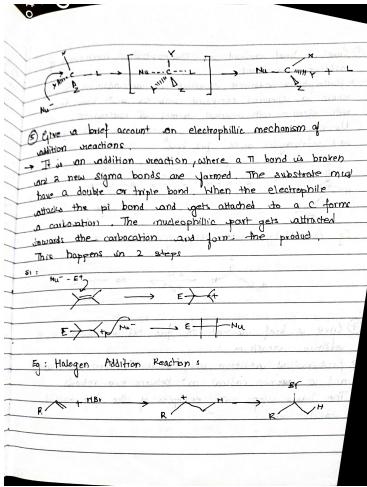
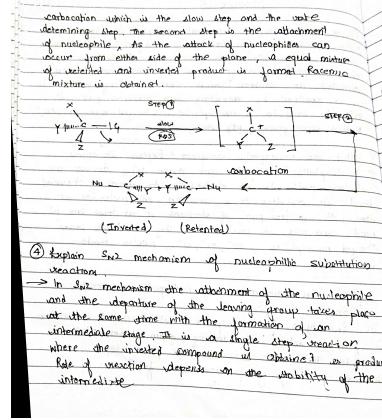


(3) Explain $\text{S}_{\text{N}}2$ mechanism of nucleophilic substitution reactions.

In $\text{S}_{\text{N}}2$ type of nucleophilic substitution, a carbocation is formed when the leaving group leaves the molecule. It occurs in 2 steps first step is the loss of leaving group and the formation of



define the terms i. entropy ii. Enthalpy and iii. Internal energy

What is Enthalpy?

Enthalpy is representing the heat content of a system. It is a common fact that the heat is given or not of the system. So, in a chemical reaction, the change of heat is defined as enthalpy change. This knowledge about the increase or decrease of the enthalpy of the system during a chemical reaction is also very crucial factor for understanding the reaction. Also, the change in the enthalpy of the system during a chemical reaction is termed as the sum total value of change in its internal energy and the change in the product of the pressure and volume of the system.

What is Entropy?

Any type of medium either solid or fluid always consists of molecules. The measurement of the randomness of molecules in the system is called entropy. Therefore, if the randomness of molecules is more, then there will be more increase in entropy of the process. And as a result, the percentage of heat which may be converted into work will be less. Thus, we may say that entropy is a function of the quantity of heat.

Definition of internal energy

: the total amount of kinetic and potential energy possessed by the molecules of a body and their ultimate parts owing to their relative positions and their motions inside the body and excluding the energy due to the passage of waves through the body and to vibrations of the body.

What is the relation between enthalpy and internal energy?

The change in the enthalpy of the system during a chemical reaction is equal to the change in its internal energy plus the change in the product of the pressure times the volume of the system.

$$\Delta H = \Delta E + \Delta(PV)$$

Unit 4

Give the differences between hard and soft acids

| Hard Acid vs Soft Acid | |
|------------------------|---|
| DEFINITION | Hard acids are composed of atoms with high nuclear charge and low electron density. |
| POLARISATION | Soft acids are composed of atoms with low nuclear charge and high electron density. |
| CHARGE VS. SIZE | High charge / Low size |
| METALICITY | High metallicity |
| EXAMPLES | H+, O2-, OH-, F-, Cl-, Br-, I- |

write notes on hard and soft bases with examples for each

"Hard" bases have a high charge (negative for bases) to ionic radius ratio along with higher oxidation states. Hard bases are typically small anions and neutral molecules. Some examples of hard acids and bases include: H^+ , O_2^- , OH^- , F^- , and Al^{3+} .

Soft Acids/Bases:

"Soft" bases have a low charge to radius ratio, with low oxidation states. They are normally larger ions that are polarizable. For example, I^- and S^{2-} are soft bases.

energetic) region

As a result, energy becomes evenly distributed across the two regions, and the temperature of the two regions becomes equal.

The same thing happens on a much larger scale. The Sun and every other star are radiating energy into the universe.

However, they can do it forever. Eventually the stars will cool down, and heat will have spread out so much that there won't be warmer objects and cooler objects.

Everything will be the same very cold temperature.

Once everything is at the same temperature, there's no reason for anything to change its state.

The universe will have run down completely, and the entropy of the universe will be as high as it is ever going to get.

If you want to think it mathematically consider the total energy q that is transferred from a hot region at temperature T_1 to a cold region at temperature T_2 .

The entropy S_1 of the hot region is defined as $S_1=T_1q$.

The entropy S_2 of the cold region is

Therefore, during the energy transfer, the change in entropy is S_1-T_1q (S_2) of the cold region is $S_2=T_2q$ ($S_2-S_1=T_2q-T_1q=T_2-T_1$)

S_2-T_2q Since $T_2 < T_1$, S_2-T_2q is positive.

The total entropy of the system increases.

Since energy never flows spontaneously in the other direction, the total entropy of the universe is always increasing

Explain how Gibbs's free energy for water formation is determined?

Let's look at the reaction of the formation of water: $2\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

The Gibbs's Free Energy relates the spontaneity of various reactions by looking at the change in enthalpy, temperature, and entropy.

spontaneous chain reaction takes place, an increase in the disorder occurs and therefore entropy increases.

What is the significance of Gibbs's free energy?

Significance of Gibbs Free Energy Change:

ΔG is a measure of the spontaneity of a chemical reaction. Gibbs energy change is also related to useful work other than pressure-volume work that can be obtained from the system. It can be shown that Gibbs energy of a process is equal to maximum possible useful work that can be derived from the process as given below:

From the first law of thermodynamics, we know-

$$\Delta U = q - w$$

$$\text{or } q = \Delta U + w$$

$$\text{.....(i)}$$

Where q is the heat absorbed by the system, ΔU is the change in internal energy and w is the work done by the system. The work may be expansion work as well as non-expansion work.

$$\Delta U = \Delta U + W_{\text{exp}} + W_{\text{non-exp}}$$

$$\text{But } W_{\text{non-exp}} = -\Delta V$$

$$q = \Delta U + \Delta V + W_{\text{non-exp}}$$

$$\text{But, } \Delta U + \Delta V = \Delta H$$

$$\text{Thus, } q = \Delta H + W_{\text{non-exp}}$$

$$\text{.....(ii)}$$

For a process carried out reversibly at a constant temperature,

$$\Delta S = q_{\text{rev}}/T \text{ or } q_{\text{rev}} = \Delta S \cdot T$$

Substitute the value of q in equation (ii) we get,

$$\text{TAS} = \Delta H + W_{\text{non-exp}}$$

rearranging(iii)

or $\Delta H - \text{TAS} = -W_{\text{non-exp}}$

But $\Delta H - \text{TAS} = \Delta G$ so that

$$\Delta G = -W_{\text{non-exp}}$$

$$-\Delta G = W_{\text{non-exp}}$$

$$-\Delta G = W_{\text{useful}}$$

Thus, the decrease in the free energy change of a system is the measure of work done by the system. This is the significance of the Gibbs free energy change.

What is the significance of Helmholtz free energy?

Many real-life based open systems in thermodynamics exist as the process of exchanging heat and work with respect to the environment compared to closed systems. Open systems are more complex because they would be of the living systems and attain an inherent reduction in their entropy as they grow mature. The Helmholtz function is the second thermodynamic potential used to measure the work done in a closed system at a constant temperature and volume. The other three thermodynamic potentials are internal energy, enthalpy, and Gibbs free energy.

Comment on the statement, "the entropy of the Universe is always increasing"

The entropy of the universe increases because energy never flows uphill spontaneously

Explanation:

Energy always flows downhill, and this causes an increase of entropy

Entropy is the spreading out of energy, and energy tends to spread out as much as possible

It flows spontaneously from a hot (i.e. highly energetic) region to a cold (less

What is entropy? Explain its significance

What is Entropy?

Any type of medium either solid or fluid always consists of molecules. The measurement of the randomness of molecules in the system is called entropy. Therefore, if the randomness of molecules is more, then there will be more increase in entropy of the process. And as a result, the percentage of heat which may be converted into work will be less. Thus, we may say that entropy is a function of the quantity of heat.

Significance of Entropy

Entropy is very significant in thermodynamics. The significances mentioned below:

- Entropy is a physical quantity. It is equal to the ratio of heat absorbed or rejected to the temperature at which the process takes place.
- In individual processes, entropy always increases. A spontaneous process is also known as an irreversible process because these processes take place at a very fast rate. All the natural processes are spontaneous processes.
- It helps in determining the thermodynamic state of an object. A little consideration shows that a spontaneous process takes place from a less probable state to a more probable state.
- like temperature, volume, pressure, internal energy, magnetic behavior it expresses the state of a body.
- The orderliness of an object decreases with the increase of entropy. Hence spontaneous processes are accompanied by an increase in entropy as well as an increase in the disorder of the system.
- like temperature or pressure, it cannot be felt. Hence the state of the order of the molecules gets disturbed and gives rise to greater disorder.
- It is a measure of the disorder or randomness in the system. When a gas expands into a vacuum, water flows out of a reservoir,

Whenever there is a difference in ionic concentration between any two local areas of a metal, a localized form of corrosion known as crevice corrosion can occur. In a simple instance, this form of corrosion mostly occurs in confined spaces (crevices). Examples of areas where crevice corrosion can occur are gaskets, the undersurface of washers, and bolt heads. All grades of stainless alloys and stainless steel also undergo crevice corrosion. This is mainly because of the formation of a differential aeration cell that leads to the formation of corrosion inside the crevices.

(ii) Stress Corrosion Cracking

Stress Corrosion cracking can be abbreviated as "SCC" and refers to the cracking of the metal as a result of the corrosive environment and the tensile stress placed on the metal. It often occurs at high temperatures.

Example: Stress corrosion cracking of austenitic stainless steel in chloride solution.

(iii) Intergranular Corrosion

Intergranular corrosion occurs due to the presence of impurities in the grain boundaries that separate the grain formed during the solidification of the metal alloy. It can also occur via the depletion or enrichment of the alloy at these grain boundaries.

Example: Aluminum-base alloys are affected by IGC.

(iv) Galvanic Corrosion

When there exists an electric contact between two metals that are electrochemically dissimilar and are in an electrolytic environment, galvanic corrosion can arise. It refers to the degradation of one of these metals at a point or at a junction. A good example of this type of corrosion would be the degradation that occurs when copper, in a salt-water environment, comes in contact with steel.

Example: When aluminum and carbon steel are connected and immersed in seawater, aluminum corrodes faster and steel is protected.

(v) Pitting Corrosion

Pitting Corrosion is very unpredictable and therefore is difficult to detect. It is considered one of the most dangerous types of corrosion. It occurs at a local point and proceeds with the formation of a corrosion cell

surrounded by the normal metallic surface. Once this 'pit' is formed, it continues to grow and can take various shapes. The pit slowly penetrates metal from the surface in a vertical direction, eventually leading to structural failure if left unchecked.

Example: Consider a droplet of water on a steel surface, pitting will initiate at the centre of the water droplet (anodic site).

(vi) Uniform Corrosion

This is considered the most common form of corrosion wherein an attack on the surface of the metal is exerted by the atmosphere. The extent of the corrosion is easily discernible. This type of corrosion has a relatively low impact on the performance of the material.

Example: A piece of zinc and steel immersed in diluted sulphuric acid would usually dissolve over its entire surface at a constant rate.

(vii) Hydrogen Grooving

This is a corrosion of the piping by grooves that are formed due to the interaction of a corrosive agent, corroded pipe constituents, and hydrogen gas bubbles. The bubbles usually remove the protective coating once it comes in contact with the metal.

(viii) Metal Ductility

Metal ductility is a damaging form of corrosion that occurs when valuable materials are exposed to certain environments with high carbon activities including synthesis gas. The corrosion results in the break-up of bulk metal to metal powder. Corrosion occurs as a graphite layer is deposited on the surface of the metals from carbon monoxide (CO) in the vapour phase. This graphite layer then goes on to form meta-stable (M₂C) species where M is the metal that usually moves away from the metal surface. In some cases, no M₂C species may be observed. This means that the metal atoms have been directly transferred into the graphite layer.

(ix) Microbial Corrosion

Microbial corrosion which is also known as microbiologically influenced corrosion (MIC), is a type of corrosion that is caused by microorganisms. The most common one is chemoautotrophs. Both metallic and non-

metallic materials either in the presence or absence of oxygen can be affected by this corrosion.

(x) High-temperature Corrosion

High-temperature corrosion as the name suggests is a type of corrosion of metals (mostly metals) due to heating. Chemical deterioration of the material can occur due to a hot atmosphere that contains gases such as oxygen, sulfur, or other compounds. These compounds are capable of oxidizing materials (metals in this case) easily. For example, materials used in car engines have to resist sustained periods at high temperatures during which they can be affected by an atmosphere containing corrosive products of combustion.

Explain the free energy for corrosion reaction

Free Energy of a Corrosion Reaction

In electrical and electrochemical processes, electrical work is done as the product of charges moved (Q) times the potential (E) through which it is moved. If this work is done in an electrochemical cell in which the potential difference between its two half-cells is E, and the charge is that of one mole of electrons (1 mol e⁻), then the electrical work (W) done by the cell must be nE. In this relationship, the Faraday constant (F) is required to obtain coulombs from moles of electrons. In an electrochemical cell at equilibrium, no current flows and the energy change occurring in a reaction is expressed in equation:

$$\Delta G = -nFE$$

Under standard conditions, the standard free energy of the cell reaction ΔG° is directly related to the standard potential difference across the cell, E^o:

$$\Delta G^\circ = -nFE^\circ$$

For solid or liquid compounds or elements, standard conditions are the pure compound or element; for gases they are 100 kPa pressure; and for solutes they are the ideal 1 mol/l concentration.

Electrode potentials can be combined algebraically to give cell potential. For a galvanic cell, such as [The Daniell cell](#), a positive cell voltage will be obtained if the difference is taken in the usual way, as equation.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The free energy change in a galvanic cell in a spontaneous cell reaction is negative and cell voltage positive. The opposite is true in an electrolytic cell that requires the application of an external potential to drive the electrolysis reaction, in which case E_{ext} would be negative.

Define Solubility product [K_s]. Explain with an example

What is Solubility Product, K_s?

The solubility product constant is the equilibrium constant for the dissolution of a solid substance into an aqueous solution. It is denoted by the symbol K_s.

What is an Electrochemical cell or Galvanic cell? Give its representation

The devices in which electrical energy is produced from chemical reactions are called electrochemical cells or galvanic cells or voltaic cells.

In these cells, oxidation and reduction reactions occur in separate containers called half cells and the redox reaction is spontaneous. Electrical energy is produced during such reactions.

1) The arrangement consists of two beakers, one of which contains 1.0 M solution of zinc sulphate and the other 1.0 M solution of copper sulphate.

2) A zinc rod is dipped into ZnSO₄ solution while a copper rod is dipped into CuSO₄ solution. These metallic rods are known as electrodes.

3) The metallic rods in the beaker are connected to the ammeter by means of an insulated wire through a key.

4) Ammeter is used to know the passage of current which moves in opposite direction to the flow of electrons.

5) The solutions in the two beakers are connected by an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO₃, or NH₄NO₃ which does not undergo a chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.

6) The two openings of the U-tube are plugged with porous material such as glass wool or cotton. The U-tube which connects the two glass beakers is called a salt bridge.

7) When the circuit is complete by inserting the key in the circuit, it is observed that electric current flows through external circuit as indicated by the ammeter.

In an electrochemical cell, the anode is given a negative charge and cathode is given a positive charge. Give reasons.

Assertion

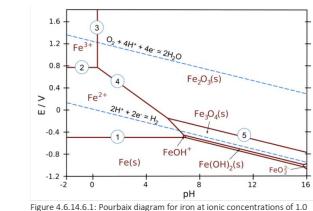


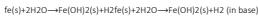
Figure 4.6.14.6.1: Pourbaix diagram for iron at ionic concentrations of 1.0 mM. (CC BY-SA 3.0 Imported; Metalls via [Wikimedia](#))

Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

1. $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ (e.g. $\text{Fe}^{2+} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2$) (pure redox reaction - no pH dependence)
2. $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{e}^-$ (e.g. $\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + \text{H}_3\text{O}^+$) (pure redox reaction - no pH dependence)
3. $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 2\text{e}^-$ (e.g. $\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + \text{H}_3\text{O}^+$)
4. $2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 2\text{e}^-$ (slope = $-59.2 \times 10^{-3} \text{ mV/pH}$)
5. $2\text{Fe}^{3+}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + 2\text{Fe}^{2+} + 2\text{e}^-$ (slope = $-59.2 \times 10^{-3} \text{ mV/pH}$)

The water redox lines have special significance on a Pourbaix diagram for an element such as iron. Recall that liquid water is stable only in the region between the dotted lines. Below the H₃O line, water is unstable relative to hydrogen gas, and above the O₂ line, water is unstable with respect to

oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H₃O line. This means that iron metal is unstable in contact with water, undergoing reactions:



Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O₂ line in the Pourbaix diagram. Here the spontaneous reactions are:



20. Define the following with example a) Plane of symmetry b) Centre of symmetry c) Alternating axis of symmetry

plane of symmetry with example



A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other, e.g. 1: In 1, the vertical plane that bisects the methyl group, the carbon atom, and the hydrogen atom bisects the molecule into halves that are mirror images of each other.

centre of symmetry

A centre of symmetry exists in a crystal if an imaginary line can be extended from any point on its surface through its centre and a similar point is present along the line equidistant from the centre.

alternating axis of symmetry with example



A molecules possess an alternating axis symmetry (Sn) of n fold if rotation of the molecule about the axis by 2π/n followed by reflection through a plane perpendicular to this axis produces an indistinguishable with the original.

It is also called rotation or reflection of symmetry. For example, 1,3,7,8-octamethyl-5-azaspiro[4.4] nonan-5-um have alternating axis of symmetry.

This compound possess alternating axis of symmetry and also has a plane of symmetry, so it is optically inactive.

Write a note on Geometrical isomerism

Geometrical isomerism

Geometrical isomerism is a type of stereoisomerism having the same molecular formula and same structure but differs in the relative arrangement of atoms. Geometrical isomerism, which arises commonly in heterocyclic complexes. This type of isomerism arises due to the different possible geometric arrangements for the ligand.

Examples

- But-2-ene

In one case, the CH₃ groups are on opposite sides of the double bond, and in the other case, they are on the same side.

In an electrochemical cell anode and cathode are respectively negative and positive electrodes.

Reason

At anode oxidation takes place and at cathode reduction takes place.

Anode (oxidation) for eq. $2\text{n} - 2\text{Zn} + 2\text{e}^- \rightarrow \text{Zn}_2^+$

Excess of electrons and hence negatively charged while cathode is positively charged.

With a neat sketch explain Pourbaix diagram for Iron

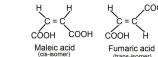
Example: Iron Pourbaix diagram

Across the in the Pourbaix diagram mark regions where a single species (Fe^{2+} (aq), $\text{Fe}_2\text{O}_3(\text{s})$, etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium.

- Pure redox reactions are horizontal lines - these reactions are not pH-dependent
- Pure acid-base reactions are vertical lines - these do not depend on potential
- Reactions that are both acid-base and redox have a slope of $-0.0592 \text{ V}/(\text{pH} - \text{pH}_0)$

Structures of maleic and fumaric acid



iii) $\text{CH}_5\text{-O-CH}_3$ and $\text{CH}_3\text{-O-CH}_3$ are metamer. So, the type of isomerism shown by diethyl ether and methyl propyl ether is metamerism.

What is Chirality? Differentiate Chirality and Achirality with example

The word chirality is used as a term to describe a molecule whose enantiomers are non-superimposable on their mirror images. A chiral molecule that contains a single stereogenic center may exist in an enantiopure form or as a mixture of enantiomers in varying ratios.

| CHIRAL VERSUS ACHIRAL | |
|--|---|
| Chiral means "asymmetric in such a way that the structure and its mirror image are not superimposable" | Molecules are always symmetric at every center |
| The molecule and its mirror image are the same | The molecule and its mirror image are superimposable |
| Molecules can rotate plane around a chiral center clockwise or anticlockwise | Molecules cannot rotate plane around a chiral center in any direction |
| Visit wikipedia | |

Difference between Enantiomers and Diastereomers.

5. Explain Sawhorse projection with an example.

Write notes on Structural isomerism with its types and give examples

Structural Isomers Definition

Structural isomers, or constitutional isomers, is a type of isomerism where isomers have same molecular formula but differ in functional group. Thus belong to different families of compounds or different homologous series. Structural isomers are also called skeletal isomers. For example dimethyl ether and ethanol are two structural isomers with the molecular formula $\text{C}_2\text{H}_6\text{O}$. Ethanol and dimethyl ether are those two functional group isomers. Here ethanol contains alcohol as functional group and dimethyl ether contains ether.

$\text{CH}_3\text{-O-CH}_3$ (skeletal structure)

$\text{CH}_3\text{-CH}_2\text{-OH}$ (Fischer projection)

\text