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Semester - II (GE2)

Topic - First law of thermodynamics

1. **Thermodynamic co-ordinates :=**

The macroscopic quantities which have bearing on the internal state of the system. These quantities are called thermodynamic co-ordinates.

Thermodynamic co-ordinates are -

Pressure (P)
Volume (V)
temperature (T)
entropy (S)

2. **Thermodynamic System :=** A thermodynamic system is one which can be described in terms of thermodynamic co-ordinates.

eg - gas, vapour.

3. **Zeroth law of thermodynamics :=** If two systems are in thermal equillibrium with the third one then they are in thermal equillibrium to each other.

## 4. Concept of temperature from Zeroth Law –



Let two system B and A are in thermal equillibrium heat transfer does not take place between them. Hence the physical parameter which determine wheather heat flow takes place or not must have the same value.

Similarly the system c must have the same value of physical parameter. This physical parameter is termed as temperature whose difference leads to flow of heat.

## 5. First law of thermodynamics :–

We know that whenever work is done an equivalent amount of heat is produced and whenever certain amount of heat disappears, it appears in the form of work. This is the keynote of first law of thermodynamics ie principle of conservation of energy.

**Statement :-** When a system is subjected to a cyclic transformation, the work produced in the surroundings is equal to the heat withdrawn from the surroundings.

ie $\oint dw = \oint dQ$

or, $\oint (dQ - dw) = 0$

Since cyclic integral of the integrand vanishes, the diff. $(dQ - dw)$ is must be an exact differential du ie u must be state function. u is known as internal energy function.

Hence first law of thermodynamics can be written mathematically as –

$$dQ - dw = du$$

or, $dQ = du + dw$

or, $\boxed{dQ = du + pdv}$

Note- ① First law is applicable to all states of matter (solid, liquid, and gas) and any type of transformation.

② First law gives the existance of internal energy function.

③ First law is based on Principle of conservation of energy.

④ First law gives the defination of heat as energy.

6. Application of first law of thermodynamics :-

1. Cyclic Process :- The Process in which the substance returns to the initial state after a series of change, is called cyclic Process.

For cyclic Process total change of internal energy must be zero. ie $\oint du = 0$

Hence 1st law for cyclic Process $\oint dQ = \oint dw$.

2. Specific heat at constant volume :-

$$c_v = \left(\frac{\partial Q}{\partial T}\right)_V$$

From 1st law, $dQ = du + pdv$

$$\text{or, } \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V$$

$$\text{or, } c_v = \left(\frac{\partial u}{\partial T}\right)_V$$

$$\text{or, } du = c_v dT$$

3. Specific heat at constant Pressure :-

$$c_p = \left(\frac{\partial Q}{\partial T}\right)_P$$

From 1st law. $dQ = du + dw$

$$\text{or, } dQ = du + pdv$$

or, $\left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial T}\right)_P$

or, $C_P = \left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial T}\right)_P$

4. **Difference between two specific heats :-**

$$c_p - c_v = \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V$$

$$= \left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial T}\right)_P - \left(\frac{\partial u}{\partial T}\right)_V \quad \cdots (1)$$

Again, $u = f(v, T)$

Differentiating partially; $du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_V dT$

or, $\left(\frac{\partial u}{\partial T}\right)_P = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial u}{\partial T}\right)_V \quad \cdots (2)$

From equation (1) and (2)

$$c_p - c_v = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial u}{\partial T}\right)_V + P\left(\frac{\partial v}{\partial T}\right)_P - \left(\frac{\partial u}{\partial T}\right)_V$$

$$\therefore c_p - c_v = \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right]\left(\frac{\partial v}{\partial T}\right)_P$$

5. **Prove that for 1 mole of ideal gas $c_p - c_v = R$**

Ans:- For ideal gas $\left(\frac{\partial u}{\partial v}\right)_T = 0$

Hence for ideal gas $c_p - c_v = P\left(\frac{\partial v}{\partial T}\right)_P$

For one mole ideal gas, ~~$c_p - c_v = P\left(\frac{\partial v}{\partial T}\right)_P$~~

$PV = RT$

or, $V = \frac{RT}{P}$

or, $\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$

$\therefore \quad c_p - c_v = P \cdot R/P = R$ (Proved)

6. Prove that for n mole of ideal gas $c_p - c_v = nR$

Ans:- For ideal gas, $\left(\frac{\partial u}{\partial v}\right)_T = 0$

Hence for ideal gas $c_p - c_v = P\left(\frac{\partial v}{\partial T}\right)_P$

For n mole of ideal gas, $PV = nRT$

or, $V = \frac{nRT}{P}$

or, $\left(\frac{\partial v}{\partial T}\right)_P = \frac{nR}{P}$

$\therefore \quad c_p - c_v = P \cdot \frac{nR}{P} = nR$ (Proved)

7. Internal energy :- Depending on the nature of the body and also at a particular state on the internal condition of the body, it posses some energy, called internal energy.

The internal energy is a single valued state

ie if the body comes back to the initial state after a cycle of operation, the change of internal energy is zero.