III YEAR

SEMESTER-V

Paper – V: (INORGANIC, PHYSICAL & ORGANIC CHEMISTRY)

UNIT- V. Thermodynamics

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Thermodynamics

Definition:-

The term thermodynamics is made up of two words thermo means heat and dynamic means motion leading to work as it is a branch of science which deals with conversion of heat into mechanical work and vice versa.

First law of thermodynamics:-
Different statements of law

1.The first law of thermodynamics is simply the law of conservation of energy that is energy can neither be created nor be destroyed but it can be converted from one form to another.

2. There is an exact equivalence between heat and work that is a quantity of some form of energy disappears and exactly equivalent amount of a some other form of energy will appear.

3. It is impossible to construct a perpectual motion machine that could produce work without consuming any energy.

4. The sum of energies of the system and the surroundings remains constant however energy is shared differently between the two.

5. The total energy of an isolated system remains constant although it can change from one form to another.

Mathematical form of first law of thermodynamics is given below

The First Law of Thermodynamics

The internal energy E of a system tends to increase, if energy is added as heat Q and tends to decrease if energy is lost as work W done by system

$$dE = dQ - dW \text{ (first law)}$$

(*Q* is the heat absorbed and *W* is the work done by the system)

- ✓ The quantity *(Q - W)* is the same for all processes
- ✓ It depends only on the initial and final states of the system
- ✓ Does not depend at all on how the system gets from one to the other
- ✓ This is simply conservation of energy

Internal energy (U):-

1.Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temperature, pressure and volume.

2.This energy is known as internal energy the exact magnitude of this energy is not known but the internal energy of a substance or a system is a definite quantity and it is a function only of the state of the system at the given the moment irrespective of the manner in which the state has been brought about.

3. It is a denoted by the letter U or E

Change in internal energy:-

- Let UAand UB are the internal energies of a system at state A and state B.
- suppose the system while undergoing change from state A to state B absorbs some q amount of heat and also performs some work w.
- The mathematical form is given below

- $\Delta U = q + w$

- Here ΔU is the change in internal energy
- q amount of heat supplied to the system
- W is the work done

- If work is done by the surroundings on this system w is taken as positive$\Delta U=q+w$ (compression of a gas)

- If work is done by the system on the surroundings w is taken as negative so that$\Delta U=q-w$ (expansion of gas)

Enthalpy:-

Like internal energy enthalpy is also a heat or energy term so that we can measure the change in enthalpy only.

The total amount of heat content or energy of a system at constant pressure is called as enthalpy.

Suppose a system of volume VA expands to volume VB at constant pressure then the work done by the system will be given by

$W=-P(VB-VA)$_____ 1

From internal energy definition

$\Delta U=q- p(VB-VA)$

$UB-UA=q-pVB+pVA$

$UB+pVB=q+UA+pVA$

$(UB+pVB)-(UA+pVA)=q$_____2

Here

ΔU is change in internal energy

VA and VB are volumes of the system at state A and State B

UA and UB are internal energies in state A and state B
P pressure

q amount of heat absorbed

The quantity U+PV is known as enthalpy of the system and is denoted by **H**

It represents the total energy stored in the system.

In the above expression U P V are definite quantities so that H is also definite quantity so that change in enthalpy is given by

$H_A - H_B = \Delta H = q$ _____ 3

$$HA-HB=\Delta H=q \quad \underline{\qquad\qquad} \quad 3$$

$$\Delta H=(UB+pVB)-(UA+pVA)$$

$$\Delta H=(UB-UA)+(pVB+pVA)$$

$$\Delta H=\Delta U+p\Delta V$$

- If the quantity ΔH=+ve then the reaction is endothermic

- If the quantity ΔH=-ve then the reaction is exothermic.

Thank you