

①

Dr. Hazi Darrkhom Sijm.

Asso. Prof.

Dept. of Physics.

D.P.I Physics -Applications of First Law of Thermodynamics:-

In case of gas, any two of the variables

P, V, T are sufficient to define completely its state.

If V and T are chosen as the independent variables,

Internal energy,

$$U = f(V, T) \rightarrow \text{①}$$

Differentiating this equation,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \rightarrow \text{②}$$

If an amount of heat  $\delta Q$  is supplied to a thermodynamical system, say an ideal gas and if the volume increases by  $dV$  at a constant pressure

P, then according to the first law of thermodynamics,

$$\delta Q = dU + \delta W$$

where,  $\delta W = P \cdot dV$ .

$$\therefore \delta Q = dU + P dV$$

Substituting the values of  $dU$  from equation ②.

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV \rightarrow \text{③}$$

②

Dividing both sides by  $\delta dT$ .

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + P \frac{dV}{dT}$$

$$\text{or, } \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \frac{dV}{dT} \rightarrow \textcircled{IV}$$

If the gas is heated at constant volume,

$$\left(\frac{\delta Q}{dT}\right)_V = C_V$$

$$\text{and, } \frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \rightarrow \textcircled{V}$$

When the gas is heated at constant pressure,

$$\frac{\delta Q}{dT} = C_P$$

From equation (IV) we have,

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_P = C_V + \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P \rightarrow \textcircled{VI}$$

From Joule's experiment, for an ideal

(3)

On opening the stopcock, ~~no~~ no-work was done and no heat transfer took place.

So,  $\delta Q = 0 = dU \neq 0$ , therefore,  $dU = 0$

Even though the volume changed while the temp. is constant, there is no change in internal energy;

$$\left(\frac{\partial U}{\partial T}\right)_T = 0$$

For an ideal gas equation,

$$PV = RT.$$

$$\text{or } P \left(\frac{\partial V}{\partial T}\right)_P = R. \rightarrow \text{(vi)}$$

$$\therefore C_p - C_u = P \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

$$\text{But, } \left(\frac{\partial U}{\partial V}\right)_T = 0.$$

$$\therefore C_p - C_u = P \left(\frac{\partial V}{\partial T}\right)_P = R.$$

$$\text{or } \boxed{C_p - C_u = R}. \rightarrow \text{(vii)}$$

This formula is known as Mayer's relation. Here,  $C_p$ ,  $C_u$ , and  $R$  are expressed in the same unit.

(4)

From equation (iii),

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \rightarrow (ix)$$

For a process at constant temperature,

$$dT = 0.$$

$$\therefore (\delta Q)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \rightarrow (x)$$

This equation represents the amount of heat energy supplied to a system in an isothermal reversible process and is equal to the sum of the work done by the system and increase in its internal energy.

For a Reversible Adiabatic process -

For this,  $\delta Q = 0$ .

Since  $Q$  is constant during adiabatic process

therefore, from equation (ix)

$$C_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV = 0$$

$$\therefore C_V dT = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV.$$

Dividing through-out by  $dV$ .

$$C_V \left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \rightarrow (xii)$$

(5)

The isobaric volume coefficient of expansion,

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P.$$

$$\alpha V = \left( \frac{\partial V}{\partial T} \right)_P.$$

we have,  $C_p - C_v = P \left( \frac{\partial V}{\partial T} \right)_P.$

$$\therefore \frac{C_p - C_v}{\alpha V} = P.$$

But,  $\left( \frac{\partial U}{\partial V} \right)_T = 0 = P - P.$

$$\text{or, } \left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{C_p - C_v}{\alpha V} \right) - P \quad \text{--- (iii)}$$

$$\text{or, } \left( \frac{C_p - C_v}{\alpha V} \right) = - \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \quad \text{--- (iv)}$$

From equation (iii) and (iv) we get,

$$C_v \left( \frac{\partial T}{\partial V} \right) = - \left( \frac{C_p - C_v}{\alpha V} \right)$$

$$\text{or } \left( \frac{\partial T}{\partial V} \right) = \frac{C_v - C_p}{\alpha V \cdot C_v}.$$

This expression holds good for  
an adiabatic reversible process.