

## Science 1 - Ch 2

### ★ The First Law :-

#### → Internal Energy :-

- Internal Energy is defined as the total energy of a system.  
(total kinetic and potential energy of its constituents).
- First Law of Thermodynamics :-

$$\Delta U = q + W$$

q - Heat Supplied to system

W - Work done on system

- Heat and Work are equivalent ways of changing the internal energy of the system.
- If a system is isolated, ie  $q = W = 0$ , then the internal energy of the system is constant.
- Heat - Energy Transfer using Random motion.  
Work - Energy Transfer using Uniform motion.

- Expansion Work :

- Work done by the change in volume of the system, against an external pressure  $P_{ext}$ .

$$W = - \int_{V_1}^{V_2} P_{ext} dV$$

- Free expansion :  $P_{ext} = 0 \quad \nabla \Rightarrow W = 0$

- Maximum work is obtained when the process is reversible, ie, when internal pressure  $P = P_{ext} + \text{steps of the process}$ .

- Properties of U :-

- $U$  is a state function - depends only on the current state of the system.

- Heat transferred at const  $V = \Delta U$

- Calorimetry : The study of heat transfer during a process, usually at constant volume.

$C_V$  - Heat capacity of the system at constant volume.

$$\Delta U = C_V \Delta T \rightarrow \text{At constant volume.}$$

→ Enthalpy :-

$$H = U + PV$$

$$\Rightarrow \Delta H = \Delta U + \Delta PV$$

° At constant pressure,  $\Delta H = q$ .

° For condensed reaction (involving solids and liquids only)  $\Delta H \approx \Delta U$   
since  $\Delta V = 0$ .

For gaseous reaction,  $\Delta H = \Delta U + RT \cdot \Delta n_g$   $\Delta n_g$  - Change in Gaseous mole.

°  $C_p$  - Heat capacity of the system at constant pressure.

$$\Delta H = C_p \Delta T \longrightarrow \text{At constant pressure.}$$

° Generally  $C_p > C_v$  since a change in volume may lead to some energy going back into the surroundings via work.

For a perfect gas,  $C_p - C_v = R$

→ Thermochimistry :-

° The study of heat transfer during chemical reaction.

° Standard State: The standard state of a substance is its pure form at 1 bar.

- Standard Enthalpy Change : The change in enthalpy of a reaction where the products and reactants are in their standard form. ( $\Delta_r H^\circ$ )

$\Delta H < 0 \rightarrow$  Exothermic

$\Delta H > 0 \rightarrow$  Endothermic

- Enthalpies of Transition : The standard molar enthalpy of the physical change of state of a substance. (fusion and vaporization) ( $\Delta_{\text{fus}} H^\circ$ ) ( $\Delta_{\text{vap}} H^\circ$ )

- Hees' Law : Enthalpy is a state function, so enthalpy of a reaction with same products and reactants are the same, irrespective of the mechanism of the reaction.

- Standard Enthalpy of Formation : The standard reaction enthalpy of forming a substance from its reference state (most stable state at the reaction temperature and 1 bar) ( $\Delta_f H^\circ$ )

- By Hees' Law, the standard reaction enthalpy is given by,

$$\Delta_r H^\circ = \Delta_f H^\circ_{\text{products}} - \Delta_f H^\circ_{\text{reactants}}$$

- Kirchoff's Law:  $\frac{d(\Delta_r H)}{dT} = C_p(\text{products}) - C_p(\text{reactants}) = \Delta(C_p)$

$$\Rightarrow \Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta(C_p) dT$$

## → State and Path Functions :-

- ° H, V are state functions, which only depend on the current state of the system. dH and dV are exact differentials.
- ° q, W are path functions, which depend on the process path between the states. dq and dW are inexact differentials.
- ° Internal Pressure :-

$$\pi(T) = \frac{\delta U}{\delta V} \Big|_T$$

- $\pi(T)$  measures how the internal energy varies with volume at a certain temperature.  $\pi(T) = 0$  for an ideal gas.
- Heat Capacity :  $C_p - C_v = nR$  for an ideal gas.  
 $= \frac{\alpha^2 TV}{k_T}$ ,  $\alpha$  - expansion coefficient  
 $k_T$  - isothermal compressibility

## Joule - Thomson Effect :

$$\mu = \frac{\delta T}{\delta P} \Big|_H$$

$\mu$  measures the change in temperature when a gas undergoes isenthalpic expansion (expansion at constant enthalpy)

- Used in Gas Liquefaction.  $\mu = 0$  for ideal gas.

→ Adiabatic Process :-

- Processes that occur without the transfer of heat. ( $q = 0$ )

- $\Delta U = W \Rightarrow W = C_V \Delta T$  in an adiabatic process.

- Reversible Adiabatic Expansion :-

- In a reversible expansion,

$$T_f V_f \frac{C_{V,m}}{R} = T_i V_i \frac{C_{V,m}}{R}$$

- Adiabate:  $PV^\gamma = \text{constant}$  in an adiabatic process. ( $\gamma = \frac{C_p m}{C_{V,m}}$ )

Proof of above 2:

$$W = -pdV$$

$$W_{\text{adiabat}} = C_V dT$$

$$\Rightarrow C_V dT = -pdV$$

$$\Rightarrow C_V dT = -\frac{nRT}{V} dV \quad (\text{Ideal Gas Law})$$

$$\Rightarrow C_V \frac{dT}{T} = -\frac{nR}{V} \frac{dV}{V}$$

$$\Rightarrow \int_{T_i}^{T_f} C_V \frac{dT}{T} = \int_{V_i}^{V_f} nR \frac{dV}{V}$$

$$\Rightarrow C_V \ln \frac{T_f}{T_i} = nR \ln \frac{V_i}{V_f}$$

$$\Rightarrow C_V \ln \frac{P_f V_f}{P_i V_i} = nR \ln \frac{V_i}{V_f}$$

$$C_V \ln \left( \frac{P_f V_f}{P_i V_i} \right) = (C_p - C_V) \ln \frac{V_i}{V_f}$$

$$\ln \frac{P_f V_f}{P_i V_i} = \left( \frac{C_p}{C_V} - 1 \right) \ln \frac{V_i}{V_f} = (\gamma - 1) \ln \frac{V_i}{V_f}$$

$$\Rightarrow \frac{P_f V_f}{P_i V_i} = \frac{V_i^{\gamma-1}}{V_f^{\gamma-1}}$$

$$\Rightarrow \frac{P_f}{P_i} = \frac{V_i^{\gamma}}{V_f^{\gamma}} \Rightarrow P_f V_f^{\gamma} = P_i V_i^{\gamma}$$

## ★ Second and Third Laws :-

→ Entropy :-

- Measures the spontaneity of a process.

- Second Law of Thermodynamics : The entropy of an isolated system increases in the course of a spontaneous change.

- Change in Entropy is defined as,

$$dS = - \frac{dq_{rev}}{T} \quad (q_{rev} : \text{Reversible heat transferred})$$

- Entropy is a state function.

- For a reversible isothermal process

$$\Delta S^{\circ} = q + w \rightarrow q = -w$$

$$w = - \int pdV = - \int \frac{nRT dV}{V} = - nRT \ln \frac{V_f}{V_i}$$

$$q_{\text{rev}} = nRT \ln \frac{V_f}{V_i}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \Rightarrow \Delta S = nR \ln \frac{V_f}{V_i}$$

- Entropy of surroundings :-  $\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}}$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}}$$

- Clausius Inequality : For any process,

$$dS \geq \frac{dq_{\text{sur}}}{T} \quad (q_{\text{sur}} - \text{Actual heat transfer of the process})$$

- An implication of the above inequality is that spontaneous processes are necessarily irreversible ( $dS_{\text{tot}} > 0$ ), and a reversible process is at equilibrium ( $dS_{\text{tot}} = 0$ )

Why ? ,

$$dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{sur}}$$

If process is reversible,  $dS_{\text{sys}} = -\frac{dq}{T}$

$$\Rightarrow dS_{\text{tot}} = -\frac{dq}{T} + \frac{dq}{T} = 0$$

If process is irreversible,  $dS_{\text{sys}} = -\frac{dq_{\text{rev}}}{T}$

$$dS_{\text{tot}} = -\frac{dq_{\text{rev}}}{T} + \frac{dq}{T} \geq 0 \quad (\text{By Clausius Inequality})$$

- Statistical Definition of Entropy :-

$$S = k \ln W$$

$W$  - No. of microstates (possible distributions of energy)

- Main Result : Higher disorder,  $W \uparrow \Rightarrow S \uparrow$

- Phase Transitions :-

At the transition temperature of a phase transition,  
the entropy change is given by,

$$\Delta S_{\text{trs}} = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

- The entropy change in heating a substance is,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \ln\left(\frac{T_2}{T_1}\right) \rightarrow \text{If } C_p \text{ is constant.}$$

Debye Extrapolation :  $C_p \propto T^3$  for small T

- Third Law: The entropy of a perfectly crystalline solid is zero at  $T=0$ .

- The entropy of any general substance at  $T=0$  is termed as residual entropy.

- Standard Reaction Entropy: The difference between the molar entropies of the products and reactants of a process ( $\Delta_r S^\circ$ ).

- The temperature dependence of  $\Delta_r S^\circ$  is similar to Kirchoff's law.

$$\Delta_r S^\circ(T_2) = \Delta_r S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT$$

- Spontaneity of the System :-

- Helmholtz Energy :  $A = U - TS$

- At constant T and V, for spontaneity we need  $dA \leq 0$

- $dA$  is equal to the maximum work obtainable from a system at a given T.

- Gibbs Energy:  $G = H - TS$
- At a constant  $p$  and  $T$ , for spontaneity we need  $dG \leq 0$ .
- Spontaneous chemical reaction proceed in the direction of negative Gibbs energy.
- Gibbs energy is the maximum non-expansion work obtainable at constant temperature and pressure.
- Gibbs Energy of Reaction:  $\Delta_f G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ$

Also,  $\Delta_f G^\circ = \Delta_f G^\circ_{\text{product}} + \Delta_f G^\circ_{\text{reactants}}$

$\Delta_f G^\circ$  - Gibbs energy of formation. i.e. the Gibbs energy of reaction for the formation of a substance from its reference state.

By convention  $\Delta_f G^\circ(\text{H}^+, \text{aq}) = 0$ .

→ Combining the First and Second Laws :-

- Fundamental Equations and Maxwell's Relations:

$$dU = dq + dw$$

$$ds = \frac{-dq_{\text{rev}}}{T} = \frac{dq}{T}, \quad dw = -pdV$$

$$\Rightarrow dU = TdS - pdV$$

$$\begin{aligned} dH &= dU + d(pV) \\ &= dU + pdV + Vdp \end{aligned}$$

$$\Rightarrow dH = TdS + Vdp$$

$$\begin{aligned} dG &= dH - d(TS) \\ &= dH - TdS - SdT \end{aligned}$$

$$\Rightarrow dG = Vdp - SdT$$

Fundamental Equation of  
Chemical Thermodynamics.

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \end{aligned}$$

$$\Rightarrow dA = -pdV - SdT$$

For any exact differential of the form  $df = gdx + hdy$ , it follows that

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

So, from the above 4 fundamental equations, the below relations can be stated,

$$1) \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial p}{\partial S}\right)_V \quad [ \text{From } dU ]$$

$$2) \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_T \quad [ \text{From } dH ]$$

$$3) \left( \frac{\delta V}{\delta T} \right)_P = \left( \frac{\delta S}{\delta P} \right)_T \quad [ \text{From } dG ]$$

$$4) \left( \frac{\delta P}{\delta T} \right)_V = \left( \frac{\delta S}{\delta V} \right)_T \quad [ \text{From } dA ]$$

These 4 relations are formed as Maxwell's Relations.

- Variation of  $G$  with  $T$  and  $p$  :-

$$dG = Vdp - SdT$$

$$\Rightarrow \left( \frac{\delta G}{\delta T} \right)_P = -S, \quad \left( \frac{\delta G}{\delta P} \right)_T = V$$

$\Rightarrow G$  decreases with  $T$  at constant  $P$

$G$  increases with  $P$  at constant  $T$

- Gibbs - Helmholtz Equation:  $\left( \frac{\delta (G/T)}{\delta T} \right)_P = -\frac{H}{T^2}$

Proof:  $\left( \frac{\delta (G/T)}{\delta T} \right)_P = \left( \frac{T \frac{\delta G}{\delta T} - G \frac{\delta T}{\delta T}}{T^2} \right)_P$

$$= \frac{-ST - G}{T^2}$$

$$G = H - TS \Rightarrow H = G + TS$$

$$\Rightarrow \left( \frac{\delta (G/T)}{\delta T} \right)_P = -\frac{H}{T^2}$$

## ★ Physical Transformation of Pure Substances :-

- About phase changes ( vaporization, condensation, melting, fusion, sublimation)
- Principle : Stable systems minimize their Gibbs energy at a given T and P.

## → Phase Diagrams :-

- Maps that show the pressure and temperature where each phase of a substance is most stable.
- Chemical Potential : Measure of a substance's potential for undergoing a change. Molar Gibbs energy for a pure substance. ( $\mu$ )
- Phase Equilibrium : At equilibrium the chemical potential of a substance is the same in and throughout every phase of the system. (ie 2 phases coexisting)
- Phase Boundaries : p and T values where 2 states can coexist at the same time.
- Critical Point : p and T value ( $p_c, T_c$ ) above which the liquid and gas phases merge into a single uniform supercritical fluid.

- Phase Rule:

$$F = C - P + 2$$

$F$  - No. of degrees of freedom for  $(P, T)$

$C$  - No. of components

$P$  - No. of phases at equilibrium

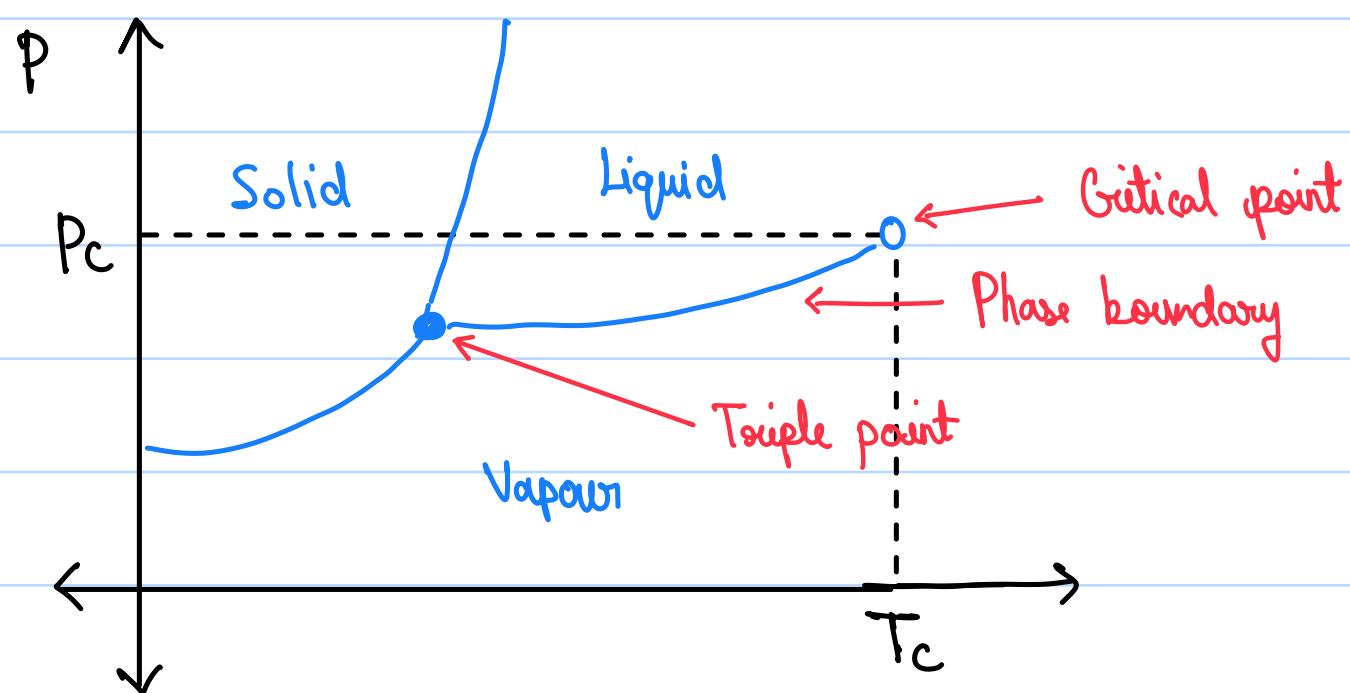
- For a one-component system,  $F = 3 - P$

A single phase ( $P=1$ ),  $F = 2 \Rightarrow$  represented by an area

Two phases coexisting ( $P=2$ ),  $F=1 \Rightarrow$  represented by a line/circle

Three phases coexisting ( $P=3$ ),  $F=0 \Rightarrow$  represented by a point (Triple State point)

> 3 phases cannot coexist at a point.



An example phase diagram. The regions of  $(P, T)$  where a solid, liquid or gas has minimum G are shown.

→ Thermodynamic Aspects of Phase Transition:

- Temperature Dependence of  $\mu$ : The chemical potential decreases as  $T$  increases.

$$\left(\frac{\delta \mu}{\delta T}\right)_P = -S \quad (\text{Hence dependence of } G \text{ and } T)$$

- Since  $S_{\text{gas}} > S_{\text{liq}} > S_{\text{solid}}$ , the chemical potential line is steepest for a gas.

- Pressure Dependence of  $\mu$ :  $\mu$  increases with increasing pressure.

$$\left(\frac{\delta \mu}{\delta P}\right)_T = V > 0 \text{ always.}$$

- Gibbs Equation :- Gives the slope of any phase boundary.

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$$

Proof,

At the phase boundary of 2 phases  $\alpha$  and  $\beta$ ,

$$d\mu(\alpha) = d\mu(\beta)$$

$$\Rightarrow dG(\alpha) = dG(\beta)$$

$$\Rightarrow V(\alpha) dp - S(\alpha) dT = V(\beta) dp - S(\beta) dT$$

$$\Rightarrow dp(V(\alpha) - V(\beta)) = dT(S(\alpha) - S(\beta))$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$$

- Clausius-Clapeyron Equation :- An approximation of the Clapeyron equation, for the boundary b/w a condensed phase and its vapour.

$$\frac{d \ln P}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

Proof,

$$\text{wkt } \Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

$$\Delta_{\text{trs}} V = V(\text{gas}) - V(\alpha) \propto V(\text{gas}) = \frac{RT}{P}$$

$$\Rightarrow \frac{dp}{dt} = \frac{\Delta_{\text{vap}} H / T}{RT/P}$$

$$\Rightarrow \frac{\left(\frac{dp}{P}\right)}{dt} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

$$\Rightarrow \underline{\underline{\frac{d \ln P}{dt} = \frac{\Delta_{\text{vap}} H}{RT^2}}}$$

- This predicts that the vapor pressure of a substance increases exponentially with temperature.

- Since  $\Delta_{\text{sub}} H > \Delta_{\text{vap}} H$  generally, the solid-vapour boundary is steeper than the liquid-vapour boundary.

- Vapour Pressure under Applied Pressure :

$$P = P^* e^{V(l)\Delta P / RT} \quad \Delta P - \text{Applied pressure.}$$

Misc Concepts :-

$$C_p = a + bT + \frac{c}{T^2}$$

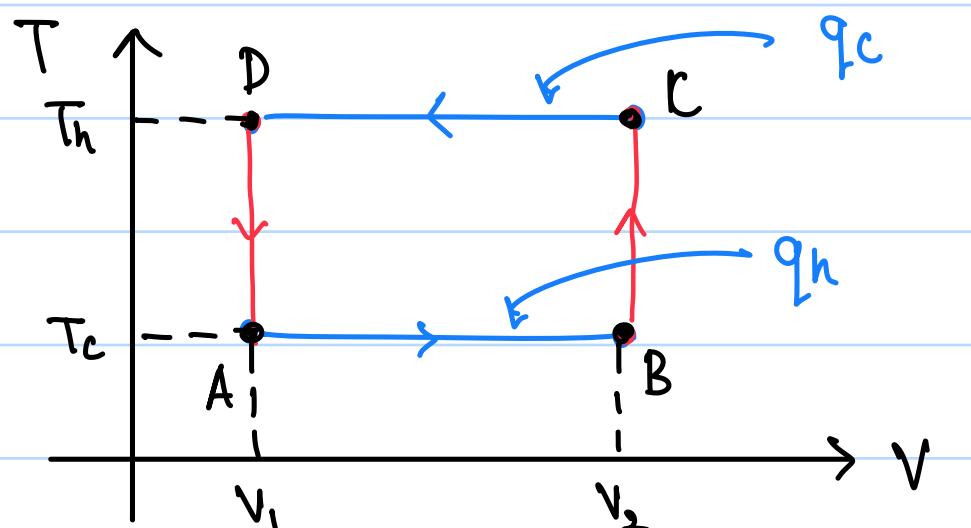
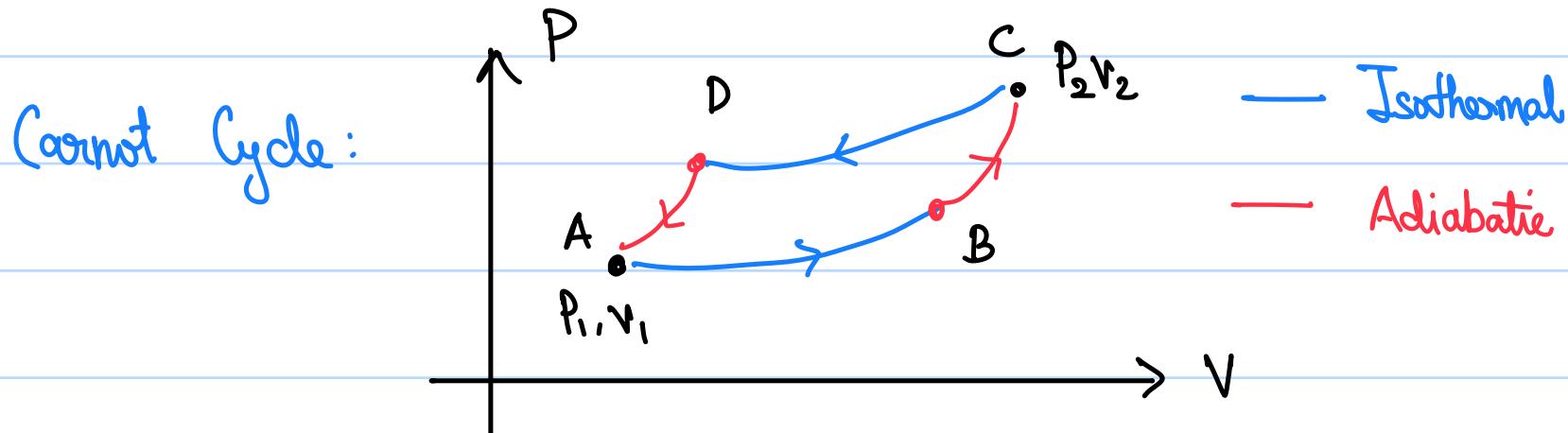
$$\text{Internal Pressure } \Pi_T = \left( \frac{\partial U}{\partial V} \right)_T$$

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

$\Pi_T > 0 \Rightarrow \text{Attraction dominant}$   
 $\Pi_T < 0 \Rightarrow \text{Repulsion dominant}$

$$\text{Isotherm. Compressibility } K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$\text{Carnot Efficiency } \eta = 1 - \frac{T_c}{T_h}$$



$$W = q_h - q_c$$

$$\eta = \frac{W}{q_{\text{supplied}}}$$

$$= \frac{q_h - q_c}{q_h}$$

$$q_h = nRT_h \ln \frac{V_2}{V_1} \quad q_c = -nRT_c \ln \frac{V_1}{V_2} \quad = 1 - \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h}$$

$$\Rightarrow \frac{q_h}{q_c} = \frac{T_h}{T_c}$$

