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Physical Chemistry

Class- F.Y.B.Sc.

Chapter 1: Chemical Energetics

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1. CHEMICAL ENERGETICS

THERMODYNAMICS:

THERMODYNAMICS IS A BRANCH OF PHYSICS THAT DEALS WITH HEAT, WORK, AND TEMPERATURE, AND THEIR RELATION TO ENERGY, RADIATION, AND PHYSICAL PROPERTIES OF MATTER. THE BEHAVIOR OF THESE QUANTITIES IS GOVERNED BY THE FOUR LAWS OF THERMODYNAMICS WHICH CONVEY A QUANTITATIVE DESCRIPTION USING MEASURABLE MACROSCOPIC PHYSICAL QUANTITIES, BUT MAY BE EXPLAINED IN TERMS OF MICROSCOPIC CONSTITUENTS BY STATISTICAL MECHANICS. THERMODYNAMICS APPLIES TO A WIDE VARIETY OF TOPICS IN SCIENCE AND ENGINEERING, ESPECIALLY PHYSICAL CHEMISTRY, BIOCHEMISTRY, CHEMICAL ENGINEERING .

STUDY OF THERMODYNAMICS IS BASED ON THREE LAWS FIRST, SECOND & THIRD LAWS OF THERMODYNAMICS.

~~ZEROTH LAW OF THERMODYNAMICS WHICH HELPS US TO UNDERSTAND THE CONCEPT OF TEMPERATURE WAS PUT FORWAORD.~~

Objective:-

Thermodynamics is very important branch of both chemistry and physics as it deals with the study of different forms of energy and conversion of energy between different forms.

- 1) To predict the feasibility of a process
- 2) To estimate yield of the products
- 3) To deduce some important relationships

LIMITATIONS OF THERMODYNAMICS

- The limitation of the first law of thermodynamics is that **it does not say anything about the direction of flow of heat.**
- It does not say anything whether the process is a spontaneous process or not. The reverse process is not possible. In actual practice, the heat doesn't convert completely into work.
- It deals with the properties like temperature, pressure etc of the matter in bulk or macroscopic quantities and not in microscopic quantities.
- Thus it deals with large groups of atoms, molecules and ions rather than individual atoms, molecules or ions.
- Its treatment is limited to the initial and final states of a system and is silent about the path by which the change is brought about that is it does not reveal the mechanism of a process.

ZEROth LAW OF THERMODYNAMICS

“The Zeroth Law of Thermodynamics states that if two bodies are each in thermal equilibrium with some third body, then they are also in equilibrium with each other”.

Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.

FIRST LAW OF THERMODYNAMICS

The **first law of thermodynamics** is a version of the law of Conservation of energy.

Statements:

- a) The law of conservation of energy states that the energy can be transformed from one form to another, but can be neither created nor destroyed.
- b) Total energy of an isolated system is constant, although it may undergo transformation from one form to the other.
- c) It is impossible to a machine which would produce work continuously without consuming energy.
- d) Whenever certain quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy must be produced.

MATHEMATICAL EXPRESSION OF FIRST LAW OF THERMODYNAMICS

IF HEAT Q IS SUPPLIED TO A SYSTEM, IT MAY BE USED UP PARTLY TO INCREASE THE INTERNAL ENERGY OF THE SYSTEM AND PARTLY TO DO SOME MECHANICAL WORK.

IF ΔU IS THE INCREASE IN INTERNAL ENERGY OF THE SYSTEM AND W IS THE WORK DONE BY THE SYSTEM, THEN

$$\Delta U = q + w$$

IF THE WORK DONE OF EXPANSION

$$W = - P \Delta V$$

FOR SMALL CHANGES IT CAN BE

$$DQ = DU + PDV$$

SECOND LAW OF THERMODYNAMICS

1. ALL SPONTANEOUS PROCESSES LIKE THE FLOW OF HEAT FROM HOT END TO COLD END, DIFFUSION OF GAS FROM HIGH PRESSURE TO LOW PRESSURE OR THE FLOW OF WATER DOWN A HILL ETC. ARE THERMODYNAMICALLY IRREVERSIBLE.
2. THE COMPLETE CONVERSION OF HEAT INTO WORK IS IMPOSSIBLE WITHOUT LEAVING SOME EFFECTS ELSEWHERE.
3. IT IS IMPOSSIBLE ~~TO CONSTRUCT A MACHINE FUNCTIONING IN CYCLES, WHICH~~ CAN CONVERT HEAT COMPLETELY INTO THE EQUIVALENT AMOUNT OF WORK WITHOUT PRODUCING CHANGES.
4. WITHOUT THE USE OF AN EXTERNAL AGENCY, HEAT CANNOT BY ITSELF PASS FROM A COLDER TO A HOTTER BODY.

DEFINATIONS OF CERTAIN THERMODYNAMICS TERMS

1.SYSTEM AND SURROUNDINGS:

THE PART OF THE UNIVERSE CONSIDERED FOR THERMODYNAMICS STUDIES,TO STUDY THE EFFECT OF TEMPRATURE,PRESSURE ETC IS CALLED **A SYSTEM**.

2.OPEN,CLOSED AND ISOLATED SYSTEM:

OPEN SYSTEM:

A SYSTEM WHICH CAN EXCHANGE BOTH MATTER AND ENERGY WITH THE SURROUNDING IS CALLED OPEN SYSTEM.

CLOSED SYSTEM:

A SYSTEM CAN EXCHANGE ONLY ENERGY WITH THE SURROUNDING BUT NOT MATTER,IS CALLED A CLOSED SYSTEM.

ISOLATED SYSTEM :

A SYSTEM WHICH CAN EXCHANGE NEITHER MATTER NOR ENERGY WITH THE SURROUNDING,IS CALLED ISOLATED SYSTEM.



Example of open, closed and isolated system :

open system- matter and energy can exchange with surroundings

beaker of water- water can evaporate and beaker does not insulate

closed system- energy can exchange with surroundings

sealed beaker of water does not insulate

isolated system- nothing exchanges with surroundings

combustion of glucose in a bomb calorimeter

3. HOMOGENEOUS SYSTEM:

A SYSTEM IS CALLED AS HOMOGENEOUS IF IT IS UNIFORM THROUGHOUT IS CALLED **HOMOGENEOUS SYSTEM**
EX- A GAS OR A MIXTURE OF GASES OR A PURE LIQUID OR SOLID OR SOLUTION OF A SOLID IN LIQUID .

4. HETEROGENEOUS SYSTEM:

A SYSTEM WHICH IS NOT UNIFORM THROUGHOUT IS CALLED **HETEROGENEOUS SYSTEM.**

EX-A SYSTEM CONSISTING A LIQUIDS & ITS VAPOUR
TWO OR MORE IMMISCIBLE LIQUIDS
A MIXTURE OF TWO OR MORE SOLIDS.

5. MACROSCOPIC SYSTEM:

A SYSTEM CONTAINING A LARGE AMOUNT OF THE SUBSTANCE IS CALLED MACROSCOPIC SYSTEM.

EX- ATOMS, IONS, MOLECULES.

6.MACROSCOPIC PROPERTY:

A PROPERTY RELATED TO THE BEHAVIOUR OF PARTICLES IN A MACROSCOPIC SYSTEM IS CALLED A MACROSCOPIC PROPERTY. EX- PRESSURE,VOLUME,TEMPRATURE,SURFACE TENSION,VISCOSITY,DENSITY,REFRACTIVE INDEX.



THERMODYNAMICS PROCESSES

1. ISOTHERMAL PROCESS:

THE **TEMPERATURE** OF THE SYSTEM REMAINS CONSTANT THROUGHOUT THE PROCESS IS CALLED ISOTHERMAL PROCESS.

2. ADIABATIC PROCESS:

IF A PROCESS IS CARRIED OUT IN SUCH A WAY THAT NO **HEAT FLOW** FROM THE SYSTEM TO THE SURROUNDING.

3. ISOCHORIC PROCESS:

THE **PRESSURE** OF THE SYSTEM REMAINS CONSTANT IS CALLED ISOCHORIC PROCESS.

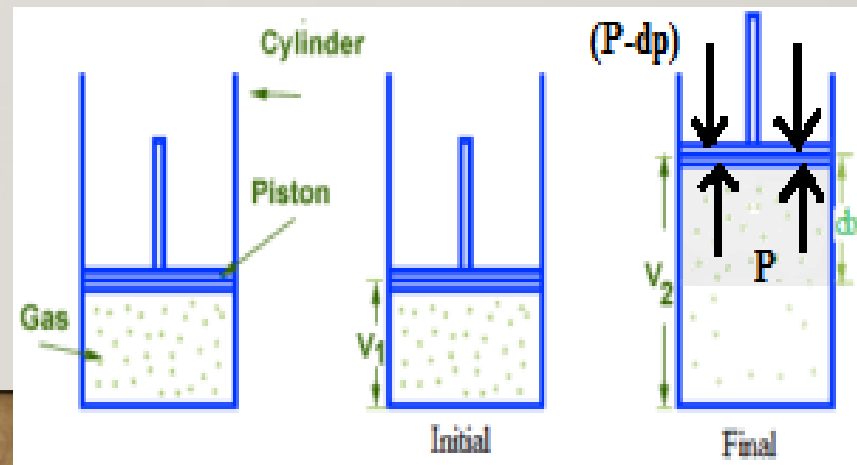
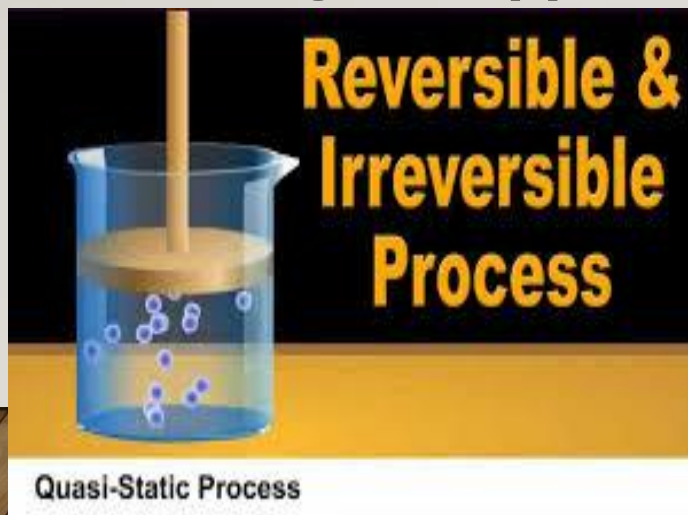
4. ISOBARIC PROCESS:

THE PROCESS IN WHICH **VOLUME** OF THE SYSTEM REMAINS CONSTANT IS CALLED ISOBARIC PROCESS.

5. REVERSIBLE PROCESS:

it is define as a process which is carried out infinitesimally slowly such that all changes occurring in the direct process can be exactly reversed and the system appears to be in a state of equilibrium at each moment.

a reversible process may also be define as “a process which is carried out in such a way that at every stage driving force is only infinitesimally greater than the opposing force and which can be reversed by increasing the opposing force by an infinitesimally



6. IRREVERSIBLE PROCESS:

AN IRREVERSIBLE PROCESS IS DEFINED AS THAT PROCESS WHICH IS NOT CARRIED OUT INFINITESIMALLY SLOWLY SO THAT THE SUCCESSIVE STEPS OF THE DIRECT PROCESS CAN NOT BE RETRACED AND ANY CHANGES IN THE EXTERNAL CONDITIONS DISTURBS THE EQUILIBRIUM.

AN IRREVERSIBLE PROCESS OCCURS WHEN CARRIED OUT RAPIDLY OR FAST.

ALL NATURALLY OCCURRING PROCESSES LIKE THE FLOW OF WATER DOWN A HILL OR THE FLOW OF HEAT FROM A HOT END TO COLD END OF AN IRON BAR ETC. ARE THERMODYNAMICALLY IRREVERSIBLE.



What is Standard State?

- Standard State: A precisely defined reference state. It is a common reference point that one can use to compare thermodynamic properties.
- Definitions of Standard State:
 - For a gas: $P = 1 \text{ atm}$.
 - For solutions: 1 M (mol/L) .
 - For liquids and solids: pure liquid or solid
 - For elements: The form in which the element exists under conditions of 1 atm and 298 K .

Caution! Not STP (for gas law problems, 273 K)

Standard Enthalpy of Formation and Reaction

Standard Enthalpy of Formation

- ΔH has no absolute value – only relative values
- ΔH_f° : 1) standard enthalpy of formation
2) Zero for any element in its most stable form at standard-state conditions (25°C & 1 atm)

e.g., $O_2 = 0$ kJ/mole

$O_3 = 143$ kJ/mol

$O = 249$ kJ/mol

Standard Enthalpies of Formation

- The **law of summation of heats of formation** states that the enthalpy of a reaction is equal to the total formation energy of the products minus that of the reactants.

$$\Delta H^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum m\Delta H_f^{\circ}(\text{reactants})$$

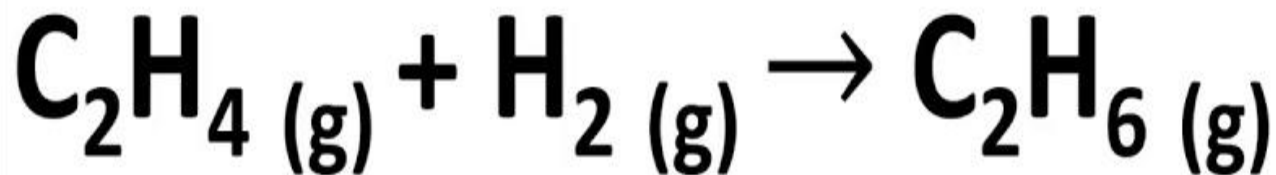
- Σ is the mathematical symbol meaning “the sum of”, and m and n are the coefficients of the substances in the chemical equation.



Formation Reactions

- In a **formation reaction**, a substance is formed from elements in their standard states.
- From what elements is water formed?
- $\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta H_f^\circ = -285.8 \text{ kJ}$
- The enthalpy change of a formation reaction is called the **standard molar enthalpy of formation**, ΔH_f° .

$$\Delta H^\ominus = \sum \Delta H_c^\ominus \text{ (reactants)} - \sum \Delta H_c^\ominus \text{ (products)}$$



$$\Delta H^\ominus = (-1411 + -286) - (-1561)$$

$$\Delta H^\ominus = -136 \text{ kJ mol}^{-1}$$

	ΔH_c^\ominus
C_2H_4	-1411
H_2	-286
C_2H_6	-1561

Standard enthalpy change of combustion



The enthalpy change when **one mole** of an element or compound reacts completely with oxygen under standard conditions.



Combustion Reaction Demonstration

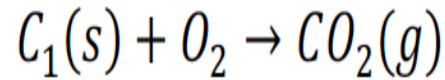
What is standard enthalpy change of combustion?

- The standard enthalpy of combustion is the enthalpy change that occurs when *one mole* of substance *burns completely* under the *standard conditions of 25 °C and 1 atm*.



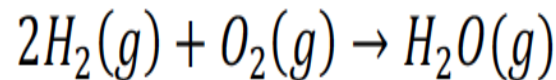
- ⊙ The standard enthalpy of combustion is always negative

-Combustion of elemental carbon :



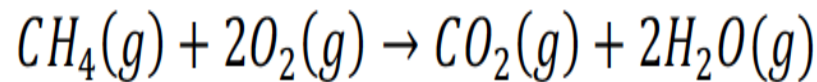
with enthalpy of combustion : $\Delta H_{form}^0(CO_2) = [-393 - (0 + 0)] \frac{kJ}{mol} \equiv -393 \frac{kJ}{mol}$

-Combustion of elemental di-atomic hydrogen:



with enthalpy of combustion: $\Delta H_{form}^0(H_2O(g)) = -286 \frac{kJ}{mol}$

-Combustion of methane:



With enthalpy of combustion:

$$\Delta H_{comb}^0(CH_4) = \Delta H_{form}^0(CO_2) + 2 \cdot \Delta H_{form}^0(H_2O(g)) - \Delta H_{form}^0(CH_4) \equiv -892 \frac{kJ}{mol}$$

$$\rightarrow \Delta H_{form}^0(CH_4) \equiv -393 \frac{kJ}{mol} + 2 \cdot \left(-286 \frac{kJ}{mol} \right) + 892 \frac{kJ}{mol} = -73 \frac{kJ}{mol}$$