Chemical Energetics
(Thermodynamics)

What is thermodynamics?

It deals with the relationship between heat and work.

Importance:

It helps us to predict the direction and feasibility of a chemical reaction.

Important Terms In Thermodynamics :-

1) System - The part of the universe under study.

- Open (Both matter and energy can be exchanged)
- Closed (Only energy can be exchanged)
- Isolated (Neither energy nor matter can be exchanged)

2) Surroundings - The part of the universed separated from the system by a boundary.

[System + Surroundings = Universe]

3) Boundary - The region separating system and surroundings.

- Diathermal (Heat transfer is allowed)
- Adiabatic (Heat transfer not allowed)

4) Processes (Path) — A path along which change of state takes place.

i) Isothermal : Temperature is constant.

$$\Delta T = 0$$

ii) Isobaric : Pressure is constant

$$\Delta P = 0$$

iii) Isochoric : Volume is constant

$$\Delta V = 0$$

iv) Adiabatic : Heat transfer not allowed

$$q = 0$$

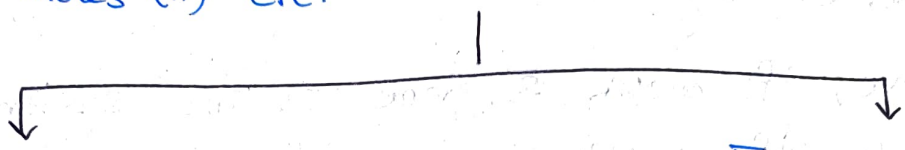
v) Cyclic : Initial and final state of the system are identical.

Reversible and Irreversible Processes :-

If both the system and surroundings return to their original state after a series of changes, the process is called reversible. It occurs in infinitesimally small steps.

Most processes take finite time to complete and are called irreversible processes.

State Variables – The state of a system can be defined by giving some values of variables e.g. – Pressure, Volume, Temperature, number of moles (n) etc.



Intensive
(Independent of mass)
e.g. P, T, density

Extensive
(Depends on mass)
e.g. V, n, energy

Zeroth Law of Thermodynamics :–

If three systems A, B and C are in thermal contact, then they have a common property i.e., temperature. If B is removed, and A and C are brought in contact, no heat exchange occurs.

Heat and Work :–

1) Heat – It is the energy transfer due to the temperature difference between system and surroundings. It appears at the boundary of the system only when the system undergoes any change in state. It is represented by 'q'.

q = +ve, if heat is absorbed by the system

q = –ve, if heat is released by the system

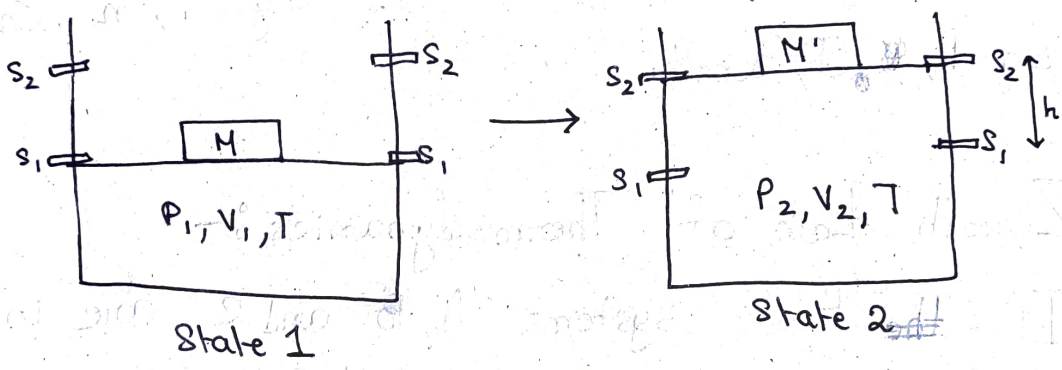
2) Work — It is the energy transfer between the system and surroundings due to macroscopic unbalanced force acting on the system. It is represented by 'w'.

w = +ve, if work is done on the system

w = -ve, if work is done by the system.

Expression of work :-

Work of expansion —



i) A cylinder containing an ideal gas is fitted with a piston.

ii) In the initial state, the variables are P_1, V_1, T. The area of cross-section is A.

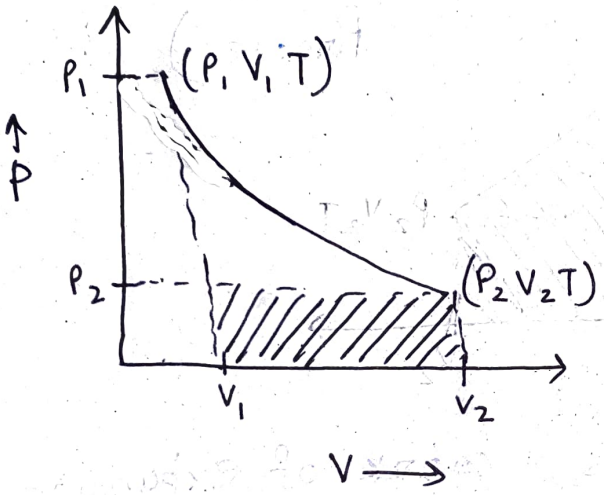
iii) Now the mass M is replaced by M' so, that the piston stops at S_2.

$$\text{Work} = -\text{Force} \times \text{displacement}$$

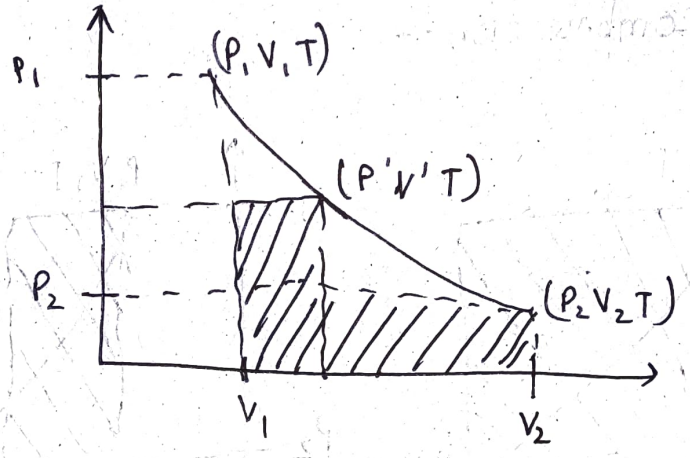
$$= -\left(\frac{F}{A}\right) \times (h \times A)$$

$$= -P_{ext} \times \Delta V$$

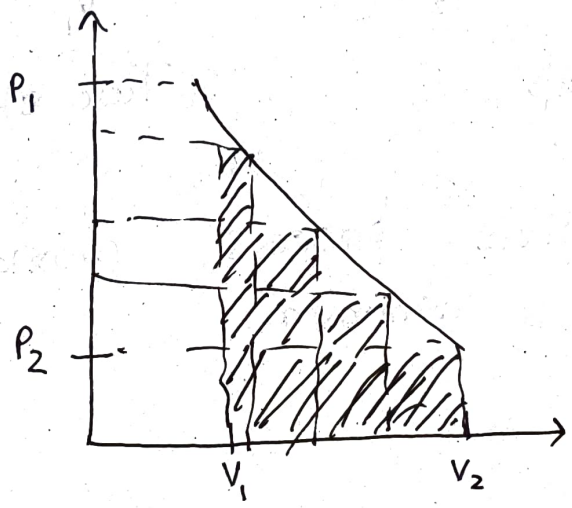
Now if the expansion is carried out in a single step, then the work done is given by the shaded area in Fig 1.



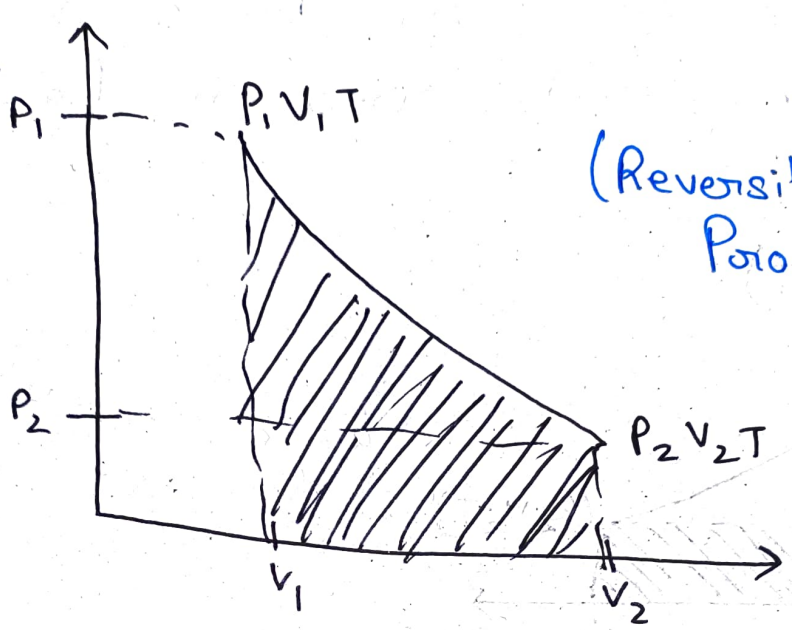
If it occurs in two steps, then



If it occurs in ~~infinites~~ multiple steps then



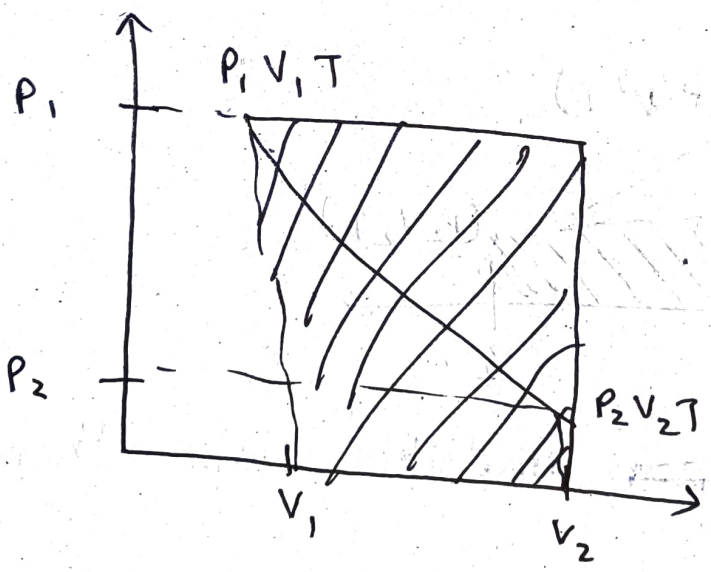
For infinitesimally number of small steps -



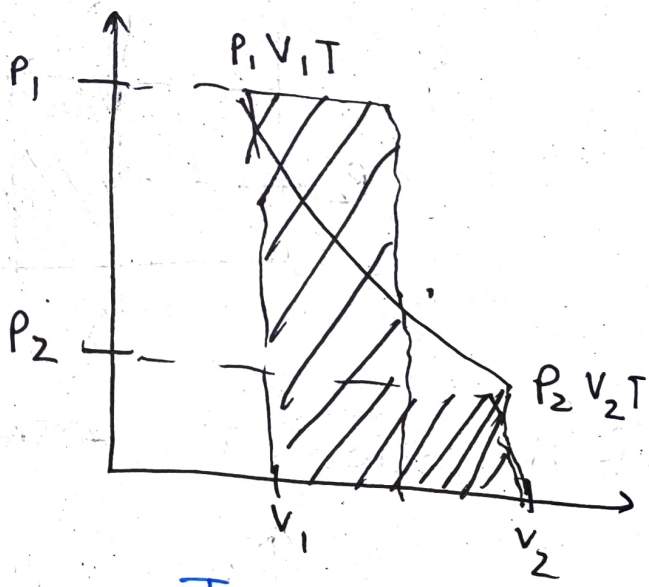
(Reversible Process)

- For a reversible process, work of expansion is maximum.

Work of compression -



One step



Two step

- For a reversible process, work of compression is minimum.

Work done during Isothermal Reversible Process :—

$$W_{rev} = -\int_{V_1}^{V_2} P_{ext} \cdot dV$$

$(P_{ext} = P_{int} \pm dP)$

$$\therefore W_{rev} = -\int_{V_1}^{V_2} (P_{int} \pm dP) \cdot dV$$

$$= -\int_{V_1}^{V_2} P_{int} \cdot dV \pm \int_{V_1}^{V_2} dP \cdot dV$$

($dP \cdot dV \to 0$)

$$= -\int_{V_1}^{V_2} P_{int} \cdot dV$$

For an ideal gas, $PV = nRT$

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

$$\therefore W_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\left[W_{rev} = -2.303\ nRT \log\left(\frac{V_2}{V_1}\right)\right]$$

For a real gas,

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\therefore W_{rev} = -\int_{V_1}^{V_2} \left[\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right] dV$$

$$\left[W_{rev} = -nRT \ln\left(\frac{V_2-nb}{V_1-nb}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \right]$$

For irreversible process—

$$W_{irr} = -P_{ext} \cdot dV$$
$$= -P_{ext}(V_2 - V_1)$$
$$= -P_2(V_2 - V_1)$$
$$= -P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$\left[W_{irr} = -nRT\left(1 - \frac{P_2}{P_1}\right) \right]$$

State Function and Path Function :—

If a function depends only on the state of the system and not on the path by which the state has been attained are called state functions. E.g. Enthalpy (H), Internal Energy (U) etc.

If the function depends on the path or, process, then it is called path function. E.g. Heat (q), Work (w).

- State functions are exact differential but path functions are not.
- The integration of exact differential over a cyclic path is zero.

$$\oint U = 0$$

Internal Energy and First Law of Thermodynamics :-

Internal Energy (U) = ~~Sum of kinetic, potential~~

The energy possessed by a system by virtue of the motion of atoms and molecules. It is an extensive property and state function.

First Law : The sum total energy of the universe is constant.

If a system is in state 1, has internal energy U_1. 'q' amount of heat is given to the system. The system does 'ω' amount of work and its internal energy becomes U_2. Then, according to first law,

$$U_1 + q = U_2 + (-\omega)$$

$$\text{or, } U_2 - U_1 = q + \omega$$

$$\text{or, } [\Delta U = q + \omega] \rightarrow \text{Mathematical form of First Law of Thermodynamics.}$$

Again $w = -P\Delta V$

or, $[\Delta U = q - P\Delta V]$

$dU = \dot{d}q + \dot{d}w$

or, $[dU = \dot{d}q - PdV]$

Enthalpy (H) :-

Enthalpy is defined as the total heat content of a system.

$$[H = U + PV]$$

It is a state function and an extensive property.

Suppose a system containing ideal gas has enthalpy H_1 and after changing its volume from V_1 to V_2, the enthalpy becomes H_2.

Initially,

$H_1 = U_1 + PV_1$

Finally,

$H_2 = U_2 + PV_2$

$\therefore H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$

or, $\Delta H = (U_2 - U_1) + P(V_2 - V_1)$

or, $[\Delta H = \Delta U + P\Delta V]$

For an ideal gas, $PV = nRT$

or, $P\Delta V = \Delta n\, RT$

$\therefore [\Delta H = \Delta U + \Delta n\, RT]$

From 1st Law, $\Delta U = q - P\Delta V$

$\therefore \Delta H = \Delta U + P\Delta V$

or, $\Delta H = q - P\Delta V + P\Delta V$

$[\text{or, } \Delta H = (q)_p]$ (At constant Pressure)

NOTE: i) If ΔH = -ve, the reaction is exothermic i.e., heat is evolved / liberated.

ii) If ΔH = +ve, the reaction is endothermic i.e., heat is absorbed.

Heat Capacity at constant volume (C_v) and constant pressure (C_p) :—

$$C_v = \frac{q_v}{\Delta T}$$

From 1st Law, $\Delta U = q - P\Delta V$

At constant volume, $\Delta V = 0$

$\therefore \Delta U = q_v$

or, $$C_v = \frac{\Delta U}{\Delta T}$$

For n moles, $[\Delta U = n \bar{C}_v \Delta T]$

$\bar{C}_v$ = molar heat capacity at constant volume.

$$C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T}$$

$$[\Delta H = n \bar{C}_p \Delta T]$$

Q) Which is greater for gases — C_p or C_v?

$$C_p - C_v = \left(\frac{\delta H}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V$$

$$= \left\{\frac{\delta (U+PV)}{\delta T}\right\}_p - \left(\frac{\delta U}{\delta T}\right)_V$$

$$= \left(\frac{\delta U}{\delta T}\right)_p + P\left(\frac{\delta V}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V$$

Again, $U = f(V, T)$

$$dU = \left(\frac{\delta U}{\delta V}\right)_T . dV + \left(\frac{\delta U}{\delta T}\right)_V . dT$$

Dividing by dT at a constant P,

$$\left(\frac{\delta U}{\delta T}\right)_p = \left(\frac{\delta U}{\delta V}\right)_T \cdot \left(\frac{\delta V}{\delta T}\right)_p + \left(\frac{\delta U}{\delta T}\right)_V$$

~~$C_p - C_v = \left(\frac{\delta U}{\delta T}\right)_p + P($~~

$$\therefore C_p - C_v = \left(\frac{\delta U}{\delta V}\right)_T \cdot \left(\frac{\delta V}{\delta T}\right)_p + \cancel{\left(\frac{\delta U}{\delta T}\right)_V} + P\left(\frac{\delta V}{\delta T}\right)_p - \cancel{\left(\frac{\delta U}{\delta T}\right)_V}$$

$$\text{or, } \left[C_p - C_v = \left[\left(\frac{\delta U}{\delta V}\right)_T + P\right]\left(\frac{\delta V}{\delta T}\right)_p\right]$$

C_V?

For an ideal gas, $\left(\frac{\delta U}{\delta V}\right)_T = 0$

and $\left(\frac{\delta H}{\delta P}\right)_T = 0$.

$\therefore C_P - C_V = P\left(\frac{\delta V}{\delta T}\right)_P$

$PV = nRT$

$\therefore \left(\frac{\delta V}{\delta T}\right)_P = \frac{nR}{P}$

or, $\left[C_P - C_V = P \times \frac{R}{P} = nR\right]$

For 1 mole i.e., $n=1$,

$\left[\overline{C}_P - \overline{C}_V = R\right]$ (ideal gas only)

For real gases,

$$\left[C_P - C_V = R\left(1 + \frac{2aP}{R^2T^2}\right)\right]$$

$\therefore C_P > C_V$

Adiabatic Reversible Process :—

For an adiabatic process, $q = 0$

$dU = -PdV$ (Since $q=0$)

or, $n\overline{C}_V dT = -PdV$

or, $n\overline{C}_V dT = -nRT\frac{dV}{V}$ $\left[PV = nRT\right]$

or, $\overline{C}_V \int_{T_1}^{T_2} \frac{dT}{T} = -R\int_{V_1}^{V_2} \frac{dV}{V}$

$$\text{or,} \quad \frac{\bar{C}_v}{R} \ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right)$$

$$\text{or,} \quad \frac{\bar{C}_v}{R} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)$$

$$\text{or,} \quad \ln\left(\frac{T_2}{T_1}\right) = (\gamma-1) \ln\left(\frac{V_1}{V_2}\right)$$

$$\bar{C}_p - \bar{C}_v = R$$

$$\text{or,} \quad \frac{\bar{C}_p - \bar{C}_v}{\bar{C}_v} = \frac{R}{\bar{C}_v}$$

$$\text{or,} \quad \frac{R}{\bar{C}_v} = (\gamma-1) \quad \text{where,} \quad \gamma = \frac{\bar{C}_p}{\bar{C}_v}$$

$$\text{or,} \quad \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{or,} \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{or,} \quad \boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$$

$$\text{or,} \quad \boxed{T V^{\gamma-1} = \text{Constant}}$$

$PV = nRT$

If $n=1$, $PV = RT$

$$\therefore \quad \frac{PV}{R} \cdot V^{\gamma-1} = \text{Constant}$$

$$\text{or,} \quad \boxed{PV^{\gamma} = \text{Constant}}$$

Also, $T\left(\frac{RT}{P}\right)^{\gamma-1} = \text{Constant}$

or, ~~$\frac{T^{\gamma-1}}{P} = \text{Constant}$~~

or, $\boxed{T^{\gamma} P^{1-\gamma} = \text{Constant}}$

Q) 3 moles of an ideal gas expands isothermally against a constant opposing pressure of 100 kPa from 20 dm^3 to 60 dm^3. Calculate q, w, ΔU and ΔH.

Q) 1 mole of an ideal gas at 27°C and 0.1 MPa is compressed adiabatically and reversibly to a final pressure of 1 MPa. Calculate the final temperature, q, w, ΔU and ΔH if $\gamma = 1.66$.

Q) 2 moles of an ideal monoatomic gas initially at 100°C and 5 atm expands adiabatically to a final pressure of 2 atm. Calculate w, molar volume and change in enthalpy.