

So, we know for 1 mole of a gas $PV = RT$ and.

Hence, $P \left(\frac{dV}{dT} \right)_P = R \cdot \left(\frac{dT}{dT} \right)_P \Rightarrow P \left(\frac{dV}{dT} \right)_P = R$

and at constant temp.

change in internal energy is zero, so,

$$\left(\frac{dU}{dV} \right)_T = 0$$

therefore $C_p - C_v = R + 0 \times \left(\frac{dV}{dT} \right)_P = R$

$$\Rightarrow \boxed{C_p - C_v = R}$$

Prove $c_p - c_v = R$

The heat required to raise the temp of 1 mole of a substance by 1K or 1°C is called molar heat capacity.

It is denoted by "c"

For gases heat can be absorbed at constant volume or at constant pressure. so for gases, there are two types of heat capacity. the heat capacity may vary with temp. it is preferable to write $c = \frac{q}{dt} \Rightarrow q = c dt$

where q is infinitesimally small. heat absorbed to raise the temp by dt . thus, the heat capacity at constant volume c_v is given by $c_v = \frac{q_v}{dt}$, or $c_v = \frac{dU}{dt}$

similarly, the heat capacity at constant pressure c_p is given by $c_p = \frac{q_p}{dt} \Rightarrow c_p = \frac{dH}{dt}$.

Difference in heat capacities \Rightarrow

$$c_p - c_v = \frac{q_p}{dt} - \frac{q_v}{dt} \Rightarrow c_p - c_v = \left(\frac{dH}{dt}\right)_p - \left(\frac{dU}{dt}\right)_v$$

we know that

$$H = U + pV$$

Differentiating both side wrt temp. at constant pressure we get

$$\left(\frac{dH}{dt}\right)_p = \left(\frac{dU}{dt}\right)_p + p\left(\frac{dV}{dt}\right)_p$$

putting this value, we get

$$c_p - c_v = \left(\frac{dH}{dt}\right)_p - \left(\frac{dU}{dt}\right)_v \Rightarrow c_p - c_v = \left(\frac{dU}{dt}\right)_p + p\left(\frac{dV}{dt}\right)_p - \left(\frac{dU}{dt}\right)_v$$

we know, internal energy U depend on v and T
 $U = f(v, T)$ and dU is an exact differential

So, we have

$$dU = \left(\frac{dU}{dv}\right)_T dv + \left(\frac{dU}{dT}\right)_v dt$$

dividing both sides by dt at constant p , we get

$$\left(\frac{dU}{dt}\right)_p = \left(\frac{dU}{dv}\right)_T \left(\frac{dV}{dt}\right)_p + \left(\frac{dU}{dT}\right)_v \frac{dt}{dt}$$

$$\Rightarrow \left(\frac{dU}{dt}\right)_p = \left(\frac{dU}{dv}\right)_T \left(\frac{dV}{dt}\right)_p + \left(\frac{dU}{dT}\right)_v$$

putting this value in $c_p - c_v$ eqⁿ we have.

$$c_p - c_v = \left(\frac{dU}{dv}\right)_T \left(\frac{dV}{dt}\right)_p + \left(\frac{dU}{dT}\right)_v + p\left(\frac{dV}{dt}\right)_p - \left(\frac{dU}{dT}\right)_v$$

$$\text{so, } c_p - c_v = p\left(\frac{dV}{dt}\right)_p + \left(\frac{dU}{dv}\right)_T \left(\frac{dV}{dt}\right)_p$$

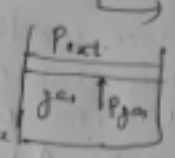
WORK → It is the form of energy which transfer with any means other than temperature difference.

Work $\xrightarrow[100\% \text{ convert in Heat}]{Q}$



Forcing $\bar{F}_{pushing}$ = Large difference
 $P_{ext} = \text{constant}$

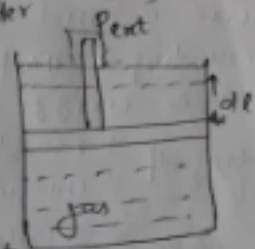
WORK → PV work as expansion or compression
 non PV work, Electrical or Mechanical work



$P_{ext} = -P_{gas}$
 $dw_{gas} = +P_{gas} \cdot dv$

Work done in a system, Isothermal irreversible process →

Suppose a cylinder vessel containing gas, the cylinder is fitted with weight less or friction less piston. the area of cross-section is $A \text{ cm}^2$



Let the pressure exerted by a gas Against surrounding = P_{ext} . then work done in Isothermal irreversible process = Force x displacement

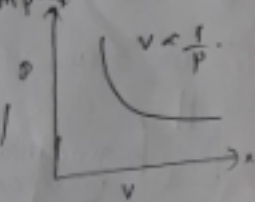
$W_{irr} = F \cdot dx$, $\therefore P = \frac{F}{A} \Rightarrow F = P \cdot A$

$\therefore W_{irr} = P_{ext} \cdot A \cdot dx$

$\Rightarrow W_{irr} = -P_{ext} \cdot dv$ $\Rightarrow W_{irr} = -P_{ext} \cdot dv$

$W_{irr} = -P_{ext} \cdot (V_2 - V_1)$

Case I $V_2 > V_1$, $\Delta V = +ve$, $W_{irr} = -P_{ext} \Delta V = -ve$ expansion work
 Case II $V_2 < V_1$, $\Delta V = -ve$, $W_{irr} = -P_{ext} \Delta V = +ve$ compression work.



work is a path function $W_{irr} \neq W_{rev}$

work done in reverse process = area under the graph = $|W|$

Problem based on 1st law of thermodynamics

work done = area under the graph

work done = area of trapezium

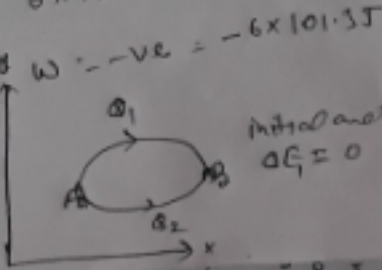
$W = \frac{1}{2} (\text{sum of parallel sides}) \times \text{height}$

$W = \frac{1}{2} (2 + 4) \times 2$

$W = 6 \text{ atm}\cdot\text{L}$

$\therefore 1 \text{ atm}\cdot\text{L} = 101.3 \text{ J}$, $\therefore 6 \times 101.3 \text{ J}$

Q2 (a) $Q_1 > Q_2$ (b) $Q_2 > Q_1$ (c) $Q_1 = Q_2$
 (d) none of the above
 1st law of thermodynamics
 $Q = \Delta U + W$
 $Q_1 + W_1 = Q_2 + W_2$
 $\therefore Q_1 > Q_2 \Rightarrow W_1 > W_2$



initial and final law
 $\Delta Q = 0$, $\Delta U = 0$