may be encountered when considering the solubility of one liquid in another. Miscible means soluble without limits; for example, alcohol is miscible with water Immiscible and insoluble mean the same; oil is immiscible with water, as in oil and vinegar salad dressing.

DETERMINING SOLUBILITY

How is the solubility of a substance determined?

A known amount of the solvent--for example, 100 mL--is put in a container. Then the substance whose solubility is to be determined is added until, even after vigorous and prolonged stirring, some of that substance does not dissolve. Such a solution is said to be saturated because it contains as much solute as possible at that temperature. In this saturated solution, the amount of solute is the solubility of that substance at that temperature in that solvent. Doing this experiment with water as the solvent and sodium chloride as the solute, we find that, at 20°C, 35.7 g of the salt dissolve in 100 mL water. The solubility of sodium chloride is, then, 35.7 g/100 mL water at 20°C. Sodium chloride is a moderately soluble salt. The solubility of sodium nitrate is 92.1 g/100 mL water at 20°C; sodium nitrate is a very soluble salt. At the opposite end of the scale is barium sulfate, which has a solubility of 2.3 X 10 \cdot g/100 mL water at 20°C. Barium sulfate is an insoluble salt.

Saturated Solutions

A Saturated solution is one in which the dissolved solute is in equilibrium with the undissolved solute. The container holds a saturated solution of sucrose (cane sugar); at the bottom of the container is some undissolved sucrose. If we could see the individual molecules in this solution, we would see that some of the molecules of sucrose are moving away from the solid crystals at the bottom of the container as they dissolve. The same number of molecules are coming out of solution to become part of the undissolved sucrose.

Factors Affecting Solubility

Many factors affect the solubility of one substance in another. We will discuss a few, in particular.

1. Forces between particles

One factor that affects solubility is the nature of the intermolecular forces or interionic forces in both the solute and the solvent. When one substance dissolves in another, the attractive forces in both must be overcome. The dissolving solute must be able to break up the aggregation of molecules in the solvent (that is, the hydrogen bonds between molecules or the dispersion forces between molecules in a nonpolar solvent), and the molecules of the solvent must have sufficient attraction for the solute particles to remove them one by one from their neighbors in the undissolved solute. If the solute is ionic, only a very polar solvent like water provides enough interaction to effect dissolution. In those ionic compounds like barium sulfate that are called insoluble, the interaction between the ions is greater than can be overcome by interaction with the polar water molecules. If the solute particles are polar molecules, polar solvents such as alcohols can usually effect dissolution. If the solute is nonpolar, it may dissolve only in nonpolar solvents, not because polar solvent molecules are unable to overcome the weak dispersion forces between the solute molecules, but because these dispersion forces are too weak to overcome thedipole-dipole interaction between the solvent molecules.

A general rule is that like dissolves like. Ionic and polar compounds are most apt to be soluble in polar solvents like water or liquid ammonia. Nonpolar compounds are most apt to be soluble in nonpolar solvents, such as carbon tetrachloride, and hydrocarbon solvents like gasoline.

The solubility of gases in water depends a great deal on the polarity of the gas molecules. Those gases whose molecules are polar are much more soluble in water than are nonpolar gases. Ammonia, a strongly polar molecule, is very soluble in water (89.9 g/100 g H₂O); so is hydrogen chloride (82.3 g/100 g H2O). Helium and nitrogen are nonpolar molecules. Helium is only slightly soluble (1.8 X 10-4 g/100 g H2O), as is nitrogen (2.9 X 10-3 g/100 g H2O).

Table shows specific examples of different kinds of compounds and their relative solubilities in water, a polar solvent; in alcohol, a less polar solvent; and in benzene, a nonpolar solvent.

Kinds of bonds	Example	Solubility in		
Ionic	Sodium chloride	Water	Alcohol	Benzene
Polar covalent	Sucrose	Very soluble	Slightly soluble	Insoluble
Nonpolar	Napthalene	Very soluble	Soluble	Insoluble
Covalent		Insoluble	soluble	Very soluble

Solubility and interparticle bonds

Table below shows the solubility of several substances in water at 20°C and 100°C. Notice that the solubilities of solids and liquids usually increase as the temperature increases, but the solubilities of gases decrease with increasing temperature. This property of gases causes our concern for the fish population of lakes, oceans, and rivers threatened with thermal (heat) pollution. Fish require dissolved oxygen to survive. If the temperature of the water increases, the concentration of dissolved oxygen decreases, and the survival of the fish becomes questionable.

TEMPERATURE :

Solubility and temperature

		Solubility (g/100mL water)	
Compound	Type of bonding	At 20°C	At 100°C
sodium chloride	Ionic	35.7	39.1
barium sulfate	Ionic	2.3 X 10-4	4.1 X 10-4
Sucrose	polar covalent	179	487
Ammonia	polar covalent	89.9	7.4
hydrogen chloride	polar covalent	82.3	56.1
Oxygen	nonpolar covalent	4.5 X 10-3	3.3 X 10-3

3. Pressure

The pressure on the surface of a solution has very little effect on the solubilities of solids and liquids. It does have an enormous effect on the solubility of gases. As the partial pressure of a gas in the atmosphere above the surface of a solution increases, the solubility of that gas increases. A carbonated beverage is bottled and capped under a high partial pressure of carbon dioxide so that a great deal of carbon dioxide dissolves. When the bottle is uncapped, the partial pressure of carbon dioxide above the liquid drops to that in the atmosphere, the solubility of carbon dioxide decreases, and the gaseous CO₂ comes out of solution as fine bubbles.

This same phenomenon is of concern in scuba diving. As divers descend, they are underever-increasing pressure due to the increasing mass of water above them. Each 33 ft of water exert a pressure of 1 atm. As the diver descends, the pressure on the air in the lungs increases rapidly, and the blood dissolves more than normal amounts of both nitrogen and oxygen. As the diver comes up, the pressure decreases and the gases come out of solution. If the change in pressure is too swift, the bubbles of gas are released into the blood stream and tissues, instead of into the lungs. The bubbles cause sharp pain wherever they occur, most notably in the joints and ligaments. This dangerous and sometimes fatal condition is called *bends*, the name deriving from the temporary deformities caused by the affected diver's being unable to straighten his or her joints. Because helium, at all pressures, is less soluble than nitrogen, divers often breathe a mixture of helium and oxygen instead of air, a nitrogen-oxygen mixture.

The term hyperbaric means greater-than-normal atmospheric pressure. In hyperbaric medical treatments, patients are subjected to a pressure greater than atmospheric. This pressure increases the amount of oxygen dissolved in the blood. Treatment in hyperbaric, or high-pressure, chambers is of particular value for patients who are suffering from severe anemia, hemoglobin abnormalities, or carbon monoxide exposure or undergoing skin grafts, for such treatment increases the amount of oxygen transported by the blood to the tissues.

Solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure 13.4). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

Solute + solvent *⇒* dissolution crystallization solution

Although the terms precipitation and crystallization are both used to describe the separation of solid solute from a solution, crystallization refers to the formation of a solid with a well-defined crystalline structure, whereas precipitation refers to the formation of any solid phase, often one with very small particles.



Figure: Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Factors Affecting Solubility

The maximum amount of a solute that can dissolve in a solvent at a specified temperature and pressure is its solubility. Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume (mol/L). Even for very soluble substances, however, there is usually a limit to how much solute can dissolve in a given quantity of solvent. In general, the solubility of a substance depends on not only the energetic factors we have discussed but also the temperature and, for gases, the pressure. At 20°C, for example, 177 g of NaI, 91.2 g of NaBr, 35.9 g of NaCl, and only 4.1 g of NaF dissolve in 100 g of water. At 70°C, however, the solubilities increase to 295 g of NaI, 119 g of NaBr, 37.5 g of NaCl, and 4.8 g of NaF. As you learned in Chapter 12, the lattice energies of the sodium halides increase from NaI to NaF. The fact that the solubilities decrease as the lattice energy increases suggests that the Δ H2 Δ H2 term in Figure 13.1 dominates for this series of compounds.

A solution with the maximum possible amount of solute is saturated. If a solution contains less than the maximum amount of solute, it is unsaturated. When a solution is saturated and excess solute is present, the rate of dissolution is exactly equal to the rate of crystallization (part (b) in Figure 13.4). Using the value just stated, a saturated aqueous solution of NaCl, for example, contains 35.9 g of NaCl per 100 mL of water at 20°C. We can prepare a homogeneous saturated solution by adding excess solute (in this case, greater than 35.9 g of NaCl) to the solvent (water), stirring until the maximum possible amount of solute has dissolved, and then removing undissolved solute by filtration.

Interactions in Liquid Solutions

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions. As we described in Section 13.1, unless some of that energy is recovered in the formation of new, favorable solute–solvent interactions, the increase in entropy on solution formation is not enough for a solution to form.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules $(\Delta H2=0\Delta H2=0)$ because the molecules are already separated. Thus we need to consider only the energy required to separate the solvent molecules (Δ H1 Δ H1) and the energy released by new solute-solvent interactions (Δ H3 Δ H3). Nonpolar gases such as N2N2, O2O2, and ArArhave no dipole moment and cannot engage in dipole-dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent– solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. In this case, Δ H1 Δ H1 and Δ H3 Δ H3 are both small and of similar magnitude. In contrast, for a solution of a nonpolar gas in a polar solvent, $\Delta H1\Delta H1$ is far greater than $\Delta H3\Delta H3$. As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N2N2 in a saturated solution of N2N2 in water. а polar solvent, is only 7.07×10–4M7.07×10–4M compared with 4.5×10–3M4.5×10–3M for saturated а solution of N2N2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table 13.3. This is precisely the trend expected: as the gas molecules become larger, the

strength of the solvent-solute interactions due to London dispersion forces increases, approaching the strength of the solvent-solvent interactions.

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; thus the enthalpy of solution is expected to be small (Δ Hsoln \approx 0 Δ Hsoln \approx 0), and the increase in entropy drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl4CCl4, and CS2CS2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H2OH2O, HFHF, and NH3NH3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an interface (Figure 13.5), the region between the two layers. Just because two liquids are immiscible, however, does not mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).



Figure Immiscible Liquids. Separatory funnel demonstrating the separation of oil and colored water. The solubilities of simple alcohols in water are given in the below Table. Only the three lightest alcohols (methanol, ethanol, and n-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.



Table: Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H ₂ O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S8S8 molecules that have no dipole moment. Because the S8S8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS2CS2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform (CHCl3CHCl3) and methylene chloride (CH2Cl2CH2Cl2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C6H5OHC6H5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its dielectric constant, a measure of its ability to separate ions in solution.

Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilic (literally, "water loving"), meaning that it has an electrostatic attraction to water, or hydrophobic ("water fearing"), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and n-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either fat soluble or water soluble. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.

Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.



WATER AS A SOLVENT

Water is also a good solvent due to its polarity. The solvent properties of water are vital in biology, because many biochemical reactions take place only within aqueous solutions (e.g., reactions in the cytoplasm and blood). In addition, water is used to transport biological molecules.

When an ionic or polar compound enters water, it is surrounded by water molecules. The relatively small size of water molecules typically allows many water molecules to surround one molecule of *solute*. The partially negative dipoles of the water are attracted to positively charged components of the solute, and vice versa for the positive dipoles.

In general, ionic and polar substances such as acids, alcohols, and salts are easily soluble in water, and nonpolar substances such as fats and oils are not. Nonpolar molecules stay together in water because it is energetically more favorable for the water molecules to hydrogen bond to each other than to engage in van der Waals interactions with nonpolar molecules.

An example of an ionic solute is table salt; the sodium chloride, NaCl, separates into Na+cations and Cl- anions, each being surrounded by water molecules. The ions are then easily transported away from their crystalline lattice into solution. An example of a nonionic solute is table sugar. The water dipoles hydrogen bond to the dipolar regions of the sugar molecule and allow it to be carried away into solution.

Water is considered the universal solvent due to its ability to dissolve or dissociate most compounds. Since water is a polar molecule with slightly positive and slightly negative charges, ions and polar molecules can readily dissolve in it. Therefore, water is referred to as a solvent: a substance capable of dissolving other polar molecules and ionic compounds. The charges associated with these molecules form <u>hydrogen bonds</u> with water, surrounding the particle with



water molecules. This is referred to as a sphere of hydration, or a hydration shell, and serves to keep the particles separated or dispersed in the water.

When ionic compounds are added to water, the individual ions react with the polar regions of the water molecules, and their ionic bonds are disrupted in the process of dissociation. Dissociation occurs when atoms or groups of atoms break off from molecules and form ions. Consider table salt (NaCl, or sodium chloride): when NaCl crystals are added to water, the molecules of NaCl dissociate into Na⁺ and Cl⁻ ions, and spheres of hydration form around the ions. The positively-charged sodium ion is surrounded by the partially-negative charge of the water molecule's oxygen. The negatively-charged chloride ion is surrounded by the partially- positive charge of the hydrogen on the water molecule.

Dissociation of NaCl in Water

When table salt (NaCl) is mixed in water, spheres of hydration are formed around the ions. Since many biomolecules are either polar or charged, water readily dissolves these hydrophilic compounds. On the other hand, water is a poor solvent for hydrophobic molecules such as <u>lipids</u>. The nonpolar molecules in water undergo hydrophobic interactions: the water changes its hydrogen bonding patterns around the hydrophobic molecules.

CLASSIFICATION OF SOLVENTS

Solvents can be broadly classified into two categories: *polar* and *non-polar*. Generally, the dielectric constant of the solvent provides a rough measure of a solvent's polarity. The strong polarity of water is indicated, at 0 °C, by a dielectric constant of 88. Solvents with a dielectric constant of less than 15 are generally considered to be nonpolar. Technically, the dielectric constant measures the solvent's ability to reduce the field strength of the electric field surrounding a charged particle immersed in it. This reduction is then compared to the field strength of the charged particle in a vacuum. In layperson's terms, dielectric constant of a solvent can be thought of as its ability to reduce the solute's effective internal charge. Generally, the dielectric constant of a solvent is an acceptable approximation of the solvent's ability to dissolve common ionic compounds, such as salts.

POLAR PROTIC AND POLAR APROTIC

Solvents with a relative static permittivity greater than 15 can be further divided into protic and aprotic. Protic solvents solvate anions (negatively charged solutes) strongly via hydrogen bonding. Water is a protic solvent. Aprotic solvents such as acetone or dichloromethane tend to have large dipole moments (separation of partial positive and partial negative charges within the same molecule) and solvate positively charged species via their negative dipole. In chemical reactions the use of polar protic solvents favors theSN1reaction mechanism, while polar aprotic solvents favor the SN2 reaction mechanism.

These solvents can be classified as:

Protic Solvent: This a solvent that undergo self-ionization and provides protons which are solvated. Examples: HF, MeOH, EtOH, H2SO4, Liquid NH3 etc

(NB: Self ionizing is when a pure liquid partially dissociates into ions.)

Aprotic Solvent: This a solvents that undergoes self-ionization without the formation of protons. Examples: N₂O₄, BrF₃, N, N-dimethylformamide, dimethyl sulfoxide, and nitrobenzene.

An **inorganic nonaqueous solvent** is a solvent other than water, that is not an organic compound. Common examples are liquid ammonia, liquid sulfur dioxide, sulfuryl chlorideandsulfuryl chloride fluoride, phosphoryl chloride, dinitrogen tetroxide, antimony trichloride, bromine pentafluoride, hydrogen fluoride, pure sulfuric acid and other inorganic acids. These solvents are used in chemical research and industry for reactions that cannot occur in aqueous solutions or require a special environment.

What are Non-aqueous Solvents?

These are solvents other than water. Their use as solvents is due to the fact that water is not always a good solvent since some reagents may react with water (eg alkali metals) during inorganic reactions.

Classifications and Examples of Non-aqueous Solvents

Examples of Non-aqueous Solvents are;

Organic solvents: Dichloromethane, Hexane, Toluene, Ethers(eg diethyl ether, diglyme,tetrahydrofuran-THF)

Exotic solvents(**Inorganic**): Liquid ammonia(NH3), Liquid Sulphur dioxide(SO2), Sulphuric acid(H2SO4), Bromine trifluoride(BrF3)

Ionic solvents: [pyBu][AlCl4]

Liquid ammonia: a non-aqueous solvent

Despite low boiling point (-33.4oC), easy to handle.

=> ionic compounds can be soluble but the lower compared to water means that salt with highly charged, non-polarisable anions such as carbonates, sulphates, and phosphates are insoluble.

NH3 is more polarisable than H2O, so salts with more polarisable anions are more soluble, hence the solubility trends.

F- < Cl- < Br- < I-

PO43- < SO42- < OAc- < NO3

Specific solvation: NH3 is a better a-donor than H2O and ammine complexes are formed, especially with the later transition (Ni2+, Cu2+) and B metals (Ag+, Zn2+).

Hence higher solubilities for compounds of these metals than those of the A-metals.

Self-ionization of ammonia is much "weaker" than water.

2NH3 → NH4+ + NH2- k @ 223K ca. 10⁻³⁰

Liquid ammonia will therefore tolerate very strong bases such as C5H5- which would otherwise be hydrolysed in water.

Ammonia is kinetically stabilized to reduction (but easily oxidized) by many reagents, e.g., the reaction;

Na + NH3 \longrightarrow NaNH2 + H2 (g)

is very favourable but slow in the absence of a catalyst such as Fe3+.

Reaction in solvents

Substitution reactions

The solvent used in substitution reactions inherently determines the nucleophilicity of the nucleophile; this fact has become increasingly more apparent as more reactions are performed in the gas phase.^[12] As such, solvent conditions significantly affect the performance of a reaction with certain solvent conditions favoring one reaction mechanism over another. For S_N1 reactions the solvent's ability to stabilize the intermediate carbocation is of direct importance to its viability as a suitable solvent. The ability of polar solvents to increase the rate of S_N1 reactions is a result of the polar solvent's solvating the reactant

intermediate species, i.e., the carbocation, thereby decreasing the intermediate energy relative to the starting material. The following table shows the relative solvolysis rates of *tert*-butyl chloride with acetic acid (CH₃CO₂H), methanol (CH₃OH), and water (H₂O).

Solvent	Dielectric Constant, ε	Relative
		Rate
CH ₃ CO ₂ H	6	1
CH ₃ OH	33	4
H ₂ O	78	150,000

The case for S_N2 reactions is quite different, as the lack of solvation on the nucleophile increases the rate of an S_N2 reaction. In either case (S_N1 or S_N2), the ability to either stabilize the transition state (S_N1) or destabilize the reactant starting material (S_N2) acts to decrease the ΔG =/=activation and thereby increase the rate of the reaction. This relationship is according to the equation $\Delta G = -RT \ln K$ (Gibb's Free Energy). The rate equation for S_N^2 reactions are bimolecular being first order in Nucleophile and first order in Reagent. The determining factor when both S_N^2 and S_N^1 reaction mechanisms are viable is the strength of the Nucleophile. Nucleophilicity and basicity are linked and the more nucleophilic a molecule becomes the greater said nucleophile's basicity. This increase in basicity causes problems for S_N2 reaction mechanisms when the solvent of choice is protic. Protic solventsreact with strong nucleophiles with good basic character in an acid/base fashion, thus decreasing or removing the nucleophilic nature of the nucleophile. The following table shows the effect of solvent polarity on the relative reaction rates of the S_N2 reaction of n-butyl bromide with azide, N_3 . Note the gross increase in reaction rates when changing from a protic solvent to an aprotic solvent. This difference arises from acid/base reactions between protic solvents (not aprotic solvents) and strong nucleophiles. It is important to note that solvent effects as well as steric effects both affect the relative reaction rates; however, for demonstration of principle for solvent polarity on S_N2 reaction rates, steric effects may be neglected.

Solvent	Dielectric Constant, ɛ	Relative Rate	Туре
CH ₃ OH	33	1	Protic
H ₂ O	78	7	Protic
DMSO	49	1,300	Aprotic
DMF	37	2800	Aprotic
CH ₃ CN	38	5000	Aprotic

A comparison of S_N1 to S_N2 reactions is to the right. On the left is an S_N1 reaction coordinate diagram. Note the decrease in $\Delta G^{=/=}_{activation}$ for the polar-solvent reaction conditions. This arises from the fact that polar solvents stabilize the formation of the carbocation intermediate to a greater extent than the nonpolar-solvent conditions. This is apparent in the ΔE_a , $\Delta \Delta G^{=/=}_{activation}$. On the right is an S_N2 reaction coordinate diagram. Note the decreased $\Delta G^{=/=}_{activation}$ for the non-polar-solvent reaction conditions. Polar solvents stabilize the reactants to a greater extent than the non-polar-solvent conditions by solvating the negative charge on the nucleophile, making it less available to react with the electrophile.



Transition-metal-catalyzed reactions

The reactions involving charged transition metal complexes (cationic or anionic) are dramatically influenced by solvation, especially in the polar media. As high as 30-50 kcal/mol changes in the potential energy surface (activation energies and relative stability) were calculated if the charge of the metal species was changed during the chemical transformation.

Free radical syntheses

Many free radical-based syntheses show large kinetic solvent effects that can reduce the rate of reaction and cause a planned reaction to follow an unwanted pathway.

Protic solvent

In chemistry, a **protic solvent** is a solvent that has a hydrogen atom bound to an oxygen (as in a hydroxyl group) or a nitrogen (as in an amine group). In general terms, any solvent that contains labile H^+ is called a protic solvent. The molecules of such solvents readily donate protons (H^+) to reagents. Conversely, **aprotic solvents** cannot donate hydrogen.

Polar protic solvents

Polar protic solvents are often used to dissolve salts. In general, these solvents have high dielectric constants and high polarity.

Common characteristics of protic solvents :

- solvents display hydrogen bonding
- solvents have an acidic hydrogen (although they may be very weak acids such as ethanol)

- solvents dissolve salts
 - cations by unshared free electron pairs
 - anions by hydrogen bonding

Examples include water, most alcohols, formic acid, hydrogen fluoride, and ammonia. Polar protic solvents are favorable for S_N1 reactions, while polar aprotic solvents are favorable for S_N2 reactions.

Polar aprotic solvents

Polar *aprotic* **solvents** are solvents that lack an acidic hydrogen. Consequently, they are not hydrogen bond donors. These solvents generally have intermediate dielectric constants and polarity. Although discouraging use of the term "polar aprotic", IUPAC describes such solvents as having both high dielectric constants and high dipole moments, an example being acetonitrile. Other solvents meeting IUPAC's criteria include DMF, HMPA, and DMSO.^[1]

Common characteristics of aprotic solvents:

- solvents that can accept hydrogen bonds
- solvents do not have acidic hydrogen
- solvents dissolve salts

The criteria are relative and very qualitative. A range of acidities are recognized for aprotic solvents. Their ability to dissolve salts depends strongly on the nature of the salt.

Polar aprotic solvents are generally incompatible with strong bases, such as Grignard reagents or *n*-butyllithium. These reagents require ethers, not nitriles, amides, sulfoxides, etc.

Properties of common solvents

The solvents are qualitatively grouped into non-polar, polar aprotic, and polar protic solvents, often ranked by dielectric constant.

Solvent	<u>Chemical formula</u>	Boiling	<u>Dielectric</u>	Density	<u>Dipole</u>
		<u>point</u>	<u>constant</u>		<u>moment</u> (<u>D</u>)
<u>Non-polar</u> solvents					
Hexane	CH ₃ -CH ₂ -CH ₂ -CH ₂ -	69 °C	2.0	0.655	0.00 D
	CH ₂ -CH ₃			g/mL	
<u>benzene</u>	C ₆ H ₆	80 °C	2.3	0.879	0.00 D
				g/ml	
toluene	C ₆ H ₅ CH ₃	111 °C	2.4	0.867	0.36 D
				g/mL	
<u>1,4-dioxane</u>	$(CH_2CH_2O)_2$	101 °C	2.3	1.033	0.45 D
				g/mL	

<u>chloroform</u>	CHCl ₃	61 °C	4.8	1.498	1.04 D
				g/mL	
diethyl ether	(CH ₃ CH ₂) ₂ O	35 °C	4.3	0.713	1.15 D
				g/mL	
dichloromethane (DCM)	CH ₂ Cl ₂	40 °C	9.1	1.3266	1.60 D
				g/mL	
Polar aprotic solvents		1		l	•
N-methylpyrrolidone	CH ₃ NC(O)C ₃ H ₆	202 °C	32.2	1.028	4.1 D
				g/mL	
tetrahydrofuran (THF)	C ₄ H ₈ O	66 °C	7.5	0.886	1.75 D
				g/mL	
ethyl acetate (EtOAc)	CH ₃ CO ₂ CH ₂ CH ₃	77 °C	6.0	0.894	1.78 D
				g/mL	
acetone	CH ₃ C(O)CH ₃	56 °C	21	0.786	2.88 D
				g/mL	
dimethylformamide (DMF)	$HC(O)N(CH_3)_2$	153 °C	38	0.944	3.82 D
				g/mL	
acetonitrile (MeCN)	CH ₃ CN	82 °C	37	0.786	3.92 D
				g/mL	
<u>dimethyl</u>	CH ₃ S(O)CH ₃	189 °C	47	1.092	3.96 D
sulfoxide (DMSO)				g/mL	
propylene carbonate (PC)	C ₄ H ₆ O ₃	242 °C	64	1.205	4.90 D
				g/mL	
Polar protic solvents			1		
formic acid	HCO ₂ H	101 °C	58	1.21	1.41 D
				g/mL	
<u><i>n</i>-butanol</u>	CH ₃ CH ₂ CH ₂ CH ₂ OH	118 °C	18	0.810	1.63 D
				g/mL	
isopropanol (IPA)	(CH ₃) ₂ CH(OH)	82 °C	18	0.785	1.66 D
				g/mL	
nitromethane	CH ₃ NO ₂	100-	35.87	1.1371	3.56 D
		103 °C		g/mL	

ethanol (EtOH)	CH ₃ CH ₂ OH	79 °C	24.55	0.789	1.69 D
				g/mL	
methanol (MeOH)	CH ₃ OH	65 °C	33	0.791	1.70 D
				g/mL	
Acetic acid (AcOH)	CH ₃ -CO ₂ H	118 °C	6.2	1.049	1.74 D
				g/mL	
Water	H ₂ O	100 °C	80	1.000	1.85 D
				g/mL	

REACTIONS AND APPLICATIONS

SOLVOLYSIS: synthesis of amides

OPCl3 + 6NH3 → OP(NH2)3 + 3NH4Cl

 $SiCl_4 + 8NH_3 \longrightarrow Si(NH_2)_4 + 4NH_4Cl$

Metatheses reactions: solubility reversals

In water,

 $RCl + AgNO_3 \longrightarrow AgCl(ppt) + RNO_3$

In ammonia

 $AgCl + KNO_3 \longrightarrow RCl(ppt) + AgNO_3$

Ba(NO3)2 + 2AgCl → BaCl_{2(ppt)} + 2AgNO3

Alkali metals in liquid ammonia

Sodamide as a base

 $Na + NH_3 \longrightarrow NaNH_2 + H_2(g)$

NaNH2 + C5H6 → NaC5H5 + NH3

NaCp (useful reagent)

Solvated electron as a reducing agent (Birch reduction), many examples of compounds in very unusual low oxidation states.

 $[Ni(CN)_4]_2 + Na/liq-NH_3 \longrightarrow [Ni(CN)_4]_4$

 $Fe(CO)_5 + Na/liq-NH_3 \longrightarrow [Fe(CO)_4]_2$ -

 $Mo(CO)_6 + Na/liq-NH_3 \longrightarrow [Mo(CO)_4]_4-$

 $[Pt(NH_3)_4]_{2+} + Na/liq-NH_3 \longrightarrow [Pt(NH_3)_4]$

Reduction of salts of Group IV and V elements give polyhedral anions, many examples.

Ge94-, Sn52-, Sn93-, Pb52-, Bi42-, P72-As64-

Liquid-SO₂

Liq.SO₂ is a non-Protonic solvent ,bcoz it does not contain any hydrogen atom.

Liq. Range (-75.5 to -10.2°C) viscosity 0.428cp at -10°C dipole moment 1.61 specific conductance 4×10⁻⁸

Its dielectric constant is small (15.6 at 0°C). Therefore its a good solvent for Covalent compounds.

Structure of SO₂



AutoIonisation of SO₂

 $2SO_2 \rightleftharpoons SO^{2+}$ (thionyl ion) + SO_3^{2-} (Sulphite ion)

Reaction Of Liq.SO₂

•Acid Base Reaction:

Compound which gives SO^{2+} is acidic and substances which gives SO_3^{2-} act as base.

Example , Acidic :- SOCl₂(thionyl Chloride) \Rightarrow SO²⁺ + 2Cl⁻

Basic :- $CsSO_3 \rightleftharpoons 2Cs + SO_3^{2-}$

Neutralisation Reaction

 $SOCl_2$ (Acid) + Cs_2SO_3 (base) $\rightarrow 2CsCl + 2SO_2$

Solvolytic Reactions

Solvolytic rxns in liqSO₂ are not as common as they are in other Protonic solvents such as NH₃,H₂O.

 $PCl_5 + SO_2(liq) \rightarrow POCl_3 + SOCl_3$

 $2CH_{3}COONH_{4} + 2SO_{2} \rightarrow (NH_{4})_{2}SO_{3} + (CH_{3}COO)_{2}SO$

 $(CH_3COO)_2SO \rightleftharpoons SO_2 + (CH_3CO_2)O$

Precipitation Reaction

A large number of precipitation reactions can be carried out in liquid Sulphur dioxide due to Selective Solubilities of Compounds.

Example:- SbCl₃ + 3LiI \rightarrow SbI₃ + 3LiCl

 $AlCl_3 + 3NaI \rightarrow 2NaCl\downarrow + AlI_3$ $2KI + SOCl_2 \rightarrow 2KCl\downarrow + SOI_2$

Complex Formation Reactions

 $2\text{AlCl}_3 + 3\text{SO}_3^{2-} \leftrightarrows \text{Al}_2(\text{SO}_3)_3 \downarrow + 6\text{Cl}_-$

 $Al_2(SO_3)_3 + 3SO_3^{2-} \rightleftharpoons 2[Al(SO_3)_3]^{3-}$, (soluble complex ion)

Similarly , SbCl₃ + 3KCl + liq SO₂ \rightarrow K₃[SbCl₆]

 $SbCl_5 + NOCl + liq.SO_2 \rightarrow NO[SbCl_6]$

Organic Reactions :

a large no. Of organic compounds are soluble in liq.SO₂ ,bcoz it is relatively inert solvent.



SO2 of Crystallisation (Salvation Reaction)

These are formed with the highly soluble salts and are analogous to hydrates.

Examples: NaI.4SO₂, LiI.2SO₂, AlCl₃.SO₂, BaI₂.4SO₂.

Redox Reaction :

liq. SO_2 does not show any marked reducing or oxidising tendency. it simply act as a medium for certain redox reaction.

Example , $6KI + 3SbCl_6 + liqSO_2 \rightarrow 2K_3[SbCl_6] + SbCl_6 + 3I_2$

Some Special Feature Of Liq.SO2 As A Solvent

•It has low boiling point and this allows its easy evaporation. ie ,removal from the reaction mixture.

•Liquid SO₂ is an inert Solvent.

•It has unusual solvating powers for both covalent and electrovalent compounds.

•It is used as dilutent for the superAcid medium (CHSO₃F-SbF₅) which helps in reducing its viscosity without affecting its acidity.

Textbooks

- 1. T2. Sathya Prakash, 2008. Modern Inorganic Chemistry. S.Chand & Company Pvt. Ltd., New Delhi.
- T3. Wahid U.Malik, G.D.Tuli, R.D.Madan; 2010. Selected topics in inorganic chemistry, S.Chand & Company Pvt. Ltd., New Delhi.
- 3. T4. Soni, P.L., 2014. Text book of Inorganic Chemistry, S.Chand & Sons, New Delhi.

Reference

- R1. F.A.Cotton, G.Wilkinson, P.L.Gaus, 2013, 3rd Edition. Basic Inorganic Chemistry; Wiley & Sons INC., Print India Press, Sahibabad.
- 2. R2. Weller, Overtone, Rourke and Armstrong, "Inorganic Chemistry", 6th Edition, 2014.

POSSIBLE QUESTIONS

<u>PART A: MULTIPLE CHOICE QUESTIONS</u> (Each question carry one mark)

1.	. The factor which do not affect the solubility of a substance					
a.	Temperature b. Nature of the solute c. Pressure d. melting point of the solute					
2.	. Ionic substances are soluble in					
a.	Polar solvents b. nonpolar solvent c. organic solvents d. non aqueous solvents					
3.	. Covalent substances are soluble in					
a.	Polar solvents b. nonpolar solvent c. organic solvents d. non aqueous solvents					
4.	Benzene is an example for					
a.	Polar solvents b. nonpolar solvent c. organic solvents d. non aqueous solvents					
5.	Chloroform is an example for					
a.	Polar solvents b. nonpolar solvent c. polar organic solvents d. non aqueous					
sol	solvents					
6.	Sodium chloride is highly soluble in					
a.	Waterb. alcoholc. benzened. carbon di sulphide					
7.	Non polar covalent compounds are soluble in					
a.	Waterb. alcoholc. benzened. carbon di sulphide					
8.	When temperature increases the solubility of a solid substance					
a.	Decreases b. not affected c. Increases d. is infinity					
9.	9. The pressure on the surface of a solution on the solubilities of liquid					
a.	Decreases b. not affected c. Increases d. is infinity					
10.	The measure of the solvent's ability to reduce the field strength of the electric field					
sur	surrounding a charged particle immersed in it.					
a.	Dipole momentb. surface tensionc. dielectric constantd. viscosity					
11.	Solvents with a dielectric constant of less than 15 are generally considered to be					
a.	Polarb. nonpolarc. semipolard. organic solvent					
12. Solvents which have large dipole moment						
a.	Protic solvents b. aprotic solvents c. nonpolar solvents d. polar solvents					
13.	13. Example for a aprotic solvent					
a.	Acetone b. ammonia c. water d. carbon di sulphide					

14. In chemical reactions the use of polar aprotic solvents favors a. SN₁ reaction **b.** SN₂reaction c. SN_i reaction d. E₂ elimination 15. The solvents which favour SN1 reaction a. Polar aprotic **b. polar protic** c. nonpolar protic d. Nonpolar aprotic 16. Aprotic solvents solvate cations strongly via a. Negative dipole b. positive dipole c. hydrogen bonding d. covalent bond 17. Among the solvents select an aprotic solvent a. HF b. Liquid ammonia d. Nitrobenzene c. EtOH 18. Among the solvents select a protic solvent a. Dimethyl sulphoxide b. Liquid ammonia c. Dimethyl formamide d. Nitrobenzene 19. Salts with more polarisable anions are more soluble in liquid ammonia than water because

a. NH₃ is more polarisable than H₂O

- b. NH₃ is less polarisable than H₂O
- c. NH_3 is equally polarisable than H_2O
- d. Polarisability is not th deciding factor
- 20. The solubility of gases in water depends on

a. molecular weightb. polarity of the moleculesc. temperatured. size of the molecules.
PART B (Each question carries 8 marks)

- 1. Discuss in detail the classification of solvents.
- 2. Explain chemical reactions in non-aqueous solvents with special reference to the reactions occurring in liquid SO₂.?
- 3. Giving two examples in each, discuss the following reactions in liq.SO₂ (i) Acid- Base reaction (ii) Precipitation reaction (iii) Complex formation reaction
- 4. (i) Compare the self-ionisation of water and liquid ammonia.
- 5. (ii) Discuss in detail the classification of solvents.
- 6. Explain the classification of non-aqueous solvents and describe their important characteristics?
- 7. What are the advantages and disadvantages of liquid ammonia as a solvent?
- 8. Using chemical equations illustrate the following types of reactions in liquid ammonia(i) Complex formation and (ii) Precipitation.
- 9. 7. Classify the solvents on the basis of their proton-donor and proton-acceptor property.
- 10. Give the following reaction in liquid ammonia. (i)Redox reaction (ii)Precipitation reaction.
- 11. 8. Write notes on the following reactions in an non-aqueous solvent.
- 12. (i) Ammonolysis (ii) Acid-base reactions (iii) Redox reactions.
- 13. 9. What are the advantages of Non-aqueous solvents? Discuss the following reactions occurring in liq.SO₂ medium. (i) Acid-base reactions (ii) Precipitation reaction
- 14. (iii) Complex formation reactions.

[15CHU502] KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER

INORGANIC CHEMISTRY

UNIT 5- OBJECTIVE TYPE QUESTIONS FOR ONLINE EXAMINATION(Each carry 1 Mark)

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answer
Ionic substances are soluble in	Polar solvents	nonpolar solvent	organic solvents	non aqueous solvents	Polar solvents
Covalent substances are soluble in	Polar solvents	nonpolar solvent	organic solvents	non aqueous solvents	Polar solvents
Water is an example for	Polar solvent	nonpolar solvent	organic solvents	non aqueous solvents	Polar solvent
Benzene is an example for	Polar solvents	nonpolar solvent	organic solvents	non aqueous solvents	organic solvents
Chloroform is an example for	Polar solvents	nonpolar solvent	polar organic solvents	non aqueous solvents	polar organic solvents
Alcohol is a	Less Polar organic solvent	Non polar organic solvent	Non-aqueous solvent	non-polar solvent	Less Polar organic solvent
Sodium chloride is highly soluble in	Water	alcohol	benzene	carbon di sulphide	Water
Sucrose is highly soluble in	Water	alcohol	benzene	carbon di sulphide	Water
Napthalene is soluble in	Water	alcohol	benzene	carbon di sulphide	benzene
Non polar covalent compounds are soluble in	Water	alcohol	benzene	carbon di sulphide	benzene
Polar covalent compounds are soluble in	Water	alcohol	benzene	carbon di sulphide	Water
When temperature increases the solubility of a solid substance	Decreases	not affected	Increases	is infinity	Increases
When temperature increases the solubility of a gaseous substance	Decreases	not affected	Increases	is infinity	Decreases
The pressure on the surface of a solution on the solubilities of solids	Decreases	not affected	Increases	is infinity	not affected
The pressure on the surface of a solution on the solubilities of liquid	Decreases	not affected	Increases	is infinity	not affected
The pressure on the surface of a solution on the solubilities of gases	Decreases	not affected	Increases	is infinity	Increases
The measure of the solvent's ability to reduce the field strength of the electric field surrounding a charged particle immersed in it.	Dipole moment	surface tension	dielectric constant	viscosity	dielectric constant
Solvents with a dielectric constant of less than 15 are generally considered to be	Polar	nonpolar	semipolar	organic solvent	nonpolar

Example for a protic solvent	Acetone	dichloromethane	water	carbon di sulphide	water
Protic solvents solvate which ions strongly via	Anions	cations	dipolar ions	zwitter ions	Anions
hydrogen bonding.					
Protic solvents solvate anions strongly via which	hydrogen bonding	electrostatic force	Van der Walls forces	London forces	hydrogen bonding
type of forces					
Solvents which have large dipole moment	Protic solvents	aprotic solvents	nonpolar solvents	polar solvents	aprotic solvents
Example for a aprotic solvent	Acetone	ammonia	water	carbon di sulphide	Acetone
Example for a aprotic solvent	Dichloromethane	ammonia	water	carbon di sulphide	Dichloromethane
Aprotic solvents solvate which ions strongly	Anions	cations	dipolar ions	zwitter ions	cations
Aprotic solvents solvate cations strongly via	Negative dipole		positive dipole	hydrogen bonding	Negative dipole
In chemical reactions the use of polar protic solvents	SN ₁ reaction	SN ₂ reaction	SN _i reaction	E ₂ elimination	SN ₁ reaction
favors					
In chemical reactions the use of polar aprotic solvents	SN ₁ reaction	SN ₂ reaction	SN _i reaction	E_2 elimination	SN ₂ reaction
favors					
The solvents which favour SN ₁ reaction	Polar aprotic	polar protic	nonpolar protic	Nonpolar aprotic	polar protic
The solvents which favour SN ₂ reaction	Polar aprotic	polar protic	nonpolar protic	Nonpolar aprotic	Polar aprotic
The solvent that undergo self-ionization and provides	aprotic	protic	nonpolar	Nonaqueous	protic
protons which are solvate					
The solvents that undergoes self-ionization without	Aprotic	protic	nonpolar	Nonaqueous	Aprotic
the formation of protons.					
Aprotic solvents solvate which ions strongly	Anions	cations	dipolar ions	zwitter ions	cations
Aprotic solvents solvate cations strongly via	Negative dipole		positive dipole	hydrogen bonding	Negative dipole
In chemical reactions the use of polar protic solvents	SN ₁ reaction	SN ₂ reaction	SN _i reaction	E_2 elimination	SN ₁ reaction
favors					
In chemical reactions the use of polar aprotic solvents	SN ₁ reaction	SN ₂ reaction	SN _i reaction	E_2 elimination	SN ₂ reaction
favors					
The solvents which favour SN ₁ reaction	Polar aprotic	polar protic	nonpolar protic	Nonpolar aprotic	polar protic
The solvents which favour SN ₂ reaction	Polar aprotic	polar protic	nonpolar protic	Nonpolar aprotic	Polar aprotic
The solvent that undergo self-ionization and provides	aprotic	protic	nonpolar	Nonaqueous	protic
protons which are solvate	-	-	_	-	-
The solvents that undergoes self-ionization without	Aprotic	protic	nonpolar	Nonaqueous	Aprotic
the formation of protons.	-	-	_	-	-
Among the solvents select an aprotic solvent	HF	МеОН	EtOH	dimethyl formamide	dimethyl formamide
Among the solvents select an aprotic solvent	HF	МеОН	liquid ammonia	dimethyl sulphoxide	dimethyl sulphoxide
Among the solvents select an aprotic solvent	HF	Liquid ammonia	EtOH	Nitrobenzene	Nitrobenzene
Among the solvents select a protic solvent	Dimethyl sulphoxide	Liquid ammonia	Dimethyl formamide	Nitrobenzene	Liquid ammonia
Among the solvents select a protic solvent	Dimethyl sulphoxide	HF	Dimethyl formamide	Nitrobenzene	HF
Among the solvents select a protic solvent	Dimethyl sulphoxide	Ethanol	Dimethyl formamide	Nitrobenzene	Ethanol
Which solvent undergo self-ionization and provides	Dimethyl sulphoxide	Liquid ammonia	Dimethyl formamide	Nitrobenzene	Liquid ammonia
protons			-		

Which solvent undergo self-ionization and provides	Dimethyl sulphoxide	HF	Dimethyl formamide	Nitrobenzene	HF
protons					
Which solvent undergo self-ionization and provides	Dimethyl sulphoxide	Ethanol	Dimethyl formamide	Nitrobenzene	Ethanol
protons					
Which solvents that undergoes self-ionization without	HF	Liquid ammonia	EtOH	Nitrobenzene	Nitrobenzene
the formation of protons					
Which solvents that undergoes self-ionization without	HF	MeOH	liquid ammonia	dimethyl sulphoxide	dimethyl sulphoxide
the formation of protons					
Which solvents that undergoes self-ionization without	HF	MeOH	liquid ammonia	dimethyl formamide	dimethyl formamide
the formation of protons					
These solvents are used in chemical research and	Aprotic	protic	nonpolar	Nonaqueous	Nonaqueous
industry for reactions that cannot occur in aqueous					
solutions or require a special environment.					
A solvent other than water, that is not an organic	Aprotic	protic	nonpolar	Nonaqueous	Nonaqueous
compound					
Example for a non aqueous solvent	HF	dimethyl formamide	aqueous ammonia	dimethyl sulphoxide	aqueous ammonia
Which among the following solvents is a non aqueous	HF	MeOH	EtOH	dinitrogen tetroxide	dinitrogen tetroxide
solvent					
Which is a non aqueous solvent	Dinitrogen tetroxide	aqueous ammonia	liquid sulfurdioxide	ethanol	ethanol
Salts with more polarisable anions are more soluble in	NH ₃ is more	NH ₃ is less polarisable	NH ₃ is equally	Polarisability is not	NH ₃ is more polarisable
liquid ammonia than water because	polarisable than H ₂ O	than H ₂ O	polarisable than H ₂ O	th deciding factor	than H ₂ O
NH_3 is more polarisable than H_2O , hence	Salts with more	Salts with more	Salts with less	Salts with less	Salts with more
	polarisable anions are	polarisable anions are	polarisable anions	polarisable cations	polarisable anions are
	more soluble	less soluble	are more soluble	are less soluble	more soluble
Carbonates are insoluble.in liquid ammonia because	highly charged, non-	less charged, non-	highly charged,	highly charged, non-	highly charged, non-
they have	polarisable anions	polarisable anions	polarisable anions	polarisable cations	polarisable anions
sulphates are insoluble.in liquid ammonia because	highly charged, non-	less charged, non-	highly charged,	highly charged, non-	highly charged, non-
they have	polarisable anions	polarisable anions	polarisable anions	polarisable cations	polarisable anions
Phosphates are insoluble.in liquid ammonia because	highly charged, non-	less charged, non-	highly charged,	highly charged, non-	highly charged, non-
they have	polarisable anions	polarisable anions	polarisable anions	polarisable cations	polarisable anions
Liquid ammonia tolerate very strong bases such as	Self-ionization of	Self-ionization of	Self-ionization of	Self ionization of	Self-ionization of
$C_5H_5^-$ which would otherwise be hydrolysed in water	ammonia is much	ammonia is equivalent to	ammonia is larger	ammonia is equal to	ammonia is much
because	"weaker" and	water	than water	the D ₂ O	"weaker" and "stronger"
	"stronger" than water				than water
The solubility of gases in water depends on	molecular weight	polarity of the molecules	temperature	size of the molecules	polarity of the molecules
Ammonia is highly soluble in water because it is	Non polar molecule	polar molecule	having a lone pair of	basic	polar molecule
			electrons		

[15CHU502]

KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER INORGANIC CHEMISTRY

INTERNAL EXAM I - ANSWER KEY

Part – A

1. c. gaseous state

2. d. either disordered or ordered

- 3. b. Interstitial solid solution
- 4. c. MO model
- 5. a. Phase
- 6. a. Bands overlap
- 7. a. Decreases
- 8. a. P-type
- 9. b. Electrons
- 10. a. Silicon
- 11. d. Schottky defect
- 12. b. Non-stoichiometric
- 13. d. Energy conversion
- 14. b. Instrinsic
- 15. b. Neutrons and protons
- 16. a. Alpha particles
- 17. a. natural radio activity
- 18. d. both protons and neutrons

19. a. short life periods

20. a. high atomic numbers

Part - B

21. (a) Explain the VB theory with examples

<u>Valence Bond Theory</u> suggests that overlap between two valence orbitals with an unpaired electron forms a covalent bond between two atoms.

Valence bond and molecular orbital theories are used to explain chemical bonding in chemistry. Two dissociated atoms that have unpaired electron in their orbitals can combine to give individual chemical bonds, forming a molecule.

When two atomic orbitals overlap head-to-head, a sigma bond is formed. Pi bonds occur when orbitals overlap parallel to each other. Single bonds have one sigma bond, double bonds consist of one sigma bond and one pi bond, and triple bonds contain one sigma bond and two pi bonds. Often, the bonding atomic orbitals have a character of several possible types of orbitals, which are called hybrid orbitals. Hybridization is the method to get an atomic orbital with the proper character for the bonding.

(b) Write a note on semiconductors and its types

A **semiconductor** is a pure crystaline material which has electrical conductivity between that of a conductor such as copper and that of an insulator such as glass. Semiconductors are the foundation for modern electronics, including transistors, solar cells, light emitting diodes (LEDs), quantum dots and digital and analog integrated circuits. The modern understanding of the properties of a semiconductor relies on quantum physics to explain the movement of electrons and holes inside a lattice. An increased knowledge of semiconductor materials and sophisticated fabrication processes has made increase in the complexity and speed of integrated semiconductor devices possible, an effect known as Moore's Law.

The electrical conductivity of a semiconductor material increases with increasing temperature, behaviour which is opposite to that of a metal conductor. Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by controlled addition of impurities (and by the application of electrical fields or light), 'devices' made from

semiconductors can be used for amplification of electrical signals, logic switching in computers, and energy control and conversion.

Current conduction in a semiconductor occurs through the movement of free electrons and "holes", collectively known as charge carriers. Adding impurity atoms to a semiconducting material, known as "doping", greatly increases the number of charge carriers within it. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type". The semiconductor materials used in electronic devices are doped under precise conditions to control the location and concentration of p- and ntype dopants. A single semiconductor crystal can have many p- and n-type regions; the p–n junctions between these regions are responsible for the useful electronic behavior. Although some pure elements and many compounds display semiconductor properties, silicon, germanium, and compounds of gallium are the most widely used in electronic devices.

22. (b) Explain the crystal defects in detail

Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by **crystallographic point defects.**

There are different types of imperfections or **defects** in the ideal arrangement of atoms in a crystal. We will see that the presence of a relatively small number of **defects have a profound impact on the macroscopic properties of materials**, and the control (and intentional introduction) of defects is important in many kinds of material processing.

•Point defects - atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).

•Linear defects - groups of atoms in irregular positions (e.g. screw and edge dislocations).

•**Planar defects** – the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).

Types of Point Defects

Interstitials – atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called **self-interstitial**. Creation of a self-interstitialcauses a substantial distortions in the surrounding lattice and costs more energy as

compared to the energy for creation of a vacancy (Ei > EV) and, under equilibrium conditions, self- interstitials are present in lower concentrations than vacancies.

Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called **interstitial impurities.** They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom replaces or substitutes for a matrix atom, it is called a **substitutional impurity**.

All point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects that we will consider next can give a directionality to an otherwise random jumps of atoms. In particular, a pressure gradient result in a flux of vacancies in the direction towards a compressed region of the sample.

In ionic crystals (e.g. table salt – Na+Cl-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Coulombic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created.

A **Frenkel defect** is a pair of cation (positive ion) vacancy and a cation interstitial. Or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form.

A **Schottky defect** is a pair of anion and cation vacancies. In both Frenkel and Schottky defects, the pair of point defects stay near each other because of strong coulombic attraction of their opposite charges.

22. (b) (i) Give an account on Hume-Rothery ratio

The **Hume-Rothery rules**, named after William Hume-Rothery, are a set of basic rules describing the conditions under which an element could dissolve in a metal, forming a solid solution. There are two sets of rules, one which refers to substitutional solid solutions, and another which refers to interstitial solid solutions.

For substitutional solid solutions, the Hume-Rothery rules are:

1. The atomic diameter of the solute and solvent atoms must differ by no more than 15%:

2. The crystal structures of solute and solvent must match.

3. Complete solubility occurs when the solvent and solute have the same valency. A metal will dissolve into a metal of higher valency to a greater extent than one of lower valency.

4. The solute and solvent should have similar electronegativity. If the electronegativity difference is too great, the metals will tend to form intermetallic compounds instead of solid solutions.For interstitial solid solutions, the Hume-Rothery rules are:

1. Solute atoms must be smaller than the interstitial sites in the solvent lattice.

2. The solute and solvent should have similar electro-negativity.

22. (b) (ii) What is meant by free electron theory?

In this model, the valence electrons are free to move through the bulk metal structure (hence the term *electron sea*) and even leave the metal, thereby producing positive ions. It is valence electrons, then, that convey electric current, and it is the motion of the valence electrons that transfers heat through a metal. However, this model is more qualitative than quantitative. Metals are good conductors of electricity because the electrons in the electron sea are free to flow and carry electric current.

Metals are ductile and malleable because local bonds can be easily broken and reformed.

Metals are shiny because light cannot penetrate their surface; the photons simply reflect off the electrons. However, there is an upper limit to the frequency at which the photons are reflected, although this frequency is generally too high to be visually perceived.

Metallic bonds can occur between different elements, forming an alloy. Aluminum foil and copper wire are examples of metallic bonding in action

Metallic bonds are mediated by strong attractive forces. This property contributes to the low volatility, high melting and boiling points, and high density of most metals. The group-XIImetals zinc, cadmium, and mercury are exceptions to this rule.

23. (a) How to detect the radio activity. Explain with suitable methods.

The **Geiger–Müller counter**, also called a **Geiger counter**, is an instrument used for measuringionizing radiation.

It detects radiation such as alpha particles, beta particles and gamma rays using the ionization produced in a Geiger–Müller tube, which gives its name to the instrument. In wide and prominent use as a hand-held radiation survey instrument, it is perhaps one of the world's best-known radiation instruments.

The Geiger counter consists of two main elements; the Geiger-Müller tube which detects the radiation, and the processing and display electronics. The Geiger-Müller tube is filled with an

inert gas such as helium, neon, or argon at low pressure, which briefly conducts electrical charge when a particle or photon of incident radiation makes the gas conductive by ionization. The ionization current is greatly amplified within the tube by the Townsend avalanche effect to produce an easily measured detection pulse. This makes the G-M counter relatively cheap to manufacture, as the subsequent electronic processing is greatly simplified.

There are fundamentally two types of radiation readout; counts or radiation dose. The counts display is the simplest and is the number of ionizing events displayed either as a count rate, commonly "counts per second", or as a total over a set time period (an integrated total). The counts readout is normally used when alpha or beta particles are being detected. There is usually an option to produce audible clicks representing the number of ionization events detected. This is the distinctive sound normally associated with hand held or portable Geiger counters. The purpose of this is to allow the user to concentrate on manipulation of the instrument whilst retaining auditory feedback on the radiation rate.

23. (b) Explain nuclear fission and fusion in detail

Nuclear fission:

When a nucleus fissions, splits into several smaller fragments. These fragments, or fission products, are about equal to half the original mass. Two or three neutrons are also emitted.

The sum of the masses of these fragments is less than the original mass. This 'missing' mass (about 0.1 percent of the original mass) has been converted into energy according to Einstein's equation. Fission can occur when a nucleus of a heavy atom captures a neutron, or it can happen spontaneously.



In nuclear physics and nuclear chemistry, **nuclear fission** is either a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller parts (lighter nuclei). The fission process often produces free neutrons and photons (in the form of gamma rays), and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission is a form of nuclear transmutation because the resulting fragments are not the same element as the original atom. The two nuclei produced are most often of comparable but slightly different sizes, typically with a mass ratio of products of about 3 to 2, for common fissile isotopes.

Nuclear fission and nuclear fusion both are nuclear phenomena that release large amounts of energy, but they are different processes which yield different products. Learn what nuclear fission and nuclear fusion are and how you can tell them apart.

This is an exothermic process releasing kinetic energy of the fission products and energy in the form of gamma radiation. Fission may be considered a form of element transmutation since changing the number of protons of an element essentially changes the element from one into another. An example for nuclear fission

$$_{92}U^{235} + _{1}n^0 \rightarrow _{90} Sr ^{38} + _{54}Xe^{143} + 3_1n^0$$

Nuclear fusion

It is a process in which atomic nuclei are fused together to form heavier nuclei. Extremely high temperatures (on the order of 1.5×10^{7} °C) can force nuclei together. Large amounts of energy are released when fusion occurs.



Nuclear Fusion Examples

The reactions which take place in the sun provide an example of nuclear fusion:

$11H + 21H \rightarrow 32He$
$_{32}\text{He} + _{32}\text{He} \rightarrow _{42}\text{He} + 2_{11}\text{H}$
$11\mathrm{H} + 11\mathrm{H} \longrightarrow 21\mathrm{H} + 0 + 1\beta$

In nuclear physics, **nuclear fusion** is a nuclear reaction in which two or more atomic nucleicollide at a very high speed and join to form a new type of atomic nucleus. During this process, matter is not conserved because some of the matter of the fusing nuclei is converted to photons(energy). Fusion is the process that powers active or "main sequence" stars.

Fusion reactions of light elements power the stars and produce virtually all elements in a process called nucleosynthesis. The fusion of lighter elements in stars releases energy (and the mass that always accompanies it). For example, in the fusion of two hydrogen nuclei to form helium, 0.7% of the mass is carried away from the system in the form of kinetic energy or other forms of energy (such as electromagnetic radiation).

Energy released in most nuclear reactions is much larger than in chemical reactions, because thebinding energy that holds a nucleus together is far greater than the energy that holds electrons to a nucleus. For example, the ionization energy gained by adding an electron to a hydrogen nucleus is 13.6 eV—less than one-millionth of the 17.6 MeV released in thedeuterium–tritium (D–T) reaction shown in the diagram to the right (one gram of matter would release 339 GJ of energy).

Fusion reactions have an energy density many times greater than nuclear fission; the reactions produce far greater energy per unit of mass even though *individual* fission reactions are generally much more energetic than *individual* fusion ones, which are themselves millions of times more energetic than chemical reactions. Only direct conversion of mass into energy, such as that caused by the annihilatory collision of matter andantimatter, is more energetic per unit of mass than nuclear fusion.

Reg No. ---

[15CHU502]

KARPAGAM UNIVERSITY (KARPAGAM ACADEMY OF HIGHER EDUCATION) COIMBATORE-641021 DEPARTMENT OF CHEMISTRY

Med Internal Test

INORGANIC CHEMISTRY

Time: 2 Hours

Maximum 50 marks

20X1-20

Date 8.8.2017 AN

Section-A

- 1 The isotopes with neutron-proton ratio under one. a Hichum-3 b Helaum-4 c chlorine -35 d calcium -20 2. The element with highest N/P ratio
- a lead-208 b calcium-40 c potassium-39 d iron-58 3 The elements having same atomic number but different mass number
- isotopes b isotones c. isobars d. isomers .
- 4 The difference in their mass number of isotopes is due to the difference in their number
- of Neutrons b protons c electrons d nucleons .
- 5 For elements with atomic number below 20, the N/P ratio is
- a. One b zero c two d 1.5 6. Atomic nuclei consisting of 2, 8, 20, 28, 50, 82, and 126 number of nucleons have a
- a high stability b lower average binding energy per nucleon c low stability d spontaneous radioactivity
- 7 Which substance is used to capture neutrons and control the number of neutrons in a nuclear reactor
- a iron rods b. copper rods c. cadmium rods d. heavy water 8. Which substance is used to capture neutrons and control the number of neutrons in a
- a iron rods b copper rods c. cadmium rods d heavy water nuclear reactor
- 9 The reaction taking place in the nuclear reactors is a Nuclear fission b Nuclear fusion c chemical reaction d artificial radioactivity 10. The reactions of light elements power the stars and produce virtually all elements in a

and the second se

- a Nuclear fission b Nuclear fusion c chemical reaction d artificial radioactivity 11. The radioactive decay of e C 14 to 2 N 14 occurs by the process of
- a bota particle emission b alpha particle emission c electron capture d neutron capture

12 Which of the following elements is utilized as a shield from sources of radiation? a Pb b Ca c Zn d As 13 Which of the following types of elements in the periodic table are always radioactive? a Noble gases b. Alkali metals c. Halogens d. Actinides 14 Each a- particle has the mass a Equal to that of hydrogen b Nearly four times that of hydrogen atom c. Half of the hydrogen atom d Nearly five times that of hydrogen atom 15 The temperature level inside a nuclear reactors is maintained using a Shielding b Coolants c Moderators d control rods 16 Which radioactive emission have a charge of -17 a Neutrons b protons c gamma rays d beta particles 17 As the temperature of a sample of a radioactive element decreases, the half-life will a Decrease b Increase c remains the same d double 18 8 - rays having a a neutral b positive charge c negative charge d partially positive 19 The nuclear reaction which of the following forms an intermediate element a Capture reaction b Fission reaction c Fusion d Spallation reaction 20. Co22 + 1H2 - 27Co61 + 1H1 is belongs to a (T,p) reaction b (p,n) reaction c (T,n) reaction d (T,α) reaction Section - B

 $3 \times 10 = 30$

· 21 (a) Explain the methods involved in detection of isotopes? -(Or) (b) What is nuclear stability and explain the factors influences the nuclear stability?

22 (a) Explain uses of radio isotopes in carbon dating method? (Or) (b) Solve the following equations (i) (n,a) reaction •B¹⁰ + --- + --- + --- + ---(ii) (a,p) reaction Na"+ ----(in) (D, T) reaction 17Ag109 + ---- -(IV) (p,y) reaction (v) (T,n) reaction 23. (a) Write a note on mechanism involved in nuclear reactor? (Or)

(b) Explain the properties and uses of radioactivity?

[15CHU502]

KARPAGAM ACADEMY OF HIGHER EDUCATION COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER INORGANIC CHEMISTRY

INTERNAL EXAM II - ANSWER KEY

Part – A

1. a.Helium-3

- 2. a. Lead-208
- 3. a. Isotopes
- 4. a. Neutrons
- 5. a. One
- 6. a. High stability
- 7. c. Cadmium rods
- 8. c. Cadmium rods
- 9. a. nuclear fission
- 10. b. nuclear fusion
- 11. d. neutron capture
- 12. a. Pb
- 13. d. Actinides
- 14. b. nearly 4 times that of hydrogen atom
- 15. b. Coolants
- 16. d. β- Particles
- 17. c. remains the same
- 18. c. negative charge

19. d. Spallation reaction

20. c. (T,n) reaction

Part – B

21. (a) Explain the methods involved in detection of isotopes?

The **Geiger–Müller counter**, also called a **Geiger counter**, is an instrument used for measuringionizing radiation.

It detects radiation such as alpha particles, beta particles and gamma rays using the ionization produced in a Geiger–Müller tube, which gives its name to the instrument. In wide and prominent use as a hand-held radiation survey instrument, it is perhaps one of the world's best-known radiation instruments.

The Geiger counter consists of two main elements; the Geiger-Müller tube which detects the radiation, and the processing and display electronics. The Geiger-Müller tube is filled with an inert gas such as helium, neon, or argon at low pressure, which briefly conducts electrical charge when a particle or photon of incident radiation makes the gas conductive by ionization. The ionization current is greatly amplified within the tube by the Townsend avalanche effect to produce an easily measured detection pulse. This makes the G-M counter relatively cheap to manufacture, as the subsequent electronic processing is greatly simplified.

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21. (b) What is nuclear stability and explain the factors influences the nuclear stability

What makes a nucleus stable?

It depends on a variety of factors and no single rule allows us to predict whether a nucleus is radioactive and might decay unless we observe it. There are some observations that have been made to help us make predictions.

Neutron to proton ratio

Strong nuclear force exists between nucleons. The more protons packed together the more neutrons are needed to bind the nucleus together. Atomic nucleus with an atomic number up to twenty has almost equal number of protons and neutrons. Nuclei with higher atomic numbers have more neutrons to protons.

The number of neutrons needed to create a stable nucleus increase more than the number of protons.

MAGIC NUMBERS

In nuclear physics, a **magic number** is a number of nucleons such that they are arranged into complete shells within the atomic nucleus. The seven most widely recognized magic numbers as of 2007 are **2**, **8**, **20**, **28**, **50**, **82**, **and 126**. Atomic nuclei consisting of such a magic number of nucleons have a higher average binding energy per nucleon than one would expect based upon predictions such as the semi-empirical mass formula and are hence more stable against nuclear decay.

The unusual stability of isotopes having magic numbers means that transuranium elements can be created with extremely large nuclei and yet not be subject to the extremely rapid radioactive decay normally associated with high atomic numbers (as of 2007, the longest- lived known isotope among all of the elements between 110 and 118 lasts only 8.9 min and the next 3.7 min). Large isotopes with magic numbers of nucleons are said to exist in an island of stability. Unlike the magic numbers 2–126, which are realized in spherical nuclei, theoretical calculations predict that nuclei in the island of stability are deformed. Before this was realized, higher magic numbers, such as 184 and 258, were predicted based on simple calculations that assumed spherical shapes. It is now believed that the sequence of spherical magic numbers cannot be extended in this way.

N/P ratio

The neutron-proton ratio (N/Z ratio or nuclear ratio) of an atomic nucleus is the ratio of its number of neutrons to its number protons. The ratio generally increases with increasing atomic numbers due to increasing nuclear charge due to repulsive forces of protons. Light elements, up to calcium (Z = 20), have stable isotopes with N/Z ratio of one except for beryllium (N/Z ratio = 1.25), and every element with odd proton numbers from fluorine to potassium. Hydrogen-1 (N/Z ratio = 0) and helium-3 (N/Z ratio = 0.5) are the only stable isotopes with neutron-proton ratio under one. Uranium-238and plutonium-244 have the highest N/Z ratios of any primordial nuclide at 1.587 and 1.596, respectively, while <u>lead-208</u> has the highest N/Z ratio of any known stable isotope at 1.537.

$$=\frac{(75.4\times34.98)+(24.6\times36.98)U}{100}$$

All nuclei with 84 or more protons are radioactive

1. Nuclei above the belt of stability. These neutron rich isotopes can lower their ratio and move to the belt of stability by emitting a beta particle. This increases number of protons and decreases neutrons

2. Nuclei below the belt of stability These proton rich nuclei increase their neutrons and decrease protons by positron emission (more common in lighter nuclei) and electron capture (more common in heavier nuclei)

3. Nuclei with atomic numbers greater than 84. These tend to undergo alpha emission. This emission decreases the number of neutrons and protons by 2 moving the nucleus diagonally toward the belt of stability

22. (a) Explain the uses of radio isotopes in carbon dating method?

The half-life of cobalt-60 is 5.3 years. How much of a 1.000 mg sample will remain after 15.9

years?

Dating

Because the half-life of any nuclide is constant, the amount of substance remaining in an artifact can serve as a nuclear clock to determine ages of objects. When an animal is alive it maintains a caron-14 to carbon-12 ratio identical to that in the atmosphere. When it dies, this ratio decreases. By measuring this ratio and contrast it to the atmosphere, we can get an approximate age. Radioactive decay is a first order process. Remember, half-life of a first order process is T1/2 = 0.693/k where k is the decay constant. We can determine the k constant by using the rate equation of a first order reaction

Example: If we start with 1.000 grams of Sr-90, 0.953 grams will remain after 2.0 years. (a) what is the half-life of strontium-90? (b) How much strontium-90 will remain after 5.00 years? (28.8 yr, 0.887g)

Energy Changes in Nuclear Reactions

$E = mc^2$

A very familiar equation that shows mass and energy change are proportional. If a system loses mass, it loses energy (exothermic) and if it gains mass, it gains energy (endothermic). The

The nuclei in this reaction have the following masses:

 $^{238}_{92}$ U = 238.0003 amu, $^{234}_{90}$ Th = 233.9942 amu and $^{4}_{2}$ He = 4.0015 amu

The)m is products minus reactants is 233.9942 + 4.0015 - 238.0003 = -0.0046g

Change in energy would be

E = $(-0.0046 \text{ g})(1\text{kg}/1000\text{g})(3.00 \times 10^8 \text{ m/s})^2$ = $-4.1 \times 10^{11}\text{kg} \cdot \text{m}^2/\text{s}^2$ = $-4.1 \times 10^{11} \text{ J}$

C2 shows a small mass loss can cause a large energy loss. This is why conservation of mass seems to hold in reactions. For example, combustion of one mole methane loses 9.9 x 10-9grams.

In nuclear reactions, these mass changes are much greater, 50,000 times greater than methane combustion.

22. (b) Solve the following equations

(i)
$${}_{5}B^{10} + {}_{0}n^{1} \rightarrow {}_{3}Li^{7} + {}_{2}He^{4}$$

(ii) ${}_{11}Na^{23} + {}_{0}n^{1} \rightarrow {}_{11}Na^{24} + \gamma$
(iii) ${}_{47}Ag^{109} + {}_{1}H^{2} \rightarrow$
(iv) ${}_{7}N^{14} + {}_{1}H^{1} \rightarrow {}_{8}O^{15} + \gamma$
(v) ${}_{1}H^{1} + {}_{16}S^{35} \rightarrow {}_{17}Cl^{34} + {}_{0}n^{1}$

23. (a) Write a note on mechanism involved in nuclear reactor?

A **nuclear reactor**, formerly known as an **atomic pile**, is a device used to initiate and control a sustained <u>nuclear chain reaction</u>. Nuclear reactors are used at <u>nuclear power</u> <u>plants</u> for <u>electricity generation</u> and in <u>propulsion of ships</u>. Heat from<u>nuclear fission</u> is passed to a working fluid (water or gas), which runs through <u>steam turbines</u>. These either drive a ship's<u>propellers</u> or turn <u>electrical generators</u>. Nuclear generated steam in principle can be used for industrial process heat or for<u>district heating</u>. Some reactors are used to produce isotopes for <u>medical</u> and <u>industrial</u> use, or for production of <u>weapons-gradeplutonium</u>. Some <u>are run only</u> <u>for research</u>. Today there are about 450 nuclear power reactors that are used to generate electricity in about 30 countries around the world

Parts of Nuclear Power Plant

A Nuclear Reactor mainly consists of

- a) Fuel
- b) Moderators
- c) Control rods
- d) Shielding
- e) Coolant
- f) Turbines
- g) Generator
- h) Cooler Pipes
- i) Water Supply



Fuel: The fissionable material used in the reactor is called as fuel. The commonly used fuels are Uranium, Plutonium or Thorium. It can be U-235, U-238, Pu-236 or Th-232. Uranium is mostly preferred as it has high melting point.

Moderators: Only neutrons of a fairly low speed should be used to have controlled chain reaction. To slow down the speed fast moving neutrons produced during the fission process, moderators are used. Moderator reduces the speed of the neutron by absorbing its energy but not absorb neutron. Graphite, Heavy water and Beryllium are common moderators.

Control Rods: These rods absorb neutrons and stop the chain reaction to proceed further. These are made up of steel containing a high percentage of material like cadmium or boron which can absorb neutrons. When control rods are completely inserted into the moderator block then all the neutrons is absorbed and reaction comes to halt.

Shielding: Shielding prevents radiations to reach outside the reactor. Lead blocks and concrete enclosure that is strong enough of several meters thickness are used for shielding.

Coolant: The coolant substance in a pipe to the steam generator where water is boiled. This is where heat-exchange process occurs. Heat is absorbed by the coolant that is produced in the reactor. Typical coolants are water, carbon dioxide gas or liquid sodium.

Turbines: Steam produced in the boiler is now passes to a turbine. The force of the steam jet causes the turbine to rotate. Heat energy (steam) is converted to mechanical energy (moving turbine).

Generator: The generator consists of coils that change the mechanical energy into electric energy. The turbine moves and the change in magnetic flux cause electricity. This is transmitted to substations for distribution of electric power.

23. (b) Explain the properties and uses of radioactivity	
Properties of alpha beta and gamma radiations	

Property	Alpha(a)	Beta(β)	Gamma(y)
Composition	Alpha particles (Helium Nucleus)	Beta particles (electrons)	High energy electromagnetic radiations
Symbol	А	β	γ
Charge	2+	1-1	0
Mass	4	1/1837	0
Energy	5 MeV	0.05 to 1 Mev	1 MeV
Penentrating power	low	moderate	Very high
Shielding	Paper, cloth	Metal foil	Lead, concrete

Uses of radioactivity

In medicine

Radioisotopes have found extensive use in diagnosis and therapy, and this has given rise to a rapidly growing field called nuclear medicine. These radioactive isotopes have proven particularly effective astracers in certain diagnostic procedures. As radioisotopes are identical chemically with stable isotopes of the same element, they can take the place of the latter in physiological processes. Moreover, because of their radioactivity, they can be readily traced even in minute quantities with such detection devices as gamma-ray spectrometers and proportional counters. Though many radioisotopes are used as tracers, iodine-131, phosphorus-32, and technetium-99*m* are among the most important. Physicians employ iodine-131 to determine cardiac output, plasma volume, and fat metabolism and particularly to measure the activity of the thyroid gland where this isotope accumulates. Phosphorus-32 is useful in the identification of malignant tumours because cancerous cells tend to accumulate phosphates more than normal cells do. Technetium-99*m*, used with radiographic scanning devices, is valuable for studying the anatomic structure of organs.

Such radioisotopes as cobalt-60 and cesium-137 are widely used to treat cancer. They can be administered selectively to malignant tumours and so minimize damage to adjacent healthy tissue.

In industry

Foremost among industrial applications is power generation based on the release of the fission energy of uranium (*see* nuclear fission; nuclear reactor: Nuclear fission reactors). Other applications include the use of radioisotopes to measure (and control) the thickness or density of metal and plastic sheets, to stimulate the cross-linking of polymers, to induce mutations in plants in order to develop hardier species, and to preserve certain kinds of foods by killing microorganisms that cause spoilage. In tracer applications radioactive isotopes are employed, for example, to measure the effectiveness of motor oils on the wearability of alloys for piston rings and cylinder walls in automobile engines. For additional information about industrial uses, *see* radiation: Applications in science and industry.

Reg. No.

[15CHU502]

KARPAGAM UNIVERSITY (KARPAGAM ACADEMY OF HIGHER EDUCATION) COIMBATORE-641021 (For the candidates admitted on 2015 onwards) DEPARTMENT OF CHEMISTRY V - SEMESTER

MODEL EXAMINATION INORGANIC CHEMISTRY

Time: 3 Hours Date:

Maximum: 60 marks

20X1=20

Answer all the questions

Section-A

1.	Materials which display the pro	operty of semiconductors and u	sed in electronic circuits are
	(a) Silicon (b) copper (C) Iron (d) Nichrom	
2.	In the substitutional solid solut	ions, the substitution can be	
	(a) disordered (b) ordered	(c) either disordered or ordere	d (d) in random
3.	The pair of orbitals interacts or node between the nuclei result	ut of phase with one another, th ing in a	e resulting wave will have a
	(a) bonding molecular orbital	(b) antibonding molecu	lar orbital
	© nodal plane	(d) Pi-bond	
4.	Materials which display the pro-	operty of semiconductors and u	sed in electronic circuits ar
	(a) Germanium (b) cop	per (c) Iron (d) Nichrome
5.	The scintillator for the detection	on of neutrons	

(a) Cesium iodide (b) sodium iodide (c) zinc sulphide (d) Lithium iodide

- A radioactive decay process in which the nucleus of an atom splits into smaller parts
 (a) Nuclear fission
 (b) Nuclear fusion
 (c) Radioactive decay
 (d) artificial radioactivity
- 7. The percentage of U-235 in naturally occurring uranium is (a) 93.70% (b) 7% (c) 80% (d) 20%
- Nuclear reactions involve

 (a) Small amounts of energy
 (b) Large amount of energy
 - C affected by temperature (d) affected by concentration
- 9. Fissionable plutonium-239 are used in nuclear reactors as

 (a) Coolants
 (b) control rods
 (c) moderators
 (d) fuel

 10. The energy which holds the nucleus together is known as the
- (a) nuclear binding energy (b) mass defect (c) critical mass (d) fusion energy
- 11. The fissionable nuclei used in Fast breeder nuclear reactors
- (a) Uranium-235 (b) uranium-236 (c) thorium-232 (d) Thorium-235
- 12. By which method isotopes cannot be separated
 - (a) Electromagnetism (b) Centrifuge and distillation (c) Oxidation
 - (d) Thermal diffusion



	(b) acidic solution	(c) standard solution	
(d) indicating solution	(o) acruic solution	(c) standard solution	
14. HSAB is widely use	d in chemistry for explainin	10	
(a) reaction Pathway	(b) Reactivity	of compounds	
Common ion effe	ct (d) solubility pr	oduct of the compou	nds
15. The conjugate base	of acetic acid is		
(a) CH ₃ COO ⁻ (d) Ethyl aceto acet	(b) Sodium acetate ate	(c) acetic anhyd	riđe
16. According to the HS	SAB concept, among the fo	llowing which is a b	orderline base
(a) Nitrate ion	(b) OH (c)	F (d) ferrou	$s Fe^{2+}$
 The measure of the surrounding a charge 	solvent's ability to reduce t ged particle immersed in it.	the field strength of	he electric field
(a) Dipole moment	(b) surface tension (c) d	lielectric constant	(d) viscosity
18. Solvents with a did	electric constant of less than	n 15 are generally co	insidered to be
(a) Polar (b) n	onpolar (c) semipolar	(d) organic solvent	
19. Chloroform is an o	example for	· · ·	
(a) Polar solvents	(b) nonpolar solvent (c) r	olar organic solven	S
(d) non aqueous so	olvents		
20. Alcohol is a			
(a) Less Polar orga	nic solvent (b) Non polar	organic solvent (c) Non-aqueous solvent
(d) non-polar solve	mt		
	Section - I	3	$5 \times 8 = 40$
	Answer all the	questions	
21. (a) What is metalli	ic bond explain it accordin	g to the VB and MC	theory?
21.(4)	(Or)		
(b) Explain the cr	vstal defects and its types?		
22. (a) How the fissio	n mechanism used in the a	tomic power station	s?
	(Or)		
(b) How to synthe	sis the radioactive element	ts?	
(0) 11011 10 0) 1111	- disastinity series and i	ts types	
23 (a) Write a note of	I FACTORCUVILY SCITCS AND I		
23. (a) Write a note of	(Or)		
23. (a) Write a note of (b) What are the	(Or) (Or)	naration of isoloors	2
 (a) Write a note of (b) What are the size of the	(Or) methods involved in the se fluencing factors of a acid	naration of isotopes	strengths ?
(a) Write a note of(b) What are the s24. (a) Explain the in	(Or) methods involved in the se ifluencing factors of a acid (Or)	naration of isotopes	strengths ?
 23. (a) Write a note of (b) What are the s 24. (a) Explain the in (b) Give a pote of 	(Or) methods involved in the se ifluencing factors of a acid (Or) n hard and soft acids and i	naration of isotopes is and bases relative	strengths ?
 (a) Write a note of (b) What are the size 24. (a) Explain the in (b) Give a note of (c) Explain the in 	(Or) methods involved in the se ifluencing factors of a acid (Or) n hard and soft acids and i metonic schemets and empla	naration of isotopes is and bases relative bases?	strengths ?
 (a) Write a note of (b) What are the size 24. (a) Explain the in (b) Give a note of 25. (a) Explain the property of the property	(Or) methods involved in the se ifluencing factors of a acid (Or) m hard and soft acids and i rotonic schemts and expla	naration of inotopes is and bases relative bases? in the reactions of 1	strengths ?
 (a) Write a note of (b) What are the size 24. (a) Explain the in (b) Give a note of 25. (a) Explain the p 	(Or) methods involved in the se ifluencing factors of a acid (Or) m hard and soft acids and i rotenic schuerts and expla (Or)	naration of isotopes is and bases relative bases? in the reactions of l	strengths ? NH ₃ ?

Reg. No.....

KARPAGAM UNIVERSITY

[14CHU502]

Karpagam Academy of Higher Education (Established Under Section 3 of UGC Act 1956) COIMBATORE - 641 021 (For the candidates admitted from 2014onwards) **B.Sc., DEGREE EXAMINATION, NOVEMBER 2016**

Fifth Semester

CHEMISTRY

INORGANIC CHEMISTRY

Time: 3 hours

Maximum : 60 marks

PART - A (20 x 1 = 20 Marks) (30 Minutes)(Question Nos. 1 to 20 Online Examinations)

PART B (5 x 8 = 40 Marks) (2 ½ Hours) Answer ALL the Questions

21. a. What are substitutional and interstitial solid solutions? Explain them with suitable examples.

Or

b. What are instrinsic and extrinsic semi conductors? Explain them with suitable examples.

22. a. i. Distinguish between natural and artificial radio activity.

ii. Mention any four atomic energy projects in India.

Or

- b. i. Differentiate between nuclear fission and fussion reactions.
- ii. Explain the principle of working nuclear reactor.

23. a. Discuss any two methods are used for the detection of isotopes.

Or b. Explain the uses of isotopes in various fields.

24. a. i. What are Bronsted acids and bases? Give example.

ii. State and explain Lewis acid and base concept.

Or b. Discuss the applications and limitations of HSAB concept.

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25. a. Illustrate with examples the classification of solvents.

Or

b. i. Explain any two reactions of liquid ammonia as a solvent.

ii. What are the merits and demerits in using liquid ammonia as a solvent?

Reg. No.....

[13CHU502]

KARPAGAM UNIVERSITY

Karpagam Academy of Higher Education (Established Under Section 3 of UGC Act 1956) COIMBATORE - 641 021 (For the candidates admitted from 2013 onwards)

B.Sc., DEGREE EXAMINATION, NOVEMBER 2015

Fifth Semester

CHEMISTRY

INORGANIC CHEMISTRY

Time: 3 hours

Maximum : 60 marks

PART - A (20 x 1 = 20 Marks) (30 Minutes) (Question Nos. 1 to 20 Online Examinations)

PART B (5 x 8 = 40 Marks) (2 1/2 Hours) Answer ALL the Questions

21. a. Explain in detail of stoichiometric and non- stoichiometric metal defects.

Or

- b. What is semiconductors? What are the classification of semiconductors? Give the details of N and P type semiconductors.
- 22. a. i. Discuss liquid drop model and magic numbers.
 - ii. Explain binding energies.
 - Or
 - b. i. Draw and sketch Aston's mass spectrograph.
 - ii. Discuss any two methods of separation of isotopes.
- 23. a. Discuss the process of nuclear fission, controlled fission reactions and nuclear reactor.
 - Or b. Explain Gieger-Muller counter and Wilson cloud chamber methods of detection of radioactivity.

24. a. i. Discuss the strength of Lewis acids and bases. ii. Explain Solvolytic reactions.

Or

b. Discuss in detail of HSAB principle, applications and limitations.

25. a. i. What is the role of water as a solvent?

ii. What are the general behavior and properties of ionizing solvents? Or

b. Discuss non-aqueous solvents with two examples.

Reg. No....

KARPAGAM UNIVERSITY [12CHU502]

(Under Section 3 of UGC Act 1956) COIMBATORE - 641 021 (For the candidates admitted from 2012 onwards)

B.Sc. DEGREE EXAMINATION, NOVEMBER 2014

Fifth Semester

CHEMISTRY

INORGANIC CHEMISTRY

Time: 3 hours

Maximum : 100 marks

PART - A (15 x 2 = 30 Marks)Answer ALL the Ouestions

- 1. What are the general properties of a metal?
- 2. Explain the electron sea model of the metallic bond
- 3. What is meant by Hume-Ruthory Ratio?
- 4. What is meant by radio activity?
- 5. What is meant by artificial disintegration of elements?
- 6. How will you distinguish between α particle and β particle
- 7. Differentiate isotopes and isobars with suitable examples.
- 8. State Geiger-Nattal rule of radioactivity
- 9. What are magic numbers? How is the stability of nuclei related with magic numbers
- 10. What are Lewis acids? Give examples
- 11. Explain why all Bronsted bases are Lewis bases but all Bronsted acids are not
 - Lewis acids.
- 12. Write one drawback of HSAB theory.
- 13. What is meant by a solvent? Give examples.
- 14. How temperature affects the solubility of a substance 15. What are the characteristics of an organic solvent?

PART B (5 X 14= 70 Marks) Answer ALL the Questions

16. a. What are semi conductors? Explain different types of the semiconductors with

- examples.
- Or b. Explain the different types of crystal defects.

- 17. a. Mention the important uses of radioactive materials Or

 - b. Describe different methods of detection and measurement of radioactivity
- 18. a. What do you understand by soft and hard acids and bases? Explain with suitable examples. Discuss the Pearsons principle and give a brief account of the important theories which favour this principle. Or
 - b. Apply SHAB principle in : (i) occurrence of metal minerals and (ii) predicting the stability of halogen acids.

19. a. Discuss in detail the classification of solvents. Or

b. Explain chemical reactions in non-aqueous solvents with special reference to the reactions occurring in liquid SO2.

20. Compulsory : -

- i. Discuss the stability of nucleus on the basis of n/p ratio odd even rule.
- ii. What are magic numbers? How is the stability of nuclei related with magic numbers?
- iii. Which of the following nuclei would you expect to be radioactive and why? 2He4, 20Ca39, 85 At210

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