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UNIT I

MODERN CONCEPT ACIDS AND BASES AND NON-AQUEOUS SOLVENTS

Modern Concepts of Acids and Bases

Arhenius Concept – Brownsted - Lowery theory – Lewis Concept – Soft and Hard Acids – Soft and Hard Bases – SHAB Principle – Solvent System – Lux – Flood definition – Usanovic Concept Non – Aqueous Solvents Classification of Solvents – General properties of solvents – Self ionization and leveling effect – Reactions in liquid ammonia, Liquid sulfur dioxide, Liquid hydrogen fluoride.

UNIT II

CHEMISTRY OF d AND f BLOCK ELEMENTS

d-Block Elements General Characteristic of Transition metals , Metallic character, oxidation states, size, density, melting and boiling points, ionization energy, colour, magnetic properties, reducing properties, catalytic properties, complex formation and alloy formation. Difference between first and other two rows. F-Block Elements: General Characteristics of f- block elements – Comparitive study of lanthanides and actinides – Electronic configuration, oxidation states, colour, spectral and magnetic properties – Lanthanide contraction and its consequences.

UNIT III

METALLURGY

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UNIT V

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UNIT 1

MODERN CONCEPT ACIDS AND BASES AND NON AQUEOUS SOLVENTS

ARRHENIUS CONCEPT

Arrhenius theory, theory, introduced in 1887 by the Swedish scientist Svante Arrhenius, that acids are substances that dissociate in water to yield electrically charged atoms or molecules, called ions, one of which is a hydrogen ion (H^+), and that bases ionize in water to yield hydroxide ions (OH^-). It is now known that the hydrogen ion cannot exist alone in water solution; rather, it exists in a combined state with a water molecule, as the hydronium ion ($H3O^+$). In practice the hydronium ion is still customarily referred to as the hydrogen ion.

The acidic behaviour of many well-known acids (e.g., sulfuric, hydrochloric, nitric, and acetic acids) and the basic properties of well-known hydroxides (e.g., sodium, potassium, and calcium hydroxides) are explained in terms of their ability to yield hydrogen and hydroxide ions, respectively, in solution. Furthermore, such acids and bases may be classified as strong or weak acids and bases depending on the hydrogen ion or hydroxide ion concentration produced in solution. The reaction between an acid and a base leads to the formation of a salt and water; the latter is the result of the combination of a hydrogen ion and a hydroxide ion.

Arrhenius acid in the aqueous solution increases the concentration of protons or H^+ ions. For example, hydrochloric acid in the water. HCl undergoes dissociation reaction to produce H^+ ion and $Cl^–$ ion, as explained below. The concentration of the H^+ ions is increased by forming hydronium ion.

$HCl (aq) \rightarrow H^+(aq) + Cl^–(aq)$

$HCl (aq) + H2O(l) \rightarrow H3O^+(aq) + Cl^–(aq)$

Other examples of Arrhenius acids are listed below

$NHO3(aq) + H2O(l) \rightarrow H3O^+(aq) + No3^–$

In this reaction, nitric acid dissolves in aqueous water to give hydrogen and nitrate ions.

Limitations of Arrhenius theory:

The Arrhenius theory is applicable only in aqueous solution; for example, according to the theory, HCl is an acid in the aqueous solution but not in benzene, even though it donates H^+ ion to the benzene. Also, under Arrhenius's definition, the solution of sodium amide in liquid ammonia is not alkaline, even though amide ion deprotonates the ammonia.

Bronsted-Lowry Theory of Acid and Base:

According to Bronsted-Lowry theory, acid is a substance which donates an H^+ ion or a proton and forms its conjugate base and the base is a substance which accepts an H^+ ion or a proton and forms its conjugate acid.

Bronsted-Lowry Acid

The Bronsted-Lowry acid is a substance which donates a proton or H^+ ion to the other compound.

Acid⇌Proton+Conjugatebase

A conjugate base can accept a proton and acid reforms.

$HF \rightleftharpoons H^+ + F^-$

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

$NH_4^+ \rightleftharpoons H^+ + NH_3$

$H_2O \rightleftharpoons H^+ + OH^-$

$F^- + H^+ \rightleftharpoons HF$

Bronsted-Lowry Base

The Bronsted-Lowry base is a substance which accepts a proton or H^+ ion from other compounds.

Base+Proton⇌Congatedacid

A conjugated acid can donate a proton and base reforms.

$OH^- + H^+ \rightleftharpoons H_2O$

$S^{2-} + H^+ \rightleftharpoons HS^-$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$

The Bronsted-Lowry theory of an acid-base reaction involves the transfer of protons or H^+ ions between the acid and base.

Example 1:

Consider a reaction in which ammonia (base) is dissolved in water (acid). Ammonia takes a proton from water and the reaction is as follows,

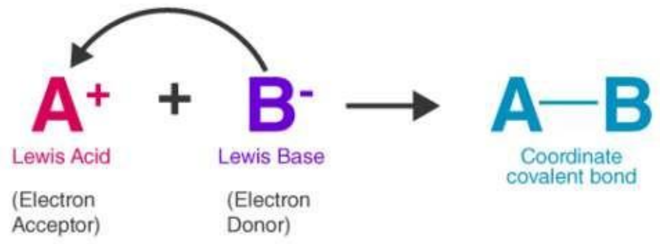
$H_2O(l)) + NH_3(Aq)) \rightleftharpoons OH^-(Aq) + NH_4^+$

Acid+Base⇌Conjugatebase+conjugateacid

- A Bronsted-Lowry acid is a substance which donates a proton or H^+ ion to the other compound and forms a conjugated base.
- A Bronsted-Lowry base is a substance which accepts a proton or H^+ ion from the other compound and forms conjugated acid.
- Strong acids and bases ionize completely in an aqueous solution, whereas weak acids and bases are partially ionized in aqueous solution.
- Water molecule is amphoteric in nature, which means it can act as Bronsted-Lowry acid as well as Bronsted-Lowry base.

Lewis acids and bases:

Lewis acids and bases are described by the Lewis theory of acid-base reactions as electron-pair acceptors and electron pair donors respectively. Therefore, a Lewis base can donate a pair of electrons to a Lewis acid to form a product containing a coordinate covalent bond. This product is also referred to as a Lewis adduct. An illustration detailing the reaction between a Lewis acid and base leading to the formation of a coordinate covalent bond between them is given below.



Lewis acids and bases are named after the American chemist Gilbert Newton Lewis, who also made invaluable contributions in the fields of thermodynamics and photochemistry.

Lewis Acid

Lewis Acids are the chemical species which have empty orbitals and are able to accept electron pairs from Lewis bases. This term was classically used to describe chemical species with a trigonal planar structure and an empty p-orbital. An example of such a Lewis acid would be BR3 (where R can be a halide or an organic substituent).

Water and some other compounds are considered as both Lewis acids and bases since they can accept and donate electron pairs based on the reaction.

Examples of Lewis Acids

Some common examples of Lewis acids which can accept electron pairs include:

- H+ ions (or protons) can be considered as Lewis acids along with onium ions like H3O+.
- The cations of d block elements which display high oxidation states can act as electron pair acceptors. An example of such a cation is Fe3+.

Apart from these chemical compounds listed above, any electron-deficient π system can act as an acceptor of electron pairs – enones, for example.

Lewis Base

Atomic or molecular chemical species having a highly localized HOMO (The Highest Occupied Molecular Orbital) act as Lewis bases. These chemical species have the ability to donate an electron pair to a given Lewis acid in order to form an addict, as discussed earlier.

The most common Lewis bases are ammonia, alkyl amines, and other conventional amines. Commonly, Lewis bases are anionic in nature and their base strength generally depends on the pKa of the corresponding parent acid. Since Lewis bases are electron-rich species that have the ability to donate electron-pairs, they can be classified as nucleophiles. Similarly, Lewis acids can be classified as electrophiles (since they behave as electron-pair acceptors).

Examples of Lewis Bases

Examples of Lewis bases which have an ability to donate an electron pair are listed below.

- Pyridine and the derivatives of pyridine have the ability to act as electron pair donors. Thus, these compounds can be classified as Lewis bases.

Applications of Lewis Acids and Bases

Some important applications of Lewis acids and bases are provided below.

Lewis acids play a vital role as a catalyst in the Friedel-Crafts reaction – AlCl3 accepts a lone pair of electrons belonging to the chloride ion leading to the formation of AlCl4– in the Friedel-Crafts alkylation process.

This also leads to the formation of the highly electrophilic carbonium ion which acts as a strong Lewis Acid. The chemical reaction can be written as follows.

RCl + AlCl3 ⟶ R+ + AlCl4–

In the field of organic chemistry, Lewis acids are widely used to encourage many cationic or pseudo-cationic chemical reactions.

Lewis bases have immense applications in the modification of the selectivity and the activity of metallic catalysts. For the production of pharmaceuticals, asymmetric catalysis is an important part of enantioselective synthesis. In order to enable asymmetric catalysis, chiral Lewis bases are often used to confer chirality on catalysts.

Several Lewis bases have the ability to form many bonds with Lewis acids. These compounds are also called ‘multidentate Lewis bases’ or ‘chelating agents’ and have a wide range of industrial and agricultural applications.

Hard and Soft Acids and Bases (HSAB) Principle is a qualitative concept introduced by Ralph Pearson to explain the stability of metal complexes and the mechanisms of their reactions. However, it is also possible to quantify this concept based on Klopman's FMO analysis using interactions between HOMO and LUMO. The principle, definitions, examples, theoretical basis, applications and limitations of Pearson's HSAB theory are presented in this document.

According to HSAB principle, the Lewis acids and bases can be further divided into hard or soft or borderline types.

Hard Lewis acids are characterized by small ionic radii, high positive charge, strongly solvated, and empty orbitals in the valence shell and with high energy LUMOs.

Soft Lewis acids are characterized by large ionic radii, low positive charge, completely filled atomic orbitals and with low energy LUMOs.

Hard Lewis bases are characterized by small ionic radii, strongly solvated, highly electronegative, weakly polarizable and with high energy HOMOs.

Soft Lewis bases are characterized by large ionic radii, intermediate electronegativity, highly polarizable and with low energy HOMOs.

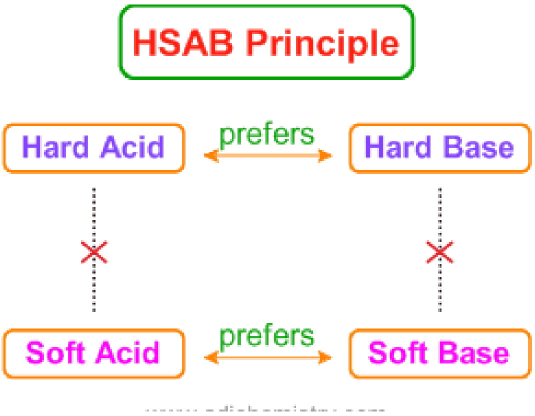
The Borderline Lewis acids and bases have intermediate properties.

Remember that it is not necessary for Lewis acid or base to possess all the properties to be classified as hard or soft or borderline.

In short, hard acids and bases are small and non-polarizable, whereas Soft acids and bases are larger and more polarizable.

HSAB PRINCIPLE:

According to HSAB concept, hard acids prefer binding to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes. It is sometimes referred to as Hard-Soft Interaction Principle (HSIP).



- ∗ The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.
- ∗ The electron negativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent.
- ∗ The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

Lux-Flood concepts for acid and base:

According to this theory, acid and base are defined as acid being an oxide acceptor and the base being an oxide donor.

Example: Calcium oxide (CaO) reacts with silicon dioxide (SiO2) to form calcium silicate (CaSiO3

$$\mathbf{CaO+SiO2 \longrightarrow CaSiO3}$$

In this reaction, CaO is an oxide donor. So, CaO acts as the base while SiO2 is an oxide acceptor. So, SiO2 acts as an acid.

Merits and demerits:

Merit:

This approach emphasizes the acid and basic-anhydride aspects. Acidic oxides are acid anhydride and in the aqueous medium generate protonic acids, while, basic oxides are basic anhydride and generate hydroxyl ions in the aqueous medium.

Demerit:

- The usefulness of this concept is limited to species that contain oxide ion.
- The concept is applicable only in the molten state of an oxide.

Usanovich Concept of Acid-Base:

In 1938, Russian physical chemist Mikhail Usanovich developed a general theory of acids and bases. According to this concept, “An acid is any species capable of giving cations, combining with anions or electrons or neutralizing a base to give a salt and a base is any species capable of giving up anions or electrons, combining with cation or neutralizing an acid to form salt.”

Examples:

Usanovich Acids: SO3, Cl2, etc.

Usanovich Bases: Na2O, Na, etc.

This concept is useful in classifying all types of acids and bases, as well as it also considers the oxidation-reduction process.

UNIT –II

CHEMISTRY OF D AND F BLOCK ELEMENTS

The d-block elements are also known as the transition elements. The IUPAC defines these transition metals as an element whose atom has a particularly filled d subshell or which can give rise to citations with uncompleted subshells.

Transition metals are defined by scientists as an element in the d-block of the periodic table. This includes groups 3 to 12 on the periodic table. The F block lanthanide, actual, and actinide series are also considered transition metals and are called inner transition metals.

Wilkinson and Cotton expanded the brief IUPAC definition by specifying which of the elements are included. The elements of groups 4 to 11 and yttrium and scandium in group 3 have partially filled d subshells in the metallic state. Actinium and lanthanum in group 3 are classified as lanthanides and actinides respectively.

Charles Bury, an English chemist, first used the word transition in this context in 1921 when he referred to a transition series of elements during the change in the inner layer of electrons from a stable group of 8 to one of 18 or from 18 to 32. These elements are known as the d block elements.

Properties of Transition Elements

The transition elements' general properties are as follows:

- They are typically metals with a high melting point.
- They have a variety of oxidation states.
- They usually combine to form coloured compounds.
- They are frequently paramagnetic.
- They have a high charge/radius ratio.
- High density and hardness.
- The boiling and melting points are both very high.
- Construct paramagnetic compounds.
- Variable oxidation states are displayed.
- Coloured compounds and ions are common.
- Create catalytically active compounds.
- Create stable complexes

Oxidation States

The number of electrons that an atom loses, gains, or appears to use when joining with another atom in a compound is related to its oxidation state. It also determines an atom's ability to oxidise (lose electrons) or reduce (gain electrons) other atoms or species. Almost all transition metals have multiple oxidation states that have been experimentally observed. Ions are formed by adding or subtracting negative charges from an atom. Keeping the atomic orbitals in mind when assigning oxidation numbers aids in understanding that transition metals are a special case, but not an exception to this convenient method.

An atom with an oxidation number of -1 accepts an electron to achieve a more stable configuration. The electron donation is then +1. When a transition metal loses electrons, it usually loses s orbital electrons first, followed by d orbital electrons. See Formation of coordination complexes for a more detailed discussion of how these compounds form. Most transition metals have multiple oxidation states because transition metals lose electron(s) more easily than alkali metals and alkaline earth metals. The valence s-orbital of alkali metals contains one electron, and their ions almost always have oxidation states of +1. (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valence s-orbitals, resulting in +2 oxidation state ions (from losing both). Transition metals, on the other hand, are more complex and exhibit a variety of observable oxidation states, owing primarily to the removal of d-orbital electron.

General Characteristics of f-block elements

The Lanthanide Series

The Lanthanide series include fifteen elements i.e. lanthanum (57 La) to lutetium (71 Lu). Lanthanum and Lutetium have no partly filled 4f- subshell but have electrons in 5d-subshell. Thus these elements should not be included in this series. However, all these elements closely resemble lanthanum and hence are considered together.

General properties of Lanthanides

Electronic configuration

The electronic configuration of Lanthanides are listed in the table 5.1. The fourteen electrons are filled in Ce to Lu with configuration [54 Xe]4f1-14 5d1 6s2

Oxidation states

The common oxidation state exhibited by all the lanthanides is +3 (Ln3+) in aqueous solutions and in their solid compounds. Some elements exhibit +2 and +4 states as uncommon oxidation states.

La - +3

Ce - +3, +4, +2

Pr - +3, +4

Nd - +3, +4, +2

Radii of tripositive lanthanide ions

The size of M3+ ions decreases as we move through the lanthanides from lanthanum to lutetium. This steady decrease in ionic radii of M3+ cations in the lanthanide series is called Lanthanide contraction.

Cause of lanthanide contraction

The lanthanide contraction is due to the imperfect shielding of one 4f electron by another in the same sub shell. As we move along the lanthanide series, the nuclear charge and the number of 4f electrons increase by one unit at each step. However, due to imperfect shielding, the effective nuclear charge increases causing a contraction in electron cloud of 4f-subshell.

Consequences of lanthanide contraction

Basicity of ions

Due to lanthanide contraction, the size of Ln^{3+} ions decreases regularly with increase in atomic number. According to Fajan's rule, decrease in size of Ln^{3+} ions increase the covalent character and decreases the basic character between Ln^{3+} and OH^- ion in $Ln(OH)_3$. Since the order of size of Ln^{3+} ions are

$La^{3+} > Ce^{3+}$................$> Lu^{3+}$

- There is regular decrease in their ionic radii.
- Regular decrease in their tendency to act as reducing agent, with increase in atomic number.
- Due to lanthanide contraction, second and third rows of d-block transistion elements are quite close in properties.
- Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.

The Actinide Series (5f block elements)

In 1923 Neils Bohr postulated the existence of an actinide series analogous to the lanthanide series.The fifteen elements from actinium to lawrencium constitute the actinide series of the periodic table.

1. **General Properties of Actinide Series**

   The general electronic configuration of actinides is [Rn] $5f^{0,1-14}\ 6d^{0,1-2}\ 7s^2$ where Rn stands for radon core.

2. **Oxidation states**

   These elements shows the oxidation states of +2, +3, +4, +5 and +6. Out of these, +4 oxidation state is most common state.

3. **Radii of M^{3+} and M^{4+} ions**

   The ionic radii of actinide elements decrease gradually as we move along the actinide series. The steady decrease in the ionic radii with increase in nuclear charge is called actinide contraction and is analogous to lanthanide contraction.

Cause of actinide contraction

Cause of actinide contraction is the imperfect shielding by 5f-electrons. As we proceed from one element to the next one in actinide series, the nuclear charge increases by +1 at each next element which is not compensated due to poor shielding effect of 5f orbitals due to their more diffuse shape. Hence as the atomic number increases, the inward pull experienced by 5f-electrons increase. Consequently, steady decrease in size occurs in the actinide series.

Difference between Lanthanides and Actinides

- Lanthanoids are involved in the filling of 4f- orbitals whereas actinoids are involved in the filling of 5f-orbitals. The binding energy of 4f electrons is comparatively less than that of 5f-electrons. The shielding effect of 5f-electrons is less effective as compared to that of 4f-electrons.
- The paramagnetic properties of lanthanoids can be easily explained but this explanation is difficult in the case of actinoids.
- Lanthanides are non-radioactive in nature except promethium whereas all actinide series elements are radioactive.
- Lanthanides do not have a tendency to form oxo-cations, but several oxo-cations of actinide series exist. The compounds formed by lanthanides are less basic on the other hand the compounds of actinides are highly basic.

Similarities between Lanthanides and Actinides

The elements of lanthanide and actinide series are characterized by filling of (n-2) f subshell. They possess almost similar outermost electronic configuration hence have similar properties. Following are the significant similarities:

- Both have a prominent oxidation state of +3.
- They are involved in the filling of (n-2) f orbitals.
- They are highly electropositive and very reactive in nature.
- With an increase in atomic number, there is a decrease in atomic and ionic size.
- Both show magnetic properties.

UNIT - III

METLLURGY

Metallurgy:

Metallurgy is defined as a process that is used for the extraction of metals in their pure form. The compounds of metals mixed with soil, limestone, sand, and rocks are known as minerals. Metals are commercially extracted from minerals at low cost and minimum effort. These minerals are known as ores. A substance which is added to the charge in the furnace to remove the gangue (impurities) is known as flux. Metallurgy deals with the process of purification of metals and the formation of alloys.

Principles of Metallurgy:

The metallurgical process can be classified as the following:

1. **Crushing and grinding**

   The first process in metallurgy is crushing of ores into a fine powder in a crusher or ball mill. This process is known as pulverization.

2. **The concentration of ores:**

   The process of removing impurities from ore is known as a concentration of minerals or ore dressing. In metallurgy, we concentrate the ores mainly by the following methods.

3. **Hydrolytic method:**

   In this method, we pour the ore over a sloping, vibrating corrugated table with grooves. A jet of water is allowed to flow over the surface. The denser ore particles settle in the grooves, and the impurities are washed away by water.

4. **Magnetic separation:**

   In this case, the crushed ore is placed on a conveyor belt. This belt rotates around two wheels in which one of the wheels is magnetic, and therefore the magnetic particles get attracted to the magnetic wheel and fall apart from the non-magnetic particles.

5. **Froth floatation:**

   In this process, we take the crushed ore in a large tank which contains oil and water. A current of compressed air is passed through it. The ore gets wet by oil and is separated from the impurities in the form of froth. Ore is lighter, and so it comes on the surface and impurities are left behind.

6. **Roasting and calcination:**

   In metallurgy, the process of heating a concentrated ore in the presence of oxygen is known as roasting. This process is applied in the case of sulfide ores. For ores containing carbonate or hydrated oxides, heating is done in the absence of air to melt the ores, and this process is known as calcination.

Zone refining

Zone refining is also known as zone melting, floating-zone process, or traveling melting zone. Zone refining process was first invented by John Desmond Bernal. Zone refining was first commercially used for germanium. As zone refining by using electrical heating coils did not work well with silicon because of its high melting point.

Electrolytic refining

Electrolytic refining is a process of refining a metal (mainly copper) by the process of electrolysis. As far as the mechanism of the process is concerned, during electrolysis, a large chunk or slab of impure metal is used as the anode with a thin strip of pure metal at the cathode. In this setup, an electrolyte (metal salt aqueous solution) depending on the metal is often used.

The clean or pure metal is formed at the cathode when the electrical current of a sufficient voltage is applied by dissolving impure metal at the anode. Electrolytic refining is also sometimes referred to as Electro refining.

Electrolytic Refining of Copper

Copper is usually mined from its coal known as blister copper. It is about 98 to 99 per cent pure. However, the electro-refining process can easily make it 99.95% pure which makes it a good product to be used in electrical components.

A block of impure copper is taken as an anode or positive electrode. Copper sulfate which is acidified with sulphuric acid is used as a graphite-coated electrolyte along with pure copper tubes, as a cathode or negative electrode. In this phase of electrolysis copper sulfate divides into a positive ion of copper (Cu++) and a negative ion of sulfate (SO4—). The positive copper ion (Cu++) or cations travel towards the negative electrode made of pure copper where it absorbs the electrons from the cathode. Cu atom is deposited on the cathode’s graphite layer.

The cathode is coated with graphite in the process of electrolytic metal processing or merely electro grinding so that the concentrated material can be easily removed. This is one of the most growing electrolysis procedures.

UNIT - IV

HALOGEN FAMILY AND NOBLE GASES

Basic properties of halogen:

The group of halogens is the only periodic table group that contains elements in all three familiar states of matter at standard temperature and pressure. Fluorine (F) is a pale yellow gas. Chlorine (Cl) is a greenish gas. Bromine (Br) is a dark red liquid. Iodine (I) is a black solid and when heated it forms a purple vapour. Astatine (At) is a black solid. The halogens all have a strong and often nasty smell. The halogen elements are extremely toxic. Poor conductors of heat and electricity. Low melting and boiling points.

Oxidation and oxidising power:

Oxidation is the removal of electrons from an atom or polyatomic ion. The higher the electronegativity the greater the pull an oxidizing agent has for electrons. The higher the pull for electrons the stronger the oxidizing agent. So the element with the highest electronegativity is the strongest oxidizing agent.

Pseudohalogens :

Pseudohalogens are polyatomic analogues of halogens, whose chemistry, resembling that of the true halogens, allows them to substitute for halogens in several classes of chemical compounds. Pseudohalogens occur in pseudohalogen molecules, inorganic molecules of the general forms Ps–Ps or Ps–X (where Ps is a pseudohalogen group), such as cyanogen; pseudohalide anions, such as cyanide ion; inorganic acids, such as hydrogen cyanide; as ligands in coordination complexes, such as ferouscyanide; and as functional groups in organic molecules, such as the nitrile group. Well-known pseudo halogen functional groups include cyanide, cyanate, thiocyanate, and aside.

Cyanogen:

Cyanogen, $(CN)2$, is a toxic, colourless gas that boils at −21 °C (−6 °F). It can be prepared by oxidation of hydrogen cyanide (HCN). A variety of oxidizing agents can be used, including oxygen gas, $O2$, chlorine gas, $Cl2$, and nitrogen dioxide gas, $NO2$.… In nitrogen: Compounds.

Thiocyanogen:

Thiocyanogen, $(SCN)2$, is a pseudohalogen derived from the pseudohalide thiocyanate, $[SCN]-$. This hexatomic compound exhibits C2 point group symmetry and has the connectivity NCS-SCN. The oxidation ability is greater than bromine. It reacts with water:

$3(SCN)2 + 4H2O \rightarrow H2SO4 + HCN + 5SCN- + 5H+$

Thiocyanogen was originally prepared by the reaction of iodine with a suspension of silver thiocyanate in diethyl ether, but this reaction suffers from competing equilibria attributed to the weak oxidizing power of iodine. An improved method for generating thiocyanogen entails oxidation of plumbous thiocyanate, which precipitates when aqueous solutions of lead(II) nitrate and sodium thiocyanate are combined. A suspension of anhydrous Pb(SCN)2 is treated with bromine in glacial acetic acid to afford a 0.1M solution of thiocyanogen that is stable for days. Alternatively, a solution of bromine in methylene chloride is added dropwise to a suspension of Pb(SCN)2 in methylene chloride at 0 °C followed by filtration under argon to give a solution of thiocyanogen that should be used immediately.

$Pb(SCN)2 + Br2 \rightarrow (SCN)2 + PbBr2$

Thiocyanogen adds to alkenes to give 1,2-bis(thiocyanato) compounds and reacts with titanacyclopentadienes giving (Z,Z)-1,4-bis(thiocyanato)-1,3-butadienes, which in turn can be converted to 1,2-dithiins. Selenocyanogen, (SeCN)2, prepared from reaction of silver selenocyanate with iodine in tetrahydrofuran at 0 °C, reacts in a similar manner to thiocyanogen.

Noblegases

The noble gases (historically also the inert gases; sometimes referred to as aerogens) make up a class of chemical elements with similar properties; under standard conditions, they are all odorless, colorless, monatomic gases with very low chemical reactivity. The six naturally occurring noble gases are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and the radioactive radon (Rn).

Oganesson (Og) is a synthetically produced highly radioactive element. Although IUPAC has used the term "noble gas" interchangeably with "group 18" and thus included oganesson, it may not be significantly chemically noble and is predicted to break the trend and be reactive due to relativistic effects. Because of the extremely short 0.7 ms half-life of its only known isotope, its chemistry has not yet been investigated.

For the first six periods of the periodic table, the noble gases are exactly the members of group 18. Noble gases are typically highly unreactive except when under particular extreme conditions. The inertness of noble gases makes them very suitable in applications where reactions are not wanted. For example, argon is used in incandescent lamps to prevent the hot tungsten filament from oxidizing; also, helium is used in breathing gas by deep-sea divers to prevent oxygen, nitrogen and carbon dioxide toxicity.

The properties of the noble gases can be well explained by modern theories of atomic structure: Their outer shell of valence electrons is considered to be "full", giving them little tendency to participate in chemical reactions, and it has been possible to prepare only a few hundred noble gas compounds. The melting and boiling points for a given noble gas are close together, differing by less than 10 °C (18 °F); that is, they are liquids over only a small temperature range.

Neon, argon, krypton, and xenon are obtained from air in an air separation unit using the methods of liquefaction of gases and fractional distillation. Helium is sourced from natural gas fields that have high concentrations of helium in the natural gas, using cryogenic gas separation techniques, and radon is usually isolated from the radioactive decay of dissolved radium, thorium, or uranium compounds. Noble gases have several important applications in industries such as lighting, welding, and space exploration. A helium-oxygen breathing gas is often used by deep-sea divers at depths of seawater over 55 m (180 ft). After the risks caused by the flammability of hydrogen became apparent in the Hindenburg disaster, it was replaced with helium in blimps and balloons.

Properties of Helium (He)

Helium is a chemical element which is denoted by the symbol He. The atomic number of helium is 2. Under standard conditions for temperature and pressure (STP), helium exists as a colourless monoatomic gas that does not have any distinct odour or taste. It can be noted that helium is non-toxic in small concentrations. It is the first and the lightest noble gas. Among all elements, helium is known to possess the lowest boiling point.

Helium is an s-block element which corresponds to period 1 and group 18 of the modern periodic table. The electron configuration of helium is 1s2. Therefore, this element has a total of 2 electrons in its valence shell. The melting point of helium is approximately equal to 0.95 Kelvin (or -272.20 degrees Celsius) when it is placed under a pressure of 2.5 MPa. Under standard conditions for temperature and pressure, the density of this element corresponds to 1.7186 grams per litre. However, in its liquid state, the density of this element is approximately equal to 0.145 grams per cubic centimetre.

Properties of Neon (Ne)

Neon is a chemical element which is denoted by the symbol Ne. the atomic number of neon is 10. Under standard conditions for temperature and pressure (STP), neon exists as a colourless mono atomic gas (similar to helium). This gas does not possess any characteristic odour. Neon is the second-lightest noble gas, the lightest being helium.

Neon belongs to group 18 and period 2 of the modern periodic table. The electron configuration of this element is [He] 2s22p6. It holds a total of 8 electrons in its valence shell. The melting point of neon is approximately equal to 24.56 Kelvin (or -248.59 degrees Celsius). On the other hand, the boiling point of neon is equal to 27.104 Kelvin (or -246.046 degrees Celsius). At STP, the density of this gas corresponds to 0.9 grams per litre (approximately). However, in its liquid state (at a temperature equal to its boiling point), the density of neon is equal to 1.207 grams per cubic centimetre.

The triple point of neon occurs at a temperature of 24.556 Kelvin and under a pressure of 43.37 kilopascals. The enthalpy of fusion of this element is equal to 0.335 kilojoules per mole. It can be noted that the latent heat of vaporisation of neon is equal to 1.71 kilojoules per mole.

Properties of Argon (Ar)

Argon is the 3rd noble gas whose atomic number is equal to 18. This element is denoted by the symbol Ar. In the Earth’s atmosphere, argon is known to be the third-most abundant gas. Under standard conditions for temperature and pressure, argon is known to exist as a colourless gas that exhibits a violet or lilac-coloured glow when it is placed in an electric field.

Argon is a p-block element that corresponds to group 18 and period 3 of the modern periodic table. The electronic configuration of argon is [Ne]3s23p6. This element has a total of 8 electrons in its valence shell. The melting point of argon corresponds to 83.81 Kelvin whereas its boiling point corresponds to 87.302 Kelvin. Under standard conditions for temperature and pressure, the density of argon is roughly equal to 1.784 grams per litre.

Properties of Krypton (Kr)

Krypton is the 4th noble gas. The atomic number of krypton is 36. This element is often denoted by the symbol Kr. Under standard conditions for temperature and pressure, krypton exists as a colourless monoatomic gas that does not have any characteristic odour. This gas is also known to be tasteless.

Krypton, like argon, is a p-block element. It corresponds to group 18 and period 4 of the modern periodic table. The electron configuration of krypton can be written as [Ar]3d104s24p6. The melting point of this element is approximately equal to 115.78 Kelvin whereas the boiling point of this element is equal to 119.3 Kelvin. At STP, the density of this element is roughly equal to 3.75 grams per litre.

Properties of Xenon (Xe)

Xenon, the 5th noble gas, has an atomic number of 54. The symbol 'Xe' is often employed to denote xenon. Under standard conditions, this element is known to exist as a mono atomic gas that is colourless and odourless. This p-block element corresponds to period 5 and group 18 of the modern periodic table. The electronic configuration of xenon is [Kr]4d105s25p6. The melting point of xenon is equal to 161.4 Kelvin whereas the boiling point of this element is equal to 165.05 Kelvin. At STP, the density of xenon is roughly equal to 5.89 grams per litre.

Properties of Radon (Rn)

Radon is a noble gas whose atomic number is 86. The symbol of this element is Rn. Under standard conditions, radon (like most other noble gases) is a colourless and odourless gas that does not have any characteristic taste. It is important to note that radon is radioactive. In fact, the most stable isotope of radon, which is 222Rn, is known to have a half-life of 3.8 days.

Uses of Noble Gases

In metallurgical processes, argon is widely used in order to provide the necessary inert atmosphere. This inert atmosphere plays an important role in welding titanium, aluminium, stainless steel, and magnesium. It is also used in the production of titanium.

A limited amount of argon is used in germanium and silicon crystals which are used in electric light bulbs, transistors, etc. The boiling point of helium is the least when compared to any other liquid. It is used to obtain the lowest temperatures required in lasers. Helium is used in nuclear reactors as a cooling gas and used as a flow-gas in liquid-gas chromatography. It finds its application in airships and helium balloons.

Helium balloons are used to check the weather of a particular region. Helium is preferred over hydrogen though hydrogen is cheaper, as helium is readily available and hydrogen is highly inflammable. Hence, due to safety issues helium is preferred in aircraft. It is used by divers to dilute oxygen over nitrogen in the gas cylinders used by them as nitrogen can easily be dissolved in the blood which results in a painful condition called bends. The risk of helium causing bends is slightly lower than nitrogen.

Neon is used in discharge tubes which is the reason behind the reddish-orange glow produced by neon lights.

Xenon and krypton find their application in photographic flash units due to the generation of very bright light. It is also used in lighthouses.

Neon, xenon, and krypton are used to produce different colour lights

Clathrates:

Clathrates or gas hydrates form the largest methane sink in the world. Methane hydrate, also known as “fire ice,” is an ice-like substance which consists of a rigid lattice of water molecules that trap methane molecules. Methane hydrates occur dominantly in organic-carbon enriched hemipelagic sediments along continental margins and in continental settings. Fine grain-size of the hemipelagic sediments (clay) is an inhibiting factor for gas hydrate formation. The occurrence of methane hydrates in marine sediments enriched in organic carbon is controlled by temperature, pressure and ionic strength of the water. Therefore, gas hydrates are only stable in subsurface depths of about 500 m up to 2000 m in the temperate latitudes (Dickens and Quinby-Hunt, 1994).

Methane hydrates have also been discovered in polar regions, in shallow subsurface environments and in permafrost soils. The thickness of the zone of stability of clathrates is constrained by temperature and pressure

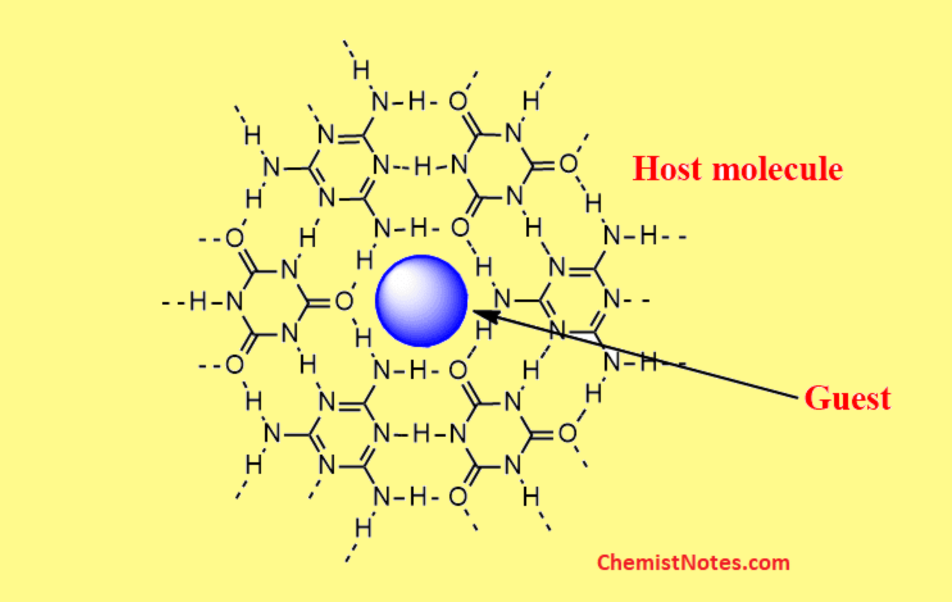
Methane in hemipelagic sediments is mainly of biogenic origin. The source of methane has been determined by isotope geochemistry (Fig 3). Stable carbon isotope compositions of − 90 to − 60‰ measured in methane point at a microbial source of methane formed below about 80oC (Schoell, 1980). Only in some cases, methane carbon isotope values of − 30 to − 50‰ were measured in gas hydrates along continental margins. These carbon isotope values indicate that some of the methane in gas hydrates is of thermogenic origin. Thermogenic methane forms at temperatures of up to 150°C or more. Thermogenic methane was transported from deeply buried carbonaceous sediments into the critical subseafloor zone of clathrate formation where it was frozen into methane ice. Today, clumped-isotope composition of methane provides additional information on the temperature of formation of thermogenic or biogenic methane.

The petroleum industry is interested in gas hydrates as a potential large source of natural gas. Estimates of reservoir size are quite variable. Early estimates of around 10,000 Gt of carbon are now considered as too high. Today estimates of around 1800 GtC seem more reasonable. Fossil fuels, for comparison, contain around 5000 GtC. Gas hydrates are considered by some authors as an important energy source for the 21st century. These authors point at the high energy value of methane ice. It has been found that 1 m3 of gas hydrate equals 164 m3 of methane under normal conditions. If gas hydrates could replace coal as a source of energy, the impact on climate would be greatly reduced. Therefore, countries like Japan are interested in using clathrates as a source of energy. Recovery of methane from clathrates remains technically challenging and, so far, only few test sites are producing natural gas from clathrates. Another problem with the exploitation of clathrates is that they are just a different source of hydrocarbons that contribute to greenhouse gas warming of the planet. Thus, they have no place in the production of energy in a future fossil fuel-free world.

Properties:

These compounds have the following characteristics in crystalline structure in addition to having a large void [84]: (1) large unit cell with high symmetry; (2) guest atoms or molecules are physically trapped in the large voids of lattice, and also stabilize the frame structure; and (3) guest atoms or molecular lattices may be nonstoichiometric, and the interaction between the main lattice frame and guest atoms or molecules will affect the performance of clathrates.Similar to skutterudites, inorganic clathrates have a three-dimensionally periodic open frame structure. For example, one or multiple host atoms of Al, Si, Ga, Ge, and Sn can form polyhedral voids by tetrahedral bonding, and appropriate guest atoms can be filled in the voids. The numbers of guest atoms and host atoms need to satisfy the Zintl–Klemm valence electron rule. According to the cage number and shape, inorganic clathrates are usually divided into different types, as shown in Table 4.5 [85]. Among them, the structure and physical properties of type I and type II clathrates are widely studied.

Structure:



Uses of clathrates:

These can be used to separate Nobel gases. For example, Ne can be separated from Ar, Kr, and Xe. This is because Ne can not form clathrate with Quinol. Kr-85 clathrate is used as a safe and useful source of β-radiation. Xe-133 clathrate is the source of gamma radiation. Clathrate play important role in some physiological actions.

UNIT-V

ERRORS AND STATISTICL ANALYSIS

Error:

Error in Chemistry is defined as the difference between the true result (or accepted true result) and the measured result. If the error in the analysis is large, serious consequences may result. As reliability, reproducibility, and accuracy are the basis of analytical chemistry.

Types of Errors

There are three types of errors that are classified based on the source they arise from; they are:

- Gross Errors
- Random Errors
- Systematic Errors

Gross Errors

This category basically takes into account human oversight and other mistakes while reading, recording, and readings. The most common human error in measurement falls under this category of measurement errors. For example, the person taking the reading from the meter of the instrument may read 23 as 28. Gross errors can be avoided by using two suitable measures, and they are written below:

Proper care should be taken in reading, recording the data. Also, the calculation of error should be done accurately. By increasing the number of experimenters, we can reduce the gross errors. If each experimenter takes different readings at different points, then by taking the average of more readings, we can reduce the gross errors

Random Errors

The random errors are those errors, which occur irregularly and hence are random. These can arise due to random and unpredictable fluctuations in experimental conditions (Example: unpredictable fluctuations in temperature, voltage supply, mechanical vibrations of experimental set-ups, etc, errors by the observer taking readings, etc. For example, when the same person repeats the same observation, he may likely get different readings every time.

Systematic Errors:

Systematic errors can be better understood if we divide them into subgroups; They are:

Environmental Errors:

This type of error arises in the measurement due to the effect of the external conditions on the measurement. The external condition includes temperature, pressure, and humidity and can also include an external magnetic field. If you measure your temperature under the armpits and during the measurement, if the electricity goes out and the room gets hot, it will affect your body temperature, affecting the reading.

Observational Errors:

These are the errors that arise due to an individual's bias, lack of proper setting of the apparatus, or an individual's carelessness in taking observations. The measurement errors also include wrong readings due to Parallax errors.

Instrumental Errors:

These errors arise due to faulty construction and calibration of the measuring instruments. Such errors arise due to the hysteresis of the equipment or due to friction. Lots of the time, the equipment being used is faulty due to misuse or neglect, which changes the reading of the equipment. The zero error is a very common type of error. This error is common in devices like Vernier callipers and screw gauges. The zero error can be either positive or negative. Sometimes the scale readings are worn off, which can also lead to a bad reading.

Accuracy

The ability of an instrument to measure the accurate value is known as accuracy. In other words, it is the the closeness of the measured value to a standard or true value. Accuracy is obtained by taking small readings. The small reading reduces the error of the calculation. The accuracy of the system is classified into three types as follows:

Point Accuracy

The accuracy of the instrument only at a particular point on its scale is known as point accuracy. It is important to note that this accuracy does not give any information about the general accuracy of the instrument.

Accuracy as Percentage of Scale Range

The uniform scale range determines the accuracy of a measurement. This can be better understood with the help of the following example:

Consider a thermometer having the scale range up to 500ºC. The thermometer has an accuracy of ±0.5 percent of scale range i.e. 0.005 x 500 = ± 2.5 ºC. Therefore, the reading will have a maximum error of ± 2.5 ºC.

Accuracy as Percentage of True Value Such type of accuracy of the instruments is determined by identifying the measured value regarding their true value. The accuracy of the instruments is neglected up to ±0.5 percent from the true value.

Precision

The closeness of two or more measurements to each other is known as the precision of a substance. If you weigh a given substance five times and get 3.2 kg each time, then your measurement is very precise but not necessarily accurate. Precision is independent of accuracy. The below examples will tell you about how you can be precise but not accurate and vice versa. Precision is sometimes separated into:

Repeatability

The variation arising when the conditions are kept identical and repeated measurements are taken during a short time period.

Reproducibility

The variation arises using the same measurement process among different instruments and operators, and over longer time periods.

Statistical treatment of error analysis:

Mean:

In statistics, the mean is one of the measures of central tendency, apart from the mode and median. Mean is nothing but the average of the given set of values. It denotes the equal distribution of values for a given data set. The mean, median and mode are the three commonly used measures of central tendency.

To calculate the mean, we need to add the total values given in a datasheet and divide the sum by the total number of values. The Median is the middle value of a given data when all the values are arranged in ascending order. Whereas mode is the number in the list, which is repeated a maximum number of time.

Median is defined as the middle value in a given set of numbers or data. In Mathematics, there are three different measures, which are used to find the average value for a given set of numbers. They are mean, median and mode. These three measures are called the measures of central tendency. The average value of the given data is given by mean. The middle value of the given data is defined by a median. The repeated value of the given data is defined by mode.Here, let us discuss one of the measures called “Median” in detail. The definition of median, its formula and examples are explained.

Range

The formula of the range in statistics can simply be given by the difference between the highest and lowest values. The range in statistics for a given data set is the difference between the highest and lowest values. Thus, the range could also be defined as the difference between the highest observation and lowest observation. The obtained result is called the range of observation. The range in statistics represents the spread of observations.

Curve Fitting

Introduction:

The objective of curve fitting is to theoretically describe experimental data with a model (function or equation) and to find the parameters associated with this model. Models of primary importance to us are mechanistic models. Mechanistic models are specifically formulated to provide insight into a chemical, biological, or physical process that is thought to govern the phenomenon under study. Parameters derived from mechanistic models are quantitative estimates of real system properties (rate constants, dissociation constants, catalytic velocities etc.). It is important to distinguish mechanistic models from empirical models that are mathematical functions formulated to fit particular curve but whose parameters do not necessarily correspond to a biological, chemical or physical property. An example of an empirical fit is a polynomial fit to the baseline of a NMR spectrum with the goal to baseline-correct the spectrum. The final coefficients are physically meaningless and also of no interest. The objective of curve fitting is different: one is just trying to draw a curve through the baseline. Other examples of empirical fitting include interpolations such as splines and smoothing. We will not be concerned with such empirical curve fitting methods in this discussion.

Curve Fitting:

The Least-Squares method:

Curve fitting finds the values of the coefficients (parameters) which make a function match the data as closely as possible. The best values of the coefficients are the ones that minimize the value of Chi-square. Chi-square is defined as:

Where y is a fitted value for a given point, yi is the measured data value for the point and σi is an estimate of the standard deviation for yi (discussed under weighting).

Correlation coefficient:

The correlation coefficient is a statistical measure of the strength of a linear relationship between two variables. Its values can range from -1 to 1. A correlation coefficient of -1 describes a perfect negative, or inverse, correlation, with values in one series rising as those in the other decline, and vice versa. A coefficient of 1 shows a perfect positive correlation, or a direct relationship. A correlation coefficient of 0 means there is no linear relationship. Correlation coefficients are used in science and in finance to assess the degree of association between two variables, factors, or data sets. For example, since high oil prices are favorable for crude producers, one might assume the correlation between oil prices and forward returns on oil stocks is strongly positive. Calculating the correlation coefficient for these variables based on market data reveals a moderate and inconsistent correlation over lengthy periods.

The significant figures of a given number are those significant or important digits, which convey the meaning according to its accuracy. For example, 6.658 has four significant digits. These substantial figures provide precision to the numbers. They are also termed as significant digits.

Rules for Significant Figures:

All non-zero digits are significant. 198745 contains six significant digits. All zeros that occur between any two non-zero digits are significant. For example, 108.0097 contains seven significant digits.

All zeros that are on the right of a decimal point and also to the left of a non-zero digit is never significant. For example, 0.00798 contained three significant digits. All zeros that are on the right of a decimal point are significant, only if, a non- zero digit does not follow them. For example, 20.00 contains four significant digits. All the zeros that are on the right of the last non-zero digit, after the decimal point, are significant. For example, 0.0079800 contains five significant digits. All the zeros that are on the right of the last non-zero digit are significant if they come from a measurement. For example, 1090 m contains four significant digits.

Rounding Significant Figures

A number is rounded off to the required number of significant digits by leaving one or more digits from the right. When the first digit in left is less than 5, the last digit held should remain constant. When the first digit is greater than 5, the last digit is rounded up. When the digit left is exactly 5, the number held is rounded up or down to receive an even number. When more than one digit is left, rounding off should be done as a whole instead of one digit at a time.There are two rules to round off the significant numbers:First, we have to check, up to which digit the rounding off should be performed. If the number after the rounding off digit is less than 5, then we have to exclude all the numbers present on the right side. But if the digit next to the rounding off digit is greater than 5, then we have to add 1 to the rounding off digit and exclude the other numbers on the right side.