

Thermodynamics.

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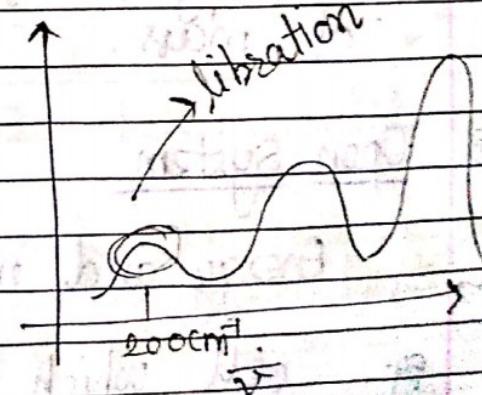
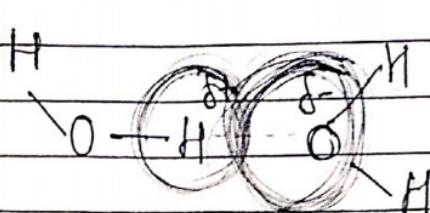
- Definition and Introduction of Thermodynamic terms
- Different systems and processes
- Reversible and Irreversible Transformations.
- First Law of Thermodynamics.
 - Enthalpy
 - Numericals
- Second Law of Thermodynamics.
 - Statements
 - Entropy
 - Carnot Cycle & its efficiency
 - Gibbs free energy, Helmholtz free energy
 - Clausius Inequality.
- Phase Transition of Matter.
- Third Law of Thermodynamics (Introduction only)

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Thermo dynamics.

Heat Energy

Work done



* Limitation

Non-Equilibrium Thermodynamics (Time limitation) (overcoming)
Statistical Thermodynamics (Exact Entropy)

* System = Part of Universe Under Investigation.

Surroundings = Universe - System

* Types of Systems.

(1) Isolated System (Practically Impossible) eg. universe
(No transfer of mass or energy) (if there is only one universe)

Conduction

Convection

Radiation

transfer of energy through vibrations w/o transfer of particles.

happens with transfer of molecules

(Can be minimized by reflecting walls)

(2) Closed system

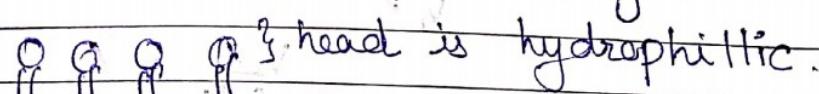
Energy transfer is possible, no transfer of mass.

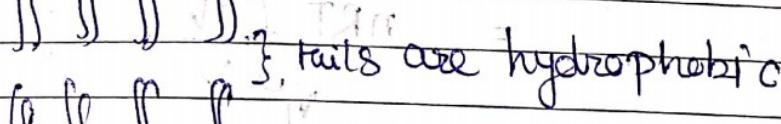
(3) Open System

Energy and mass transfer both occurs.

e.g. cell which has semipermeable membrane.

Structurecell wall \rightarrow phospholipid bilayer.


head is hydrophilic.


tails are hydrophobic

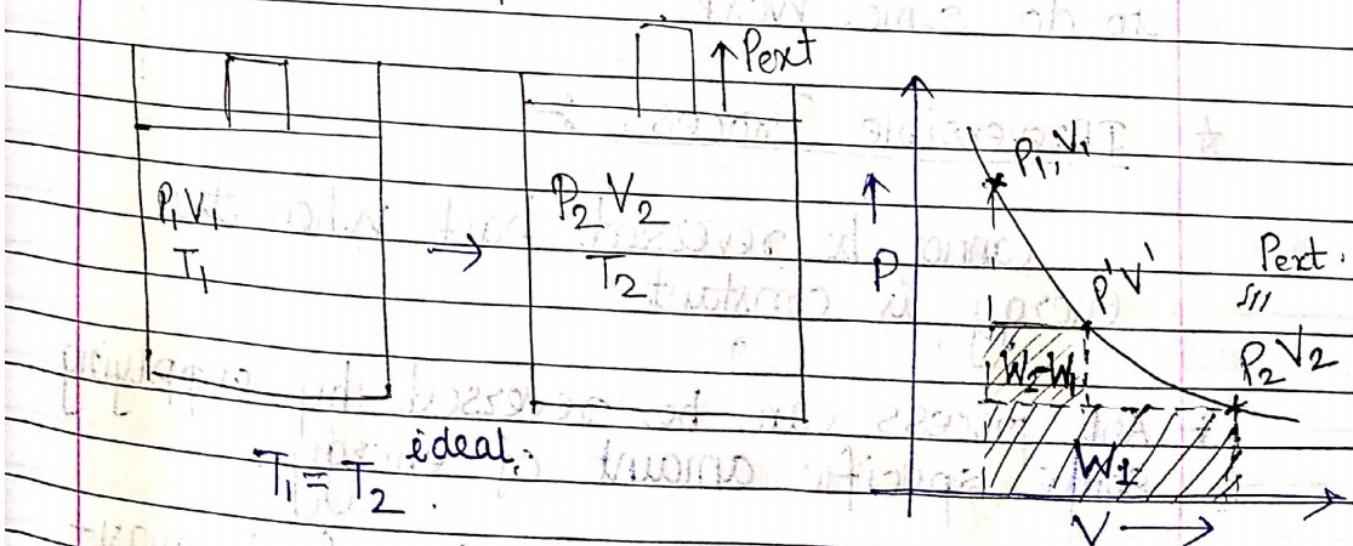
{ Thermodynamics of Variable composition }
(for open system).

* Thermodynamic Processes :-

Categorized on basis of change in P, V, T, n .

* Reversible Process :-

They are the processes where infinitesimal changes occur, which can be reversed back in infinite steps.



$$W_1 = P_{\text{ext}}(V_2 - V_1) = P_2(V_2 - V_1) \quad W_3 = \int P dV$$

$$W_2 = P'(V' - V_1) + P_2(V_2 - V')$$

$$\Delta W = (P' - P_2)(V' - V_1)$$

$$W_{\text{ext}}^e = \int_{V_1}^{V_2} P dV$$

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

$$W_{\text{ext}}^e = nRT \ln \frac{V_2}{V_1}$$

$$W_1^C = P_1(V_1 - V_2) \quad C \Rightarrow \text{Compression.}$$

$$W_{\text{ext}}^C = nRT \ln \frac{V_1}{V_2}$$

$$W_{\text{ext}}^e + W_{\text{ext}}^C = 0$$

No net work
is involved.

If done in less than ∞ steps, we have
to do some work.

* Irreversible Process :-

Cannot be reversed back when the
energy is constant.

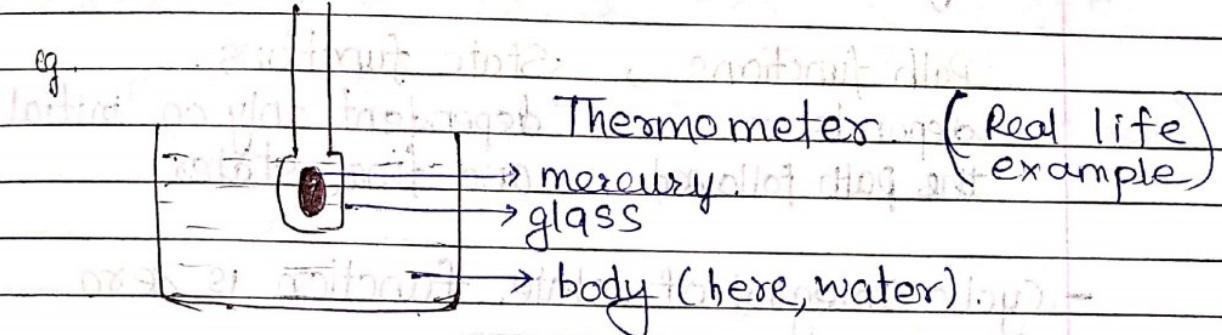
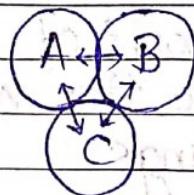
- * Any process can be reversed by supplying
some specific amount of energy.
- * In reversible process, system is in quasi-
equilibrium state always.

$T \rightarrow$ Translational
 $R \rightarrow$ Rotational
 $V \rightarrow$ Vibrational

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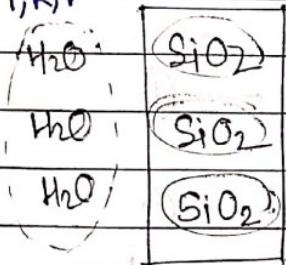
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* Zeroth Law of Thermodynamics :- If A and B are in thermal equilibrium & B and C are in thermal equilibrium then A & C are also in thermal equilibrium.



→ Law does not tell about time and how the equilibrium will actually take place.

$$T, R, V \rightarrow V \rightarrow T$$



* Equipartition principle.

$$\frac{1}{2}mv^2 = \frac{f}{2}nRT = \frac{f}{2}k_B T$$

Relates kinetic & Thermal energy

- Collisions will occur → lead to energy transfer.
Resulting into similar kinetic energy for all molecules.

2.5 ps \Rightarrow full rotation of water molecule.

- Two bodies must be in contact

- Thermal equilibrium requires contact.

Hydrogen bond (librations)

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* First law of thermodynamics :-

For a cyclic process the amount of heat absorbed by the system is equal to the work done by the system to the surroundings.

Path functions, State functions.

depends on the path followed dependent only on initial and final states.

- Cyclic Integral of state function is zero.

$$\oint dq = \oint dW \Rightarrow \oint dq - \oint dW = 0$$

$$\Rightarrow \oint (dq - dW) = 0$$

$$\Rightarrow \oint d(q - W) = 0 \quad \text{--- (1)}$$

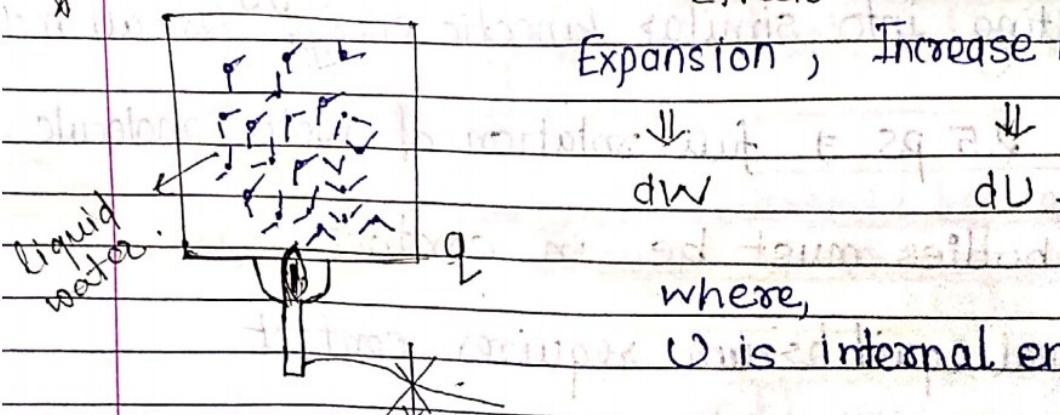
$$\oint dq - dW = \oint dU \quad \text{--- (2)}$$

$$dq = dU + dW \quad \text{Here, } U \text{ is any state function}$$



Effects.

Expansion, Increase in K.E.



$$dW = dU \quad \text{where,}$$

U is internal energy

$$\left(ds = \frac{dq_{rev}}{T} \quad \text{Energy} \right)$$

Q) Calculate the final volume of 1 mole of an ideal gas which was initially at 0°C and 1 atm pressure. The gas has absorbed 2000 calories of heat during reversible isothermal expansion (The gas is in the standard temp. & pressure condition i.e. STP).

Ans ⇒

$$P_i = 1 \text{ atm}, \quad T_i = 273K = T_f \text{ (Isothermal)}$$

$$P_i V_i = nRT_i$$

$$V_i = \frac{nRT_i}{P_i} = \frac{(1)(0.0821)(273)}{1 \text{ atm}}$$

$$V_i = 22.4 \text{ L}$$

$$W = nRT \log_e \frac{V_f}{V_i}$$

2000 cal
→ 8368 J.

$$\Rightarrow 8368 \text{ J} = (1)(8.314)(273) \log_e V_f$$

$$\Rightarrow 3.6867 = \log_e \frac{V_f}{22.4 \text{ L}}$$

$$\Rightarrow V_f = (22.4)e^{3.6867}$$

$$\Rightarrow V_f = 894.049 \text{ L}$$

Q.2) Prove mathematically that work is a path function.

Ans ⇒

$$dW = PdV, \quad V = f(T, P)$$

$$W = PdV = P \left(\frac{dV}{dT} \right)_P dT + P \left(\frac{dV}{dP} \right)_T dP$$

$$\text{Taking } \frac{\partial}{\partial P} \rightarrow P \left(\frac{\partial V}{\partial P} \right)_T$$

$$dH = d \left[\frac{\partial W}{\partial P} \right]_T = P \cdot d \left[\frac{\partial V}{\partial P} \right]_T$$

$$z \text{ is a function of } x, y \Rightarrow z = f(x, y)$$

$$\text{state function: } \left[\frac{\partial z}{\partial x} \left(\frac{\partial z}{\partial y} \right)_x \right]_y = \left[\frac{\partial z}{\partial y} \left(\frac{\partial z}{\partial x} \right)_y \right]_x$$

$$PV = RT$$

$$dV = RT \quad \Rightarrow \frac{(dV)}{(dP)} = -RT \quad \text{at } P_2$$

$$W = PdV = \frac{(dV)}{(dT/P)} = \frac{RT}{P} dT + P \left(\frac{-RT}{P^2} \right) dP$$

$$W = RT dT - \left(\frac{RT}{P} \right) dP$$

$$\frac{(dW)}{(dT/P)} = R \quad \frac{(dW)}{(dP)} = -RT \quad \frac{(dW)}{(dT/P)} = \frac{dW}{dT} = \frac{dW}{dP} \cdot \frac{dP}{dT}$$

$$dW = \frac{(dW)}{(dT/P)} dT + \frac{(dW)}{(dP)} dP \quad \frac{(dW)}{(dT/P)} = -RT \quad \frac{(dW)}{(dP)} = \frac{-1}{P} \frac{dP}{dT}$$

$$q_b = \frac{1}{2} RT_b \quad q_f = \frac{1}{2} RT_f \quad \frac{dW}{dT} = \frac{dW}{dP} \cdot \frac{dP}{dT}$$

3). Show mathematically that the magnitude of work in a reversible expansion of an ideal gas from (P_1, V_1) to (P_2, V_2) is larger than the corresponding work involved in an irreversible expansion against the constant pressure of P_2 .

4) Show that pressure is a state function for gas obeying

$$\left(\frac{P + a}{V_m^2} \right) = \frac{RT}{V_m}$$

5) For an ideal gas $PV = nRT$. Taking $V = f(n, P, T)$, verify that dV is an exact differential.

5) $\Rightarrow V = \frac{R(nT)}{P}$

$$dV = \left(\frac{\partial V}{\partial n} \right)_{P,T} dn + \left(\frac{\partial V}{\partial P} \right)_{n,T} dP + \left(\frac{\partial V}{\partial T} \right)_{n,P} dT$$

$$M = \frac{RT}{P}; N = -\frac{RnT}{P^2}; O = \frac{nR}{P}$$

$$\frac{\partial M}{\partial P} = -\frac{RT}{P^2}; \quad \frac{\partial N}{\partial n} = -\frac{RT}{P^2}; \quad \frac{\partial O}{\partial n} = \frac{R}{P}$$

$$\frac{\partial M}{\partial T} = \frac{R}{P}; \quad \frac{\partial N}{\partial T} = -\frac{nR}{P^2}; \quad \frac{\partial O}{\partial P} = -\frac{nR}{P^2}$$

As $\frac{\partial M}{\partial P} = \frac{\partial N}{\partial n}$

$$\frac{\partial M}{\partial T} = \frac{\partial O}{\partial n}$$

$$\frac{d}{dT} \left(-\frac{RT}{P} \cdot \frac{\partial P^2}{\partial n} \right)$$

$$\frac{\partial N}{\partial T} = \frac{\partial O}{\partial P}$$

\therefore for any ideal gas; dV is an exact differential.

$$4) \Rightarrow \left(\frac{P + \frac{a}{V_m^2}}{V_m} \right) V_m \neq RT \Rightarrow \frac{RT - \frac{a}{V_m^2}}{V_m} = P$$

V_m is denoted as

$$P = f(T, V)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2} + \frac{2a}{V^3}$$

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T = -\frac{R}{V^2} \quad \frac{\partial}{\partial T} \left[\left(\frac{\partial P}{\partial V} \right)_T \right]_V = -\frac{R}{V^2} \quad (2)$$

from (1) & (2) i)

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T = \frac{\partial}{\partial T} \left[\left(\frac{\partial P}{\partial V} \right)_T \right]_V .$$

P is a state function for given gas equation

$$\textcircled{3} \rightarrow W_{\text{rev}} = nRT \ln \frac{V_2}{V_1}; \quad W_{\text{irr}} = \frac{P}{2}(V_2 - V_1)$$

$$nRT \ln\left(\frac{V_2}{V_1} - 1\right) + I$$

~~Wrey~~ → Wynn

$$\text{Using } \ln(v_1v_2) = \frac{nRT}{V} \left(\frac{V_2}{V_1} - 1 \right) = P_1(V_2 - V) - P_2(V_2 - V)$$

$$\text{expansion} \quad \text{and neglecting } \frac{nRT}{V_1} (V_2 - V_1) = (P_1 - P_2) (V_2 - V_1)$$

$$\text{higher order} = P_1 (V_2 - V_1) > 0.$$

turkey

1st Law of TD.

$$dq = dU + dw$$

heat \uparrow internal energy \downarrow work done

$$dw = dw_{\text{mech}} + dw_{\text{chem}}$$

$$= PdV \quad \checkmark \text{not considered in general}$$

Amount of heat required to increase the temperature of system by 1° \rightarrow heat capacity.

$\Delta H_f^{\circ} = 1.5 A^\circ$; Heat capacity is dependent on size (it increases with increase in size)

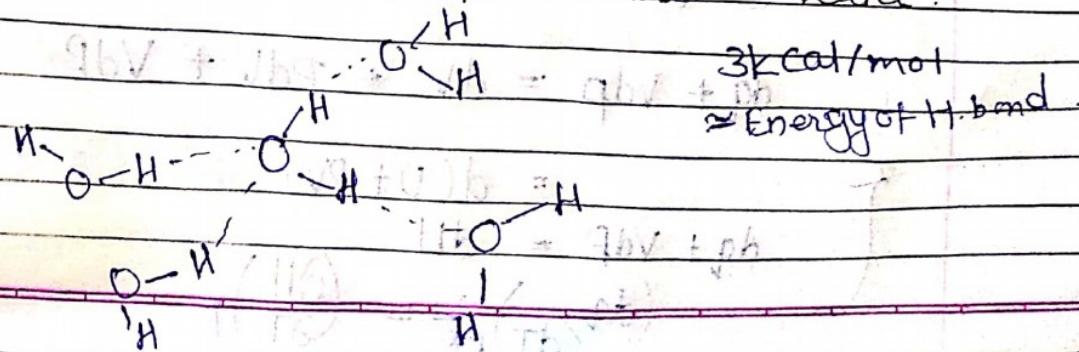
Exception: Heat capacity of water is high when compared with other molecules of similar size

Heat capacity comparison for different molecules must be done at same temperature and pressure conditions.

Average hydrogen bonds per water molecule
 ≈ 3.6 (at STP).

Due to extensive hydrogen bonding, the molecule get much more opposition for increase in vibrations which results in high heat capacity.

* Tetrahedral Network of H-bonds in water.



* Water \Rightarrow Temp. fluctuations are very less.

* Protein denatures below or above optimum temp. (37°C)

Heat capacity (C)

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} = \frac{dq}{dT}$$

Heat capacity is the

slope of the tangent to $q-T$ curve.

$$T \longleftrightarrow$$

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V ; \quad C_P = \left(\frac{\partial q}{\partial T}\right)_P$$

$$dq = dU + dW \\ = dU + PdV$$

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + 0 = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$dq + Vdp = dU + PdV + VdP$$

$$dq + Vdp = dH$$

$$\left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Numerical Problem

8. 10 dm^3 of O_2 at 101.325 kPa and 298 K is heated to 348 K . Assume ideal behaviour and calculate the heat absorbed, enthalpy change (ΔH), internal energy change (ΔU) of this process at

(a) Constant Pressure $C_p = C_v + R$

(b) Constant Volume

Given,

$$C_p / \text{JK}^{-1} \text{mol}^{-1} = 25.72 + 0.013T/\text{K}$$

$$\approx 3.86 \times 10^{-6} \left(\frac{T}{\text{K}}\right)^2$$

\Rightarrow (a) Constant Pressure (b) Constant Volume

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\checkmark \Delta H = \int_{298 \text{ K}}^{348 \text{ K}} n(C_p dT)$$

$$\checkmark \Delta U = \int_{298 \text{ K}}^{348 \text{ K}} nC_V dT$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \checkmark q = \Delta U.$$

$$\checkmark \Delta H = \Delta U + PdV + VdP = \Delta U + VdP.$$

$$\checkmark \rightarrow V_2 = V_1 \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$H = U + \underbrace{W}_{Q}$$

$$H = U + PV$$

$$\delta H = dU + PdV + VdP$$

$$V_2 = 10 \left(\frac{348}{298}\right) \text{ dm}^3$$

$$\checkmark (\delta H = \delta Q)_P$$

$$W = PdV$$

$$\checkmark \Delta U = \Delta H - W$$

$$= dQ - PdV$$

*

$C_p - C_v$ Relation :-

Final Draft (Incomplete)

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

(from first law of thermodynamics)

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

(from definition of pressure)

$$U = f(T, V); \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

(from first law of thermodynamics)

(Euler's Reciprocity Rule)

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

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

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

$$C_p - C_v = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \quad \text{--- ①}$$

The thermodynamic equation of state

$$\frac{U}{V} - \frac{P}{T} = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{--- 1st eqn}$$

Using TES ① in eqn ① ;

$$C_p - C_v = \left(\frac{\partial V}{\partial T} \right)_P \left[T \left(\frac{\partial P}{\partial T} \right)_V - P + P \right]$$

$$\boxed{C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P} \quad \text{--- ②}$$

for ideal gas ; $V = \frac{nRT}{P}$; $P = \frac{nRT}{V}$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} ; \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

$$C_p - C_v = T \left(\frac{nR}{P} \right) \left(\frac{nR}{V} \right)$$

$$\boxed{C_p - C_v = nR}$$

* Tut

A gas contained in a cylinder with a movable piston on which a heavy block is placed. Suppose the region outside the chamber is evacuated and the total mass of the block and the movable piston is 102 kg. When 2140 J heat flow into the gas, this is reduced by 1580 J. What distance S through which the piston rises? (Ans 0.54 m)

$$\rightarrow q = w + u \quad w = F \times s.$$

$$\Rightarrow 2140 = (F \times s) + 1580$$

$$\Rightarrow s = \frac{2140 - 1580}{1020}$$

$$\begin{array}{r} 2140 \\ 1580 \\ \hline 560 \end{array} \quad \Rightarrow s = \frac{560}{1020} = \frac{56}{102} = 0.54 \text{ m } \checkmark$$

* Isothermal Compressibility : (K_T)

Determines How much volume you can decrease by increasing the pressure at constant temperature

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

(Determined experimentally)

* Thermal Expansion Coefficient (α) :-

the fractional change of volume for change in temperature.

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

* Cyclic Rule :-
$$\left[\left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V + 1 \right] = 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P$$

we know, $C_P - C_V = \gamma T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V$

$$\gamma = -T \left(\frac{\partial V}{\partial T} \right)_P \cdot \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P$$

$$= -T \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2 / \left(\frac{\partial V}{\partial P} \right)_T$$

$$C_p - C_V = - \frac{T \alpha^2 V^2}{K_T V} = \frac{T \alpha^2 V^2}{K_T V}$$

$$\Rightarrow C_p - C_V = \frac{V T \alpha^2}{K_T}$$

Q) The coefficient of thermal (cubical) expansion (α) of a metal at 293K temp is $21.3 \times 10^{-6}/\text{K}$ and compressibility (K_T) is $1.56 \times 10^{-11} \text{ Pa}^{-1}$. Molar mass of metal is 63.55 g/mol, its density is 0.97 g/cm³. Calculate $(C_p - C_V)$ of metal at 293 K. (Ans 0.558 JK⁻¹mol⁻¹)

Ans :- $C_p - C_V = \frac{V T \alpha^2}{K_T}$

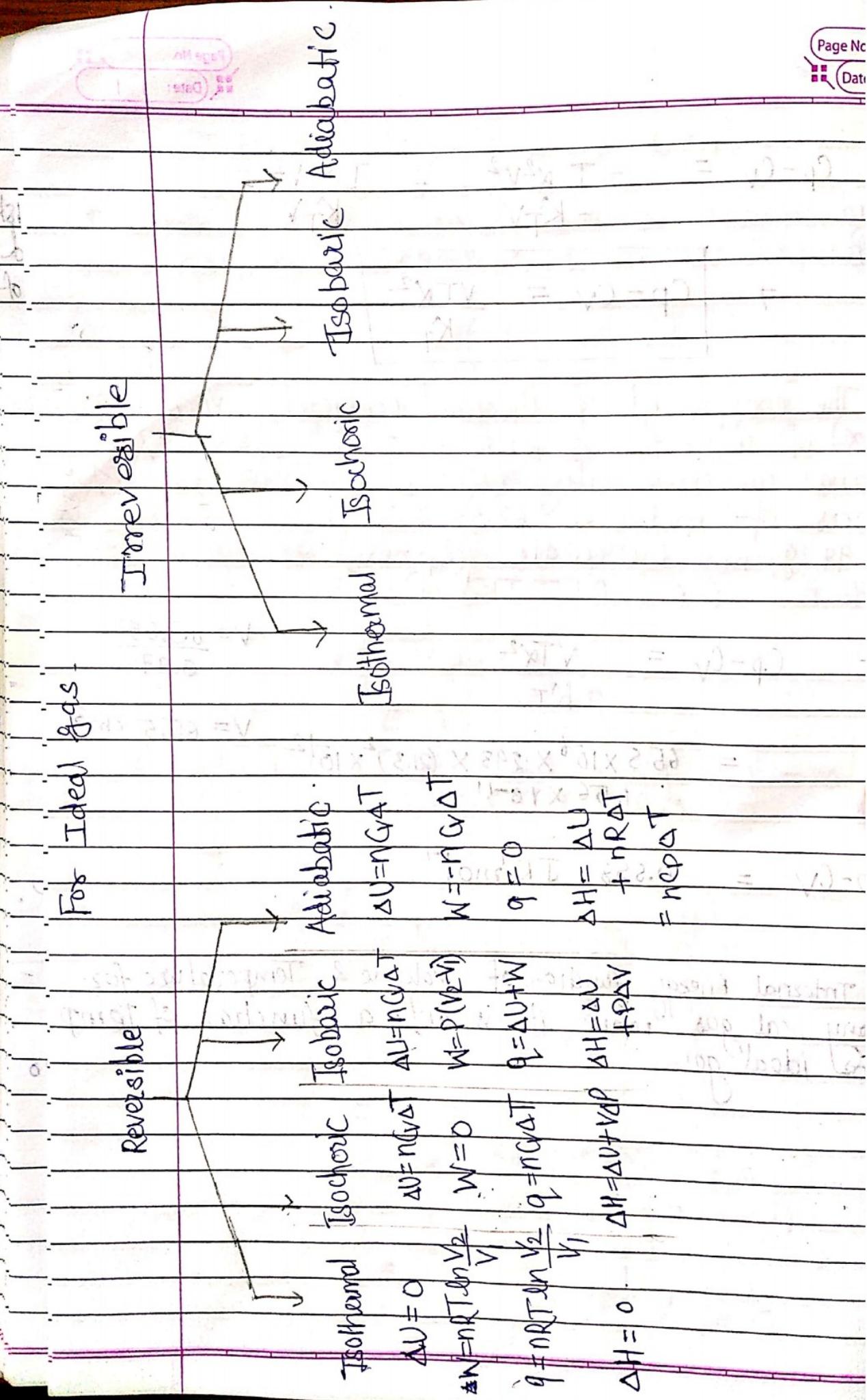
$$V = \frac{63.55}{0.97}$$

$$= 65.5 \times 10^{-6} \times 293 \times (21.3)^2 \times 10^{-12} \\ \cdot 1.56 \times 10^{-11}$$

$$V = 65.5 \text{ cm}^3$$

$$C_p - C_V = 0.558 \text{ JK}^{-1}\text{mol}^{-1}$$

* Internal Energy function of Volume & Temperature for any real gas while it is only a function of temp for ideal gas.



* Second Law of Thermodynamics :-

Importance

Our primary interest in thermodynamics is to use it to establish the criterion for the feasibility of a given chemical or physical transformation under specified conditions.

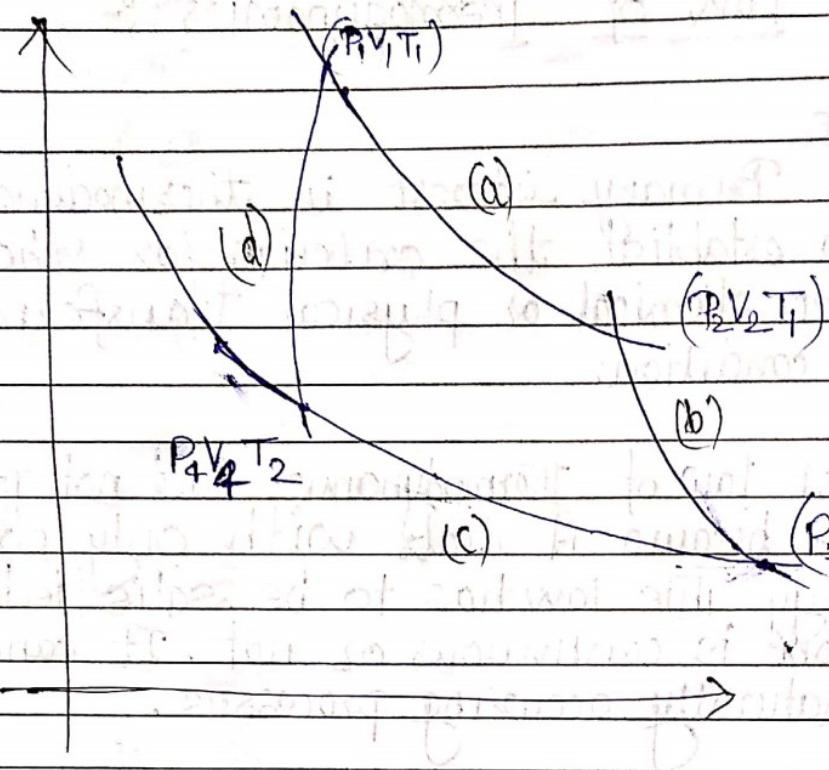
First law of thermodynamics does not provide this information because it deals with only conservation of Energy. This law has to be satisfied whether a reaction is continuous or not. It cannot however explain naturally occurring processes.

e.g. Flow of heat from a warm body to cold body.
Freezing of water, Melting of ice, feasibility of a chemical reaction, etc.

In the Second law of thermodynamics which identifies a new state function like entropy (S); Gibbs free energy (G_f); Helmholtz free energy; Chemical Potential which provide criterion for identifying continuity and equilibrium of a process.

Carnot Cycle

1. Isothermal reversible expansion for ideal gas.
2. Adiabatic reversible expansion for ideal gas.
3. Isothermal reversible compression for ideal gas.
4. Adiabatic reversible compression for ideal gas.



$$\eta = \frac{W_{\text{done}}}{Q_{\text{abs}}} \quad (a) 1. W_1 = nRT_1 \ln \frac{V_2}{V_1}$$

$$2. \Delta U_1 = Q_1, \text{ being pos.} \quad (b) 1. W_2 = -nC_V(T_2 - T_1)$$

$$2. \Delta U_2 = nC_V(T_2 - T_1)$$

$$3. q_2 = 0$$

$$(c) 1. W_3 = nRT_2 \ln \left(\frac{V_4}{V_3} \right)$$

$$2. \Delta U_3 = 0, \text{ being neg.} \quad (d) 1. W_4 = -nC_V(T_1 - T_2)$$

$$2. \Delta U_4 = nC_V(T_1 - T_2)$$

$$3. q_4 = 0$$

$$q_{\text{abs}} = q_1 = \frac{nRT_1 \ln \frac{V_2}{V_1}}{V_1}$$

(W) Net Work done = $W_1 + W_2 + W_3 + W_4$

$$= nRT_1 \ln \left(\frac{V_2}{V_1} \right) - nC_V(T_2 - T_1) + nRT_2 \ln \left(\frac{V_4}{V_3} \right)$$

$$- nC_V(T_1 - T_2)$$

$$\therefore W = nRT_1 \ln \left(\frac{V_2}{V_1} \right) + nRT_2 \ln \left(\frac{V_4}{V_3} \right)$$

for (b)

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\left(\frac{V_3}{V_2} \right)^{\gamma-1} = \left(\frac{V_4}{V_1} \right)^{\gamma-1}$$

for (d)

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\Rightarrow \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \left(\frac{V_3}{V_4} \right)^{\gamma-1}$$

$$\therefore W = nRT_1 \ln \left(\frac{V_2}{V_1} \right) + nRT_2 \ln \left(\frac{V_1}{V_2} \right)$$

$$\therefore W = nR \ln \left(\frac{V_2}{V_1} \right) [T_1 - T_2]$$

$$\eta = \frac{W}{q_{\text{abs}}} = \frac{nR \ln \left(\frac{V_2}{V_1} \right)}{nR \ln \left(\frac{V_2}{V_1} \right)} [T_1 - T_2]$$

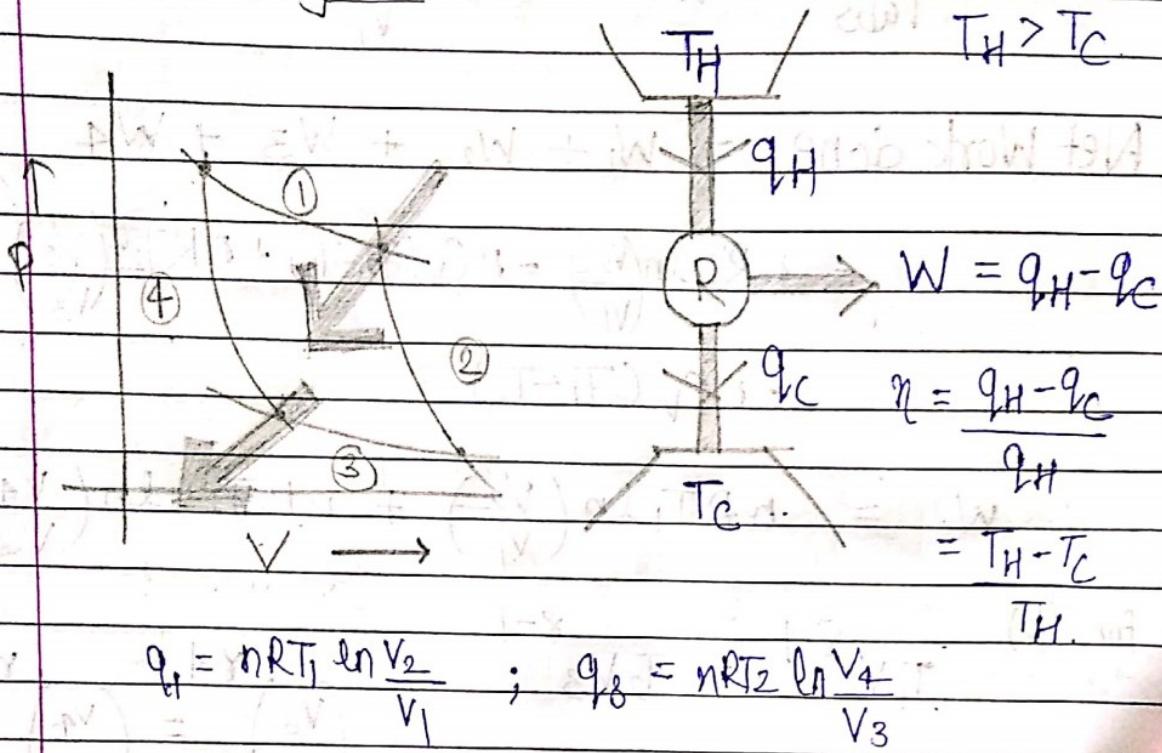
Generally, $\eta = \frac{W}{q_{\text{abs}}} = \frac{nR \ln \left(\frac{V_2}{V_1} \right)}{nR \ln \left(\frac{V_2}{V_1} \right)} [T_1 - T_2]$

for reversible process.

$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$
--

$(T_1 > T_2 \text{ always})$

* Carnot Engine :-



1. Statement I : Kelvin-Plank Statement.

It is impossible for a system/engine operating in a cycle and connected to a single heat reservoir to produce a positive amount of work in the surroundings.

Statement II : Clausius Statement

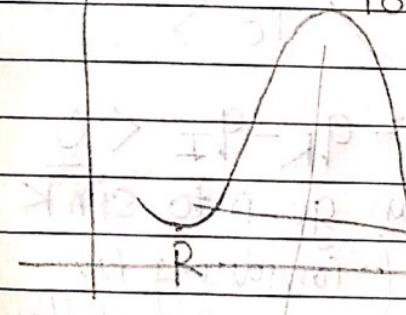
It is impossible for a cyclic process to convert heat into work without the simultaneous transfer of heat from a body at higher temp to a body at lower temp or vice-versa.

* Composition between rev. & irrev. Carnot engine :-
continuous discontinuous (PV curve)

if any one step is irrev. then the whole process is considered to be irreversible.

Free energy diagram.

TS.



Quantum

Tunneling

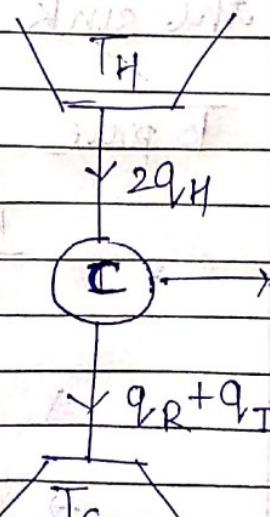
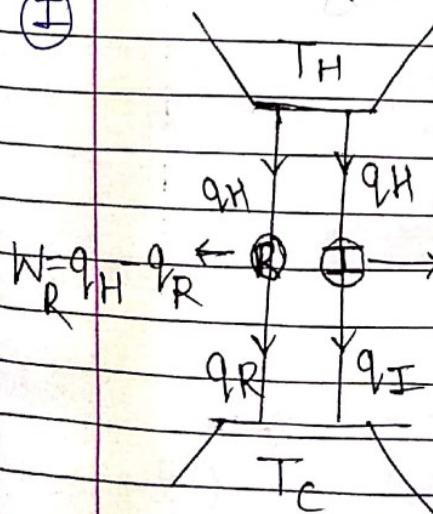
(discontinuous)

Direct conversion from reactant to product w/o TS

Classical Mechanics way
(continuous)

(conversion from P to P)
through TS

(I)



R \Rightarrow reversible

I \Rightarrow irreversible.

$$W_C = 2qH - (qR + qI)$$

If we consider

$$Q_R \geq Q_I$$

As whole heat

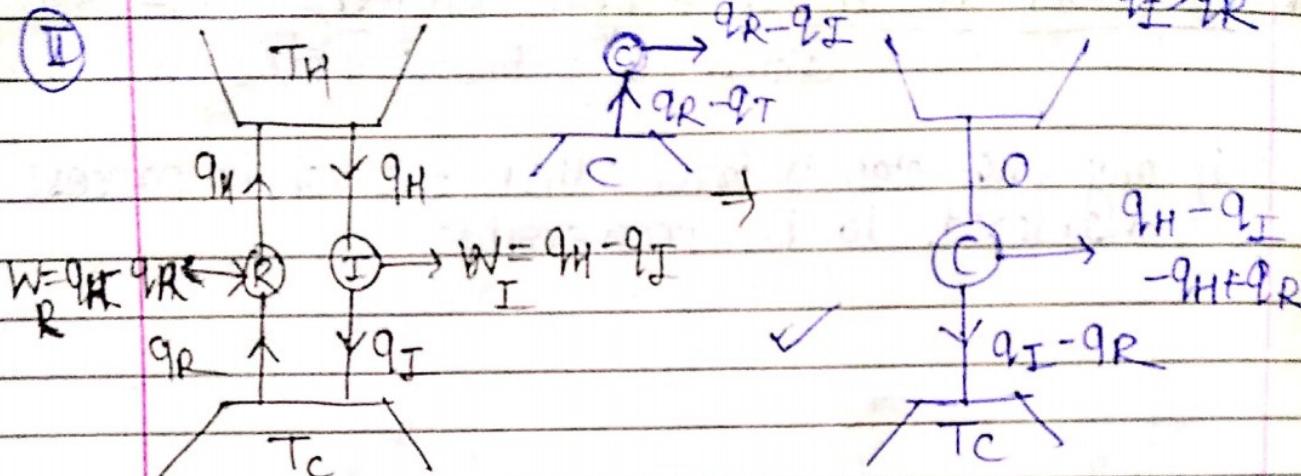
can't go into

work

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②



$$W_C = q_R - q_I < 0$$

because whole given heat can go into sink.

for ② $q_H - q_R > q_H - q_I$ (considering Rev more efficient than irrev.)

(from previous page) $q_I > q_R$.

So in ② whole amount of work goes into the sink.

To prove $\eta_R > \eta_I$.

$$\frac{W_R}{q_H} > \frac{W_I}{q_H}$$

$$\Rightarrow W_R > W_I$$

$$\Rightarrow q_H - q_R > q_H - q_I$$

$$\Rightarrow q_R < q_I$$

~~Ques~~ Tut :-

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Q1) At 27°C , two moles of an ideal monatomic gas occupy a volume V . The gas is adiabatically expanded to a volume $2V$.

(a) Calculate the ratio of final pressure to initial pressure.

(b) Calculate the final temp.

(c) Change in internal energy. ($\gamma = 5/3$)

$$\Rightarrow (b) -TV^{\gamma-1} = \text{const.}$$

$$(300)(V)^{\frac{5}{3}-1} = T_2 (2V)^{\frac{5}{3}-1}$$

$$\Rightarrow T_2 = 300 \left(\frac{V}{2V}\right)^{\frac{2}{3}}$$

$$= 300 (1/2)^{\frac{2}{3}} = 188.98$$

$$\therefore T_2 = 188.98 \text{ K.}$$

$$(a) PV^\gamma = \text{const}$$

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\Rightarrow \frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^\gamma = \left(\frac{V}{2V}\right)^{\frac{5}{3}} = 0.314^\circ$$

$$(c) dq = dU + dW$$

$$\Rightarrow dU + dW = 0 \quad (dq = 0 \text{ (adiabatic)})$$

$$\Rightarrow dU = -dW$$

$$= -P_f (V_2 - V_1)$$

$$dU = nC_V \Delta T = \frac{n}{2} f R \Delta T$$

$$\therefore = 2 \left(\frac{3}{2}\right) (R) (111.02) = 333.06 R.$$

2. Carnot engine operates with efficiency of 40%. How much must the temp. of hot reservoir increase so that the efficiency increases to 50%. The temp of cold reservoir is 9°C .

$$\Rightarrow \text{at } T_C = 9^{\circ}\text{C} = 282\text{K}, \text{efficiency} = \eta_i = 1 - \frac{T_C}{(T_H)_i}$$

$$\eta_i = 1 - \frac{282}{(T_H)_i} \quad \eta_f = 1 - \frac{282}{(T_H)_f}$$

$$\frac{40}{100} = 1 - \frac{282}{(T_H)_i} \quad \frac{50}{100} = 1 - \frac{282}{(T_H)_f}$$

$$\Rightarrow \frac{40}{50} = \frac{1 - \frac{282}{(T_H)_i}}{1 - \frac{282}{(T_H)_f}}$$

~~$$\Rightarrow 4 \left(1 - \frac{282}{(T_H)_f}\right) = 5 \left(1 - \frac{282}{(T_H)_i}\right)$$~~

~~$$\Rightarrow 4 - \frac{4 \times 282}{(T_H)_f} = 5 - \frac{5 \times 282}{(T_H)_i}$$~~

~~$$\Rightarrow 5 \times 282 - 4 \times 282 = \frac{4 \times 282}{(T_H)_i} - \frac{4 \times 282}{(T_H)_f}$$~~

$$\frac{(T_H)_i}{(T_H)_f} = \frac{100 \times 282}{60} \quad \frac{(T_H)_f}{(T_H)_i} = \frac{100 \times 282}{50}$$

$$\frac{100 \times 282}{60} \left(\frac{1}{50} - \frac{1}{70} \right)$$

$$\Rightarrow \Delta H = \frac{10.0 \times 282 \times 10}{3000} = 94^\circ\text{C}$$

3. Derive the expression of W , ΔU , q , ΔH for isothermal expansion of van der waal gas.

$$\Rightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$dW = PdV \quad \text{--- (1)} \quad \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad \text{--- (2)}$$

$$dq = dU + dW$$

$$H_1 = U_1 + PV_1$$

$$dU = dq - dW$$

$$H_2 = U_2 + PV_2$$

--- (3)

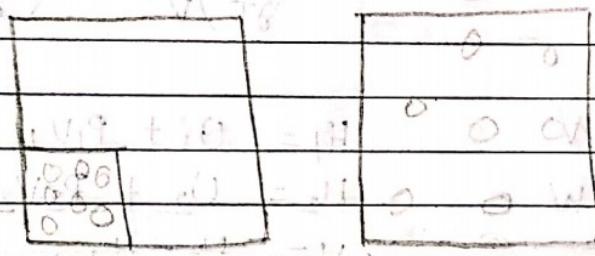
$$\Delta H = H_2 - H_1 \quad \text{--- (3)}$$

* Entropy :-

Entropy is a measure of number of possible microstates of a system.

Microstate \Rightarrow The positions and momenta of a particular particle at a particular instant.

$$(x, y, z, v_x, v_y, v_z)$$



phase space

6 dimensional

$$S = k_B \ln \Omega$$

(from third law)

Just for e.g. \rightarrow	Dice Coin	Spice	$S = k_B \ln \Omega$
	6 possible states	2 possible states.	$= -k_B \ln \frac{1}{6}$ $= -k_B \ln \frac{1}{2}$

k_B - Boltzmann constant.

Definition of Entropy (S).

$$\eta_{rev} = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H}$$

$$\Rightarrow \frac{Q_H - Q_C}{Q_H} = \frac{T_H - T_C}{T_H}$$

$$\Rightarrow \frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

$$n_I = \frac{w}{q_H} = \frac{q_H - q_C}{q_H}$$

$$n_R = \frac{T_H - T_C}{T_H}$$

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$$\Rightarrow \frac{q_H}{T_H} + \left(\frac{-q_C}{T_C} \right) = 0.$$

$$\Rightarrow \oint \frac{dq}{T} = 0 \Rightarrow dS = \frac{dq_{rev}}{T}$$

only for reversible

$$n_R > n_I$$

$$1 - \frac{T_C}{T_H} > 1 - \frac{q_C}{q_H}$$

$$\frac{T_C}{T_H} < \frac{q_C}{q_H} \Rightarrow \frac{q_H}{T_H} + \left(\frac{-q_C}{T_C} \right) < 0.$$

$$\boxed{\oint \frac{dq}{T} < 0}$$

Clausius Inequality

A

Irrev

Rev.

$$\oint \frac{dq_I}{T} = \int \frac{dq_{A \rightarrow B}}{T} + \int \frac{dq_{B \rightarrow A}}{T} < 0$$

$$\Rightarrow B \xrightarrow{I} A, B \xrightarrow{R} A$$

$$\Rightarrow \int \frac{dq_{A \rightarrow B}}{T} - \int \frac{dq_{B \rightarrow A}}{T} < 0$$

B \xrightarrow{I}

$$\Rightarrow \int \frac{dq_{A \rightarrow B}}{T} < \int \frac{dq_{A \rightarrow B}}{T}$$

B \xrightarrow{R}

Irreversible

$$\Rightarrow \int \frac{dq_{A \rightarrow B}}{T} < \int dS \quad \text{process \& only}$$

(for isolated system)

$$\Rightarrow \Delta S > \int \frac{dq_I}{T} \quad \text{d}q_{\text{ext}}$$

for isolated system; $\Delta S > 0$ describes spontaneity.

* Condition for spontaneity & equilibrium

To find on what characteristics distinguish irreversible transformations from reversible transformation we begin by asking what relation exists between the entropy change in the transformation and the irreversible heat flow that accompanies it.

In a reversible transformation at every stage the system departs from the equilibrium only infinitesimally, but in irreversible transformation at ~~no~~ point the system exists in equilibrium. Therefore, irreversible transformation is a spontaneous transformation; the reversible transformation is basically the equilibrium.

Cond'n for reversible \Leftrightarrow Cond'n for equilibrium
 Cond'n for irreversible \Leftrightarrow spontaneity.

$$\Delta S = \frac{dq_{rev}}{T}$$

$$dq_{rev} = TdS$$

$$\Delta S > \frac{dq_{irr}}{T}$$

$$dq_{irr} < TdS$$

$TdS > dq \rightarrow$ spontaneous.

$$\Rightarrow TdS - dq > 0$$

$$\Rightarrow [TdS - dU - dW > 0]$$

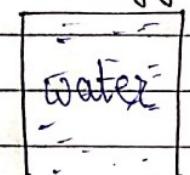
spontaneous

general eqn $\Rightarrow TdS - dU - dW_{\text{mech}} - dW_{\text{av}} > 0 \quad \text{--- (1)}$

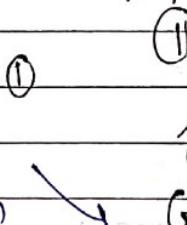
$TdS - dU - dW_{\text{mech}} - dW_{\text{av}} = 0 \rightarrow \text{for equilibrium}$

$TdS - dU - dW_{\text{mech}} - dW_{\text{av}} \geq 0$

* Free energy landscapes.

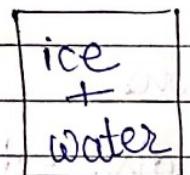


25°C, 1 atm



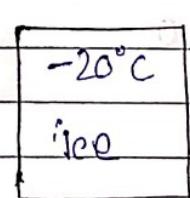
(1)

G



0°C, 1 atm

(2)

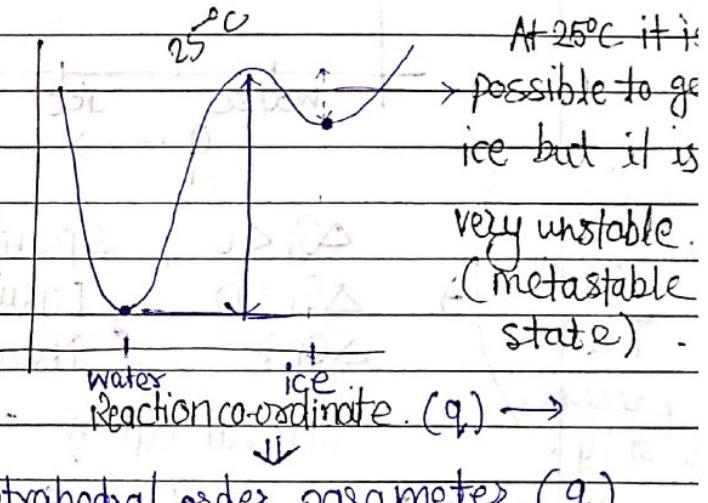


-20°C
ice

(3)

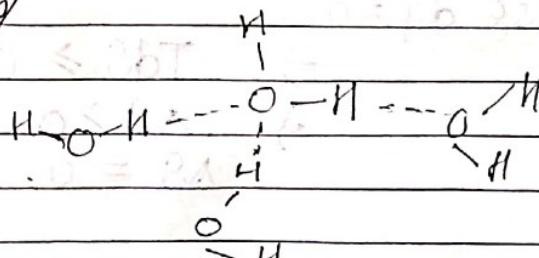
angles
distances

considers

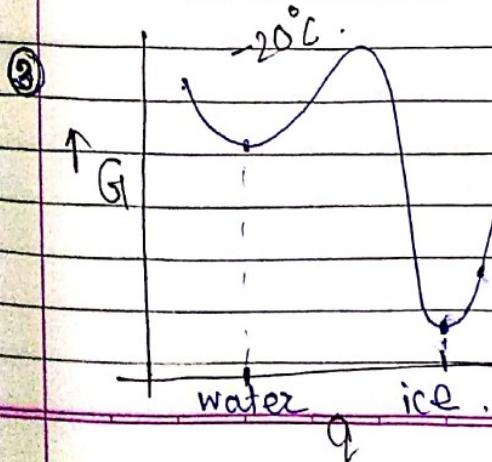


tetrahedral order parameter (q).

(It can distinguish between water and ice)

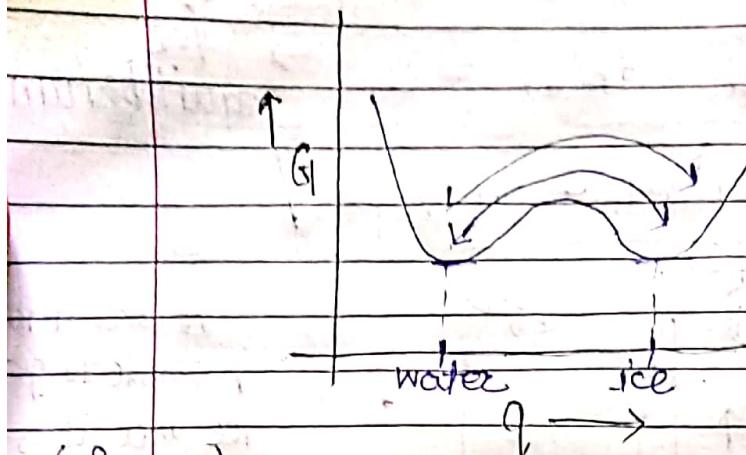


for liquid water $q \downarrow$ for ice $q \uparrow$.



metastable water (supercool water)
At -20°C.

② At 0°C. Equilibrium.



(for Constant T & P.)

- $\Delta G_1 < 0$; Spontaneous
- $\Delta G_1 = 0$; Equilibrium
- $\Delta G_1 > 0$; Non-Spontaneous

processes only.

$$\text{General eqn} \Rightarrow TdS - dU - dW_m - dW_{av} \geq 0$$

① Isolated System (~~Adiabatic~~)

$$\Delta V = 0, \Delta T = 0 \Rightarrow \Delta U = 0$$

$$\Rightarrow TdS \geq dW$$

$$\text{Also } dq = 0$$

$$\Rightarrow TdS \geq 0$$

$\Rightarrow \Delta S > 0 \Rightarrow \text{spontaneous}$

$\Delta S = 0 \Rightarrow \text{equilibrium}$

* Tut.

* Show mathematically that the magnitude of the work involved in reversible expansion of an ideal gas from (P_1, V_1) to (P_2, V_2) is larger than the corresponding work involved in an irreversible expansion against the conit pressure P_2 .

Ans.

$$|W_{rev}| = nRT \ln \frac{V_2}{V_1} = nRT \ln \left[1 + \left(\frac{V_2}{V_1} - 1 \right) \right]$$

$$\Rightarrow |W_{rev}| = nRT \left\{ \left(\frac{V_2}{V_1} - 1 \right) + \text{higher terms} \right\}$$

$$\therefore |W_{rev}| = \frac{nRT}{V_1} (V_2 - V_1) + h.t.$$

$$\therefore |W_{rev}| = P_1(V_2 - V_1) + h.t.$$

$$\therefore |W_{irr}| = P_2(V_2 - V_1)$$

$$\therefore |W_{rev}| - |W_{irr}| = P_1(V_2 - V_1) + h.t. - P_2(V_2 - V_1)$$

$$= (P_1 - P_2)(V_2 - V_1) + h.t.$$

$$P_1 > P_2 \text{ & } V_2 > V_1$$

$$\therefore |W_{rev}| - |W_{irr}| = +ve$$

* $C_p - C_V = \frac{V T \alpha^2}{K_T} ; K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T ; \alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

* Derive the T-V eqn for adiabatic expansion of van der waals gas.

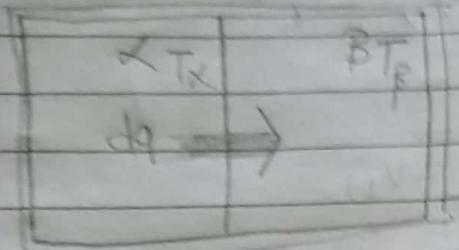
$$\Rightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\therefore W_b + (2P - U)b = \Delta H$$

$$\therefore W_b + A_b = \Delta H$$

Work and Heat of a system

* Isolated System $\Delta S \geq 0$ \rightarrow equilibrium



Entropy change for A

$$dS_A = -\frac{dq}{T_A}$$

$$\text{for } B: dS_B = \frac{dq}{T_B}$$

$$dS = dS_A + dS_B = \frac{dq}{T_B} - \frac{dq}{T_A} \geq 0$$

$$\Rightarrow T_A \geq T_B$$

Heat transfer occurs

only from high temp
to low temp

$$T_A > T_B \Rightarrow \text{spont.}$$

$$T_A = T_B \Rightarrow \text{eqm.}$$

AT constant temperature

$$\left(\begin{array}{l} TdS - dU - dW \geq 0 \\ \Rightarrow TdS - dU - dW_m - dW_{qv} \geq 0 - \textcircled{M} \end{array} \right)$$

$$\Rightarrow -d(U-TS) - dW \geq 0 - \textcircled{MI}$$

$$\Rightarrow d(U-TS) + dW \leq 0.$$

$$\Rightarrow dA + dW \leq 0$$

If there is no work

$$dA \leq -dW \Rightarrow dA \leq 0$$

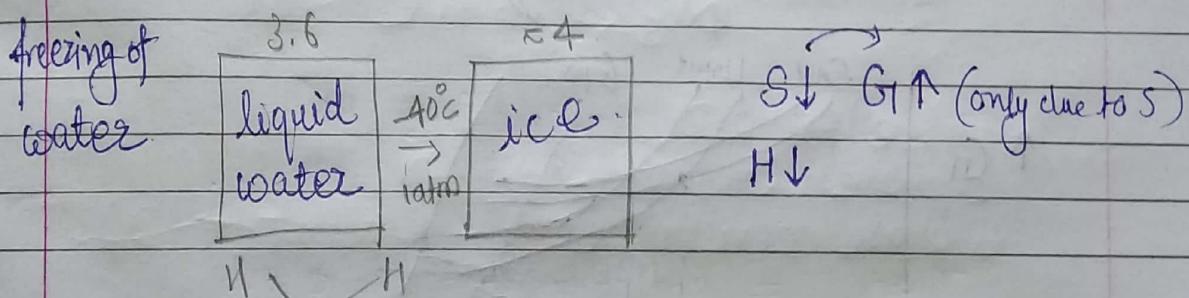
$A \Rightarrow$ Helmholtz free energy

At constant temperature and pressure;

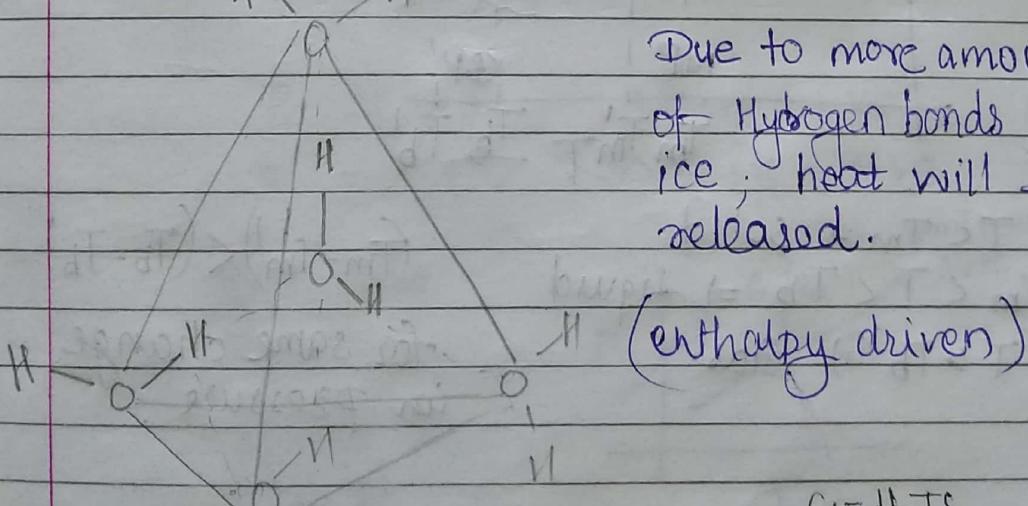
$$\begin{aligned} TdS - dU - PdV - dW_{av} &\geq 0. \\ \Rightarrow TdS - dU - d(PV) &\geq dW_{av}. \\ \Rightarrow -d(U-TS) - d(PV) &\geq dW_{av}. \\ \Rightarrow -d(U-TS + PV) &\geq dW_{av}. \\ \Rightarrow d(U+PV-TS) &\leq -dW_{av}. \\ \Rightarrow d(H-TS) &\leq -dW_{av}. \\ \Rightarrow dG &\leq -dW_{av}. \\ \Rightarrow dG &\leq 0. \end{aligned}$$

1. $TdS - dU - dW_m - dW_{av} \geq 0 \rightarrow \text{Parent}$
2. $dS \geq 0 \rightarrow \text{(B1)} \rightarrow \text{isolated}$
3. $dA \leq 0 \rightarrow \text{(B2)} \rightarrow \text{const. temp.}$
4. $dG \leq 0 \rightarrow \text{(B3)} \rightarrow \text{const. T \& P.}$

$$A = U - TS ; G = (H - TS) \quad (\text{overall}) \checkmark$$



Due to more amount of Hydrogen bonds in ice, heat will be released.



$$G = H - TS$$

Gibb's free energy

$$\delta F = H - TS$$

$$\begin{aligned} dG_1 &= dH - TdS - SdT \\ &= dU + PdV + VdP - TdS - SdT \\ &= dq + VdP - TdS - SdT \end{aligned}$$

for a reversible process, $dq = TdS$.

$$\begin{aligned} &= TdS + VdP - TdS - SdT \\ &= VdP - SdT. \end{aligned}$$

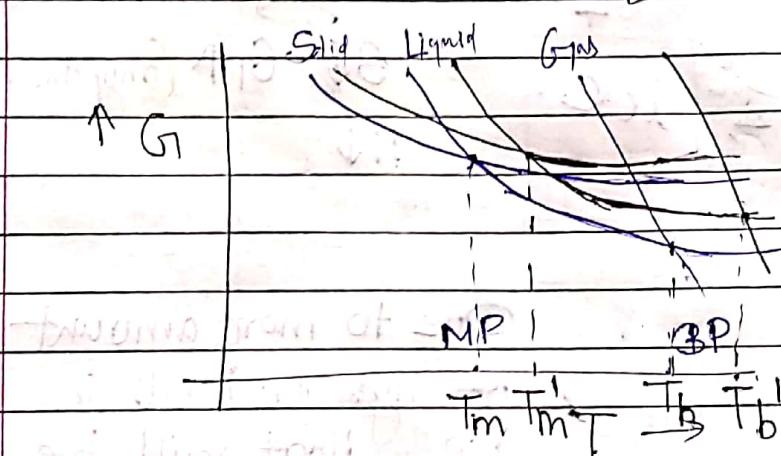
molar Gibbs' free energy change

chemical potential

$$d\bar{G} = \bar{V}dP - \bar{S}dT$$

$$dU = \bar{V}dP - \bar{S}dT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \textcircled{1} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \textcircled{2}$$



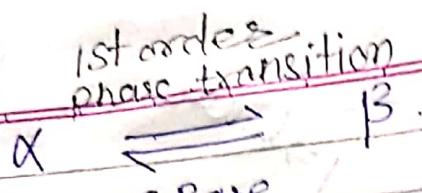
$T < T_m \Rightarrow \text{solid}$

$T_m < T < T_b \Rightarrow \text{liquid}$

$T > T_b \Rightarrow \text{gas}$

$$(T_f - T_m) < (T_b - T_f)$$

for same change
in pressure.



T & P are const.

$$\Delta \mu = \frac{d\mu}{dP}$$

$$\mu_\alpha = \mu_B \quad \text{--- (1)}$$

↑ Chem. potential of α . ↑ Chem. potential of B .

$$dP$$

$$\mu_\alpha + d\mu_\alpha = \mu_B + d\mu_B \quad \text{--- (2)}$$

$$\text{from (1) \& (2)} \Rightarrow \\ d\mu_\alpha = d\mu_B$$

$$\bar{V}_\alpha dP - S_\alpha dT \\ - \bar{V}_B dP - \bar{S}_B dT$$

$$\Rightarrow (\bar{V}_\alpha - \bar{V}_B) dP = (\bar{S}_\alpha - \bar{S}_B) dT \quad \text{--- (3)}$$

$$\left. \begin{aligned} \frac{dT}{dP} &= \frac{\bar{V}_\alpha - \bar{V}_B}{\bar{S}_\alpha - \bar{S}_B} = \frac{\Delta V_{\alpha \rightarrow B}}{\Delta S_{\alpha \rightarrow B}} \\ (4) \end{aligned} \right\}$$

$$\frac{dP}{dT} = - \frac{\Delta S_{\alpha \rightarrow B}}{\Delta V_{\alpha \rightarrow B}}$$

$$\frac{dP}{dT} = \frac{\Delta H_{\alpha \rightarrow B}}{T \Delta V_{\alpha \rightarrow B}} \quad \text{--- (4)}$$

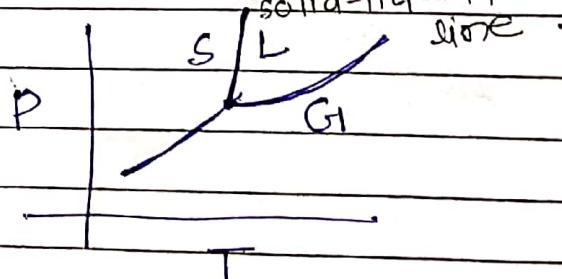
Capeyron's equation.

$$\alpha \rightleftharpoons \beta \quad \Delta S_{\alpha \rightarrow B} = +ve$$

$$S \rightleftharpoons L \quad \Delta V_{\alpha \rightarrow B} = +ve$$

$$\frac{dP}{dT} = +ve$$

Normal liquids



for general liquids (not water)

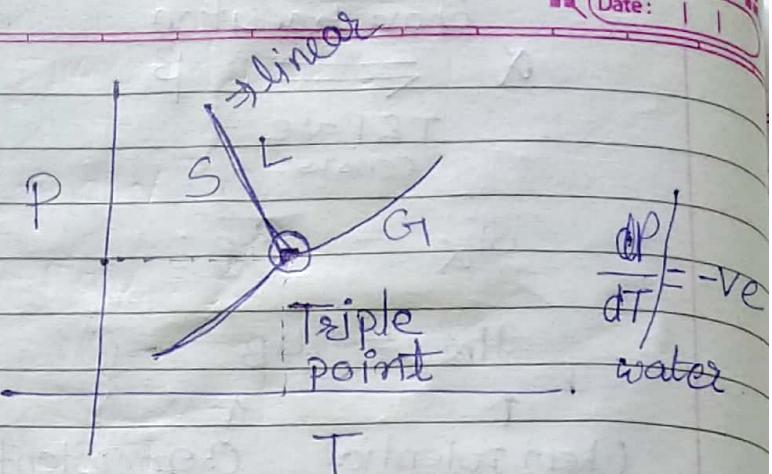
for water

$$\alpha \rightleftharpoons \beta$$

$$S \rightleftharpoons L$$

$$\Delta S_{\alpha \rightarrow \beta} = +ve$$

$$\Delta V_{\alpha \rightarrow \beta} = -ve$$



\therefore Volume of water is lower than ice at same temp. and pressure.

Normal for

liquids $L \rightleftharpoons G$ $\Delta S_{L \rightarrow G} = +ve$ $\frac{dP}{dT} = +ve$

$$\Delta V_{L \rightarrow G} = +ve$$

for

$$S \rightleftharpoons G \quad \Delta S_{S \rightarrow G} = +ve \quad \frac{dP}{dT} = +ve$$

$$\Delta V_{S \rightarrow G} = +ve$$

phase \Rightarrow 2D

2-phase coexistence \Rightarrow 1D

3-phase coexistence \Rightarrow a point (0D).

* Show that work is path function

$$\Rightarrow dW = -pdV$$

$$\text{Let, } V = f(T, P)$$

$$\Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\Rightarrow dW = -P \left\{ \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right\}$$

$$\rightarrow -\left(\frac{\partial W}{\partial P}\right)_T = P \cdot \left(\frac{\partial V}{\partial P}\right)_T \quad \text{--- (1)}$$

$$-\left(\frac{\partial W}{\partial T}\right)_P = P \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

Let, W be a state function then
we assume.

$$\frac{\partial^2 W}{\partial T \cdot \partial P} = \frac{\partial^2 W}{\partial P \cdot \partial T} \quad \text{--- (3)}$$

$$\text{i.e. } \frac{\partial}{\partial T} \left[\left(\frac{\partial W}{\partial P} \right)_T \right] = \frac{\partial}{\partial P} \left[\left(\frac{\partial W}{\partial T} \right)_P \right] \quad \text{--- (2)}$$

from (1) $\Rightarrow \frac{\partial}{\partial T} \left[-P \left(\frac{\partial V}{\partial P} \right)_T \right]_P = -P \cdot \frac{\partial^2 V}{\partial T \cdot \partial P} \quad \text{--- (4)}$

& (2) $\Rightarrow \frac{\partial}{\partial P} \left[-P \cdot \left(\frac{\partial V}{\partial T} \right)_P \right]_T = -P \cdot \frac{\partial^2 V}{\partial P \cdot \partial T} - \left(\frac{\partial V}{\partial T} \right)_P$

from (3) & (4): $-P \cdot \frac{\partial^2 V}{\partial T \cdot \partial P} = -P \cdot \frac{\partial^2 V}{\partial P \cdot \partial T} - \left(\frac{\partial V}{\partial T} \right)_P$

$$\Rightarrow P \cdot \frac{\partial^2 V}{\partial T \cdot \partial P} = P \cdot \frac{\partial^2 V}{\partial P \cdot \partial T} + \left(\frac{\partial V}{\partial T} \right)_P$$

Since, V is a state function.

$$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = 0$$

$$\Rightarrow V = k \text{ (const)} \text{ if } P = \text{const} \& T \neq \text{const}$$

which is wrong. $\therefore V \propto T$ at const P .

$\Leftrightarrow \therefore W$ is a path function.

★ Show that heat is inexact function.



$$dq = dU + dW$$

$$\Rightarrow dq = dB - PdV$$

$$\Rightarrow \left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - P$$

$$\Rightarrow \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Let, q be exact (state function) Then

$$\frac{\partial q}{\partial T \cdot \partial V} = \frac{\partial^2 q}{\partial V \cdot \partial T}$$

$$\Rightarrow \frac{\partial}{\partial T} \left[\left(\frac{\partial U}{\partial V} \right)_T - P \right]_V = \frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial T} \right)_V \right]_T$$

$$\Rightarrow \frac{\partial^2 U}{\partial T \cdot \partial V} - \left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial^2 U}{\partial V \cdot \partial T}$$

Since, U is exact.

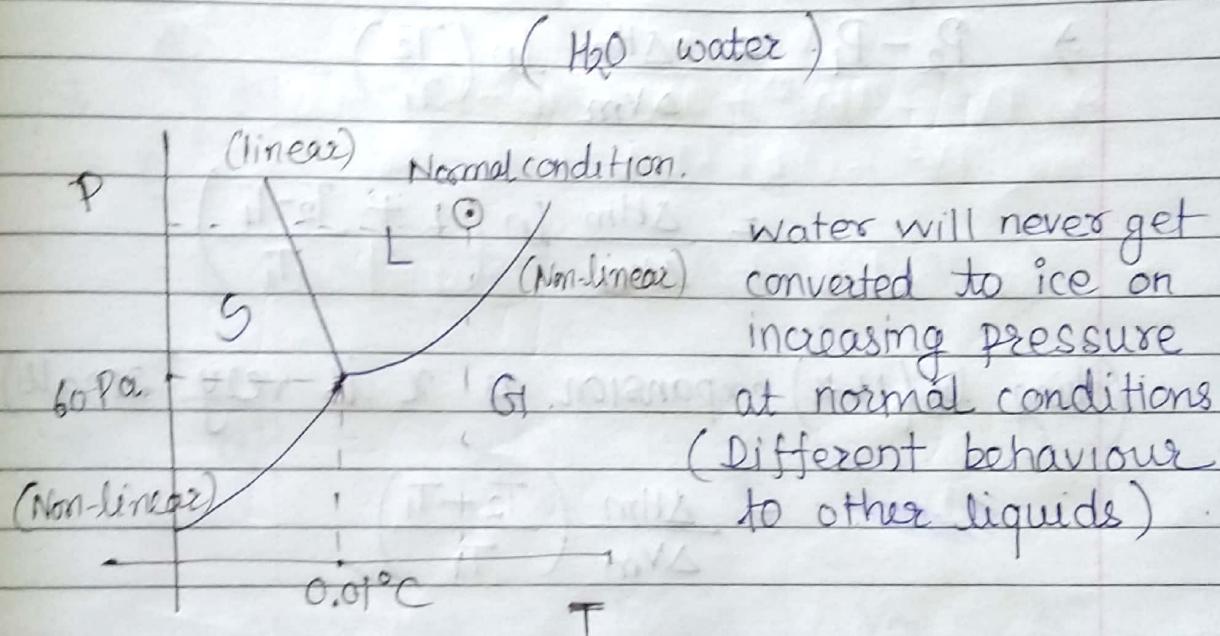
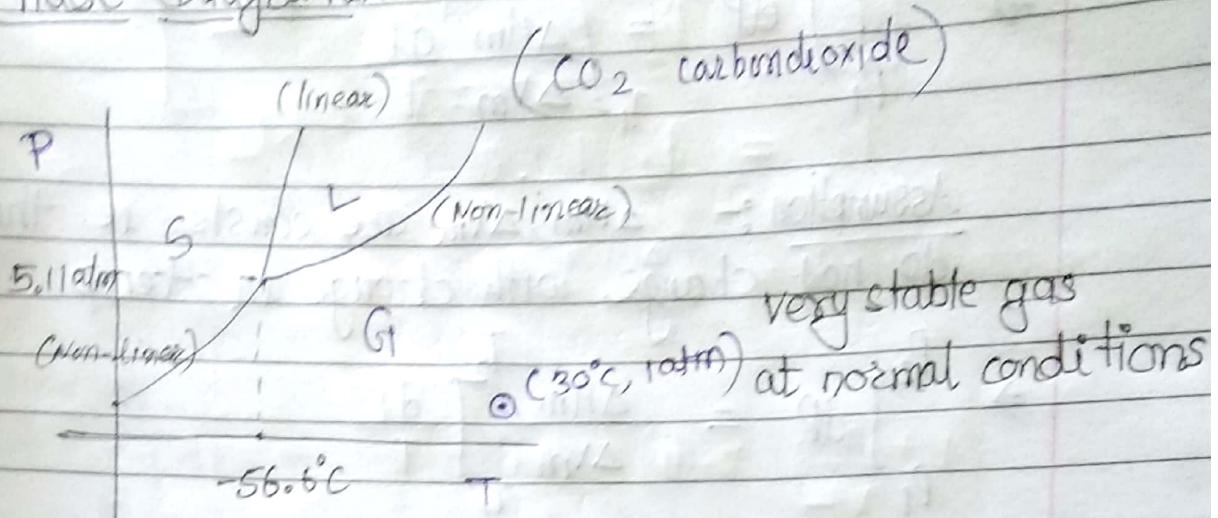
$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = 0$$

⇒ $P = \underline{k}$ if $T \neq \text{const}$ & $V = \text{const}$.
which is wrong.

⇒ $P \not\propto T$ at const. V .

∴ q is inexact

★ Phase Diagrams



(Slope of line in (P-T) plot) $\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$ (Clapeyron's Equation)

★ For Solid to liquid Transition :- $S \rightleftharpoons L$

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m} \quad \Delta H_m = H_L - H_S$$

$$\Delta V_m = V_L - V_S$$

$m \rightarrow$ melting

$$dP = \frac{\Delta H_m}{\Delta V_m} \frac{dT}{T}$$

(Volume of ice > Volume of water)

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$$\Rightarrow \int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{\Delta H_m}{\Delta V_m} dT$$

Assumption:- $\Delta H_m, \Delta V_m$ are const. i.e. they do not change with change in temp

$$\Rightarrow \int_{P_1}^{P_2} dP = \frac{\Delta H_m}{\Delta V_m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow P_2 - P_1 = \frac{\Delta H_m}{\Delta V_m} \ln \left(\frac{T_2}{T_1} \right)$$

$$= \frac{\Delta H_m}{\Delta V_m} \ln \left(1 + \frac{T_2 - T_1}{T_1} \right)$$

(Using $\ln(1+x)$ expansion as x is very small)

$$= \frac{\Delta H_m}{\Delta V_m} \left(\frac{T_2 - T_1}{T_1} \right)$$

$$\Rightarrow P_2 = P_1 - \frac{\Delta H_m}{\Delta V_m} + \frac{\Delta H_m}{\Delta V_m} \cdot \frac{T_2}{T_1}$$

Valid only
for small
 \Rightarrow

$$P_2 = \left(\frac{\Delta H_m}{\Delta V_m \cdot T_1} \right) T_2 + \left(P_1 - \frac{\Delta H_m}{\Delta V_m} \right)$$

Temperature variations. (of form $y = mx + c$)

Slope of (P-T) plot = $\frac{\Delta H_m}{\Delta V_m \cdot T_1}$
(for melting)

For liquid to Gas Transition :- $L \rightleftharpoons G_1$

$$\frac{dp}{dT} = -\frac{\Delta H_{vap}}{T \cdot \Delta V_{vap}}$$

$$dp = \frac{\Delta H_{vap}}{\Delta V_{vap}} \cdot \frac{dT}{T}$$

$$\Rightarrow \int_{P_1}^{P_2} dp = \int_{T_1}^{T_2} \frac{\Delta H_{vap}}{\Delta V_{vap}} \cdot \frac{dT}{T}$$

$$\Rightarrow \int_{P_1}^{P_2} dp = \int_{T_1}^{T_2} \frac{\Delta H_{vap}}{(V_G - V_L)} \cdot \frac{dT}{T}$$

$$(V_G \gg V_L \therefore V_G - V_L \approx V_G)$$

$$\Rightarrow dp = \frac{\Delta H_{vap}}{V_G} \cdot \frac{dT}{T}$$

$$\text{Assuming Ideal gas; } V_G = \frac{RT}{P}$$

$$\Rightarrow \int_{P_1}^{P_2} \frac{dp}{P} = \int_{T_1}^{T_2} \frac{\Delta H_{vap}}{RT} \cdot \frac{dT}{T}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Rightarrow \ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{RT_1} - \frac{\Delta H_{vap}}{RT_2}$$

$$P_2 = P_1 \cdot e^{-\frac{\Delta H_{vap}}{RT_1} - \frac{\Delta H_{vap}}{RT_2}}$$

$$P_2 = P_1 \cdot (k) \cdot e^{-\Delta H_{vap}/RT_2}$$

$$(\text{some const.}) \quad k = e^{\Delta H_{vap}/RT}$$

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$\Rightarrow PV^3 - PbV^2 + aV - ab - RTV^2 = 0$$

$$\Rightarrow PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

* for Solid to Gas Transition

$$T_b = \frac{ab}{aV - ab}$$

$$T_b = \frac{ab}{aV - ab}$$

$$T_b = \frac{ab}{aV - ab}$$

Tut

$\mu \Rightarrow$ Chemical Potential (Gibbs free energy per mole)

(i)

Calculate the effect on the chemical potentials of ice and water at increasing the pressure from 1.00 bar to 2.00 bar at 273K. The density of ice is 0.917 g/cm³ and that of liquid water is 0.999 g/cm³ under these conditions

$$\text{ice } (\Delta H) = 1.97 \text{ J/mol}^{-1}$$

$$\text{water } (\Delta H) = 1.80 \text{ J/mol}^{-1}$$

$$\rightarrow d\bar{G} = \bar{V} dP - \bar{S}dT$$

$$\rightarrow d\mu = \bar{V} \cdot dP - \bar{S}dT$$

$$\Rightarrow \frac{d\mu}{dP} = \bar{V} = V_m$$

$$\Rightarrow \Delta \mu = V_m dP$$

$$\Delta \mu = \frac{M dP}{g} \quad (g = M/V_m)$$

$$(\Delta \mu)_{\text{ice}} = \frac{(1.802 \times 10^2) \text{ kg mol}^{-1} (1 \times 10^5 \text{ Pa})}{917 \text{ kg m}^{-3}}$$

$$(\Delta \mu)_{\text{water}} = \frac{(1.802 \times 10^2) \text{ kg mol}^{-1} (1 \times 10^5 \text{ Pa})}{999 \text{ kg m}^{-3}}$$



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(2)

Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS ?

As entropy

is a state

function we can calculate it by breaking into two parts

$$\Delta S = \underset{(pressure)}{\Delta S_1} + \underset{(temp.)}{\Delta S_2}$$

$$\underset{\substack{\text{pressure} \\ \text{const.}}}{\Delta S_1} = \int \frac{dq_{rev}}{T} = \int \frac{nC_{p,m} dT}{T} = nC_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S_1 = (2 \text{ mol}) \left(\frac{7}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{(135+273)}{(25+273)} = 18.3 \text{ J K}^{-1}$$

$$\underset{\substack{\text{temp.} \\ \text{const.}}}{\Delta S_2} = \int \frac{dq_{rev}}{T} = \int \frac{q_{rev}}{T}$$

$$\Rightarrow (q_{rev} = -W = \int pdV = nRT \ln V_f = nRT \ln \frac{P_f}{P_i})$$

$$\therefore \Delta S_2 = \frac{18nRT \ln P_i}{P_f} = (2 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left(\frac{1.5 \text{ atm}}{7 \text{ atm}} \right)$$

$$\therefore \Delta S_2 = -25.6 \text{ J K}^{-1}$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = [18.3 + (-25.6)] = -7.3 \text{ J K}^{-1}$$

3. The enthalpy of fusion of mercury is 2.292 kJ/mol and its normal freezing point is 243.9 K with the change in molar volume of $0.517 \text{ cm}^3/\text{mol}$ on melting. At what temperature will the bottom of a column of mercury (density = 13.6 g/cm^3) of height 10m be expected to freeze? (297.4 K)

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}$$

$$\int dP = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \cdot \int \frac{dT}{T} \Rightarrow P_2 - P_1 = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \ln \frac{T_2}{T_1}$$

$$(13.6 \times 10^3 \text{ kg/m}^3) (9.81 \text{ m/s}^2) (10\text{m}) = 981 \text{ N/m}^2$$

$$= 1 \times \frac{2.292 \times 10^3 \text{ J/mol}}{0.517 \times 10^{-6} \text{ m}^3/\text{mol}} \cdot \ln \left(\frac{T_2}{243.9 \text{ K}} \right)$$

$$\Rightarrow \frac{981 \ln \left(\frac{T_2}{243.9 \text{ K}} \right)}{2.292 \times 10^6} = \frac{13.6 \times 9.81 \times 10 \times 0.517}{2.292 \times 10^6}$$

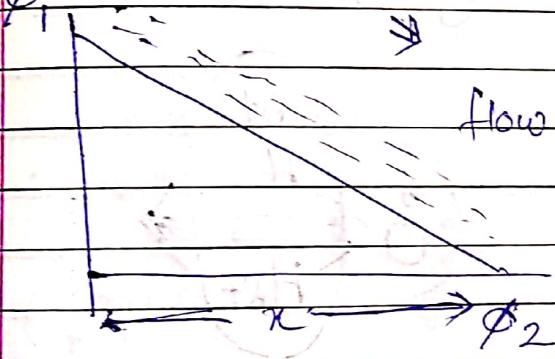
$$\Rightarrow T_2 = 243.9 e^{3.0094 \times 10^{-4}}$$

Conductance In Electrolyte solution :-

- * current (I) :- quantity of electric charge (q) that passes through a point in unit time.
- * Current Density (j) :- quantity of electric charge (q) that passes a point in unit time in unit area (Electric flux).

$$\therefore j = \frac{I}{A}; I = \frac{q}{t} \quad (1)$$

~~Conductivity is proportional to current density~~ $\Rightarrow J \propto -\frac{\partial \phi}{\partial x}$



flow of water
due to Potential
difference.
(change in
potential with
position.)

ϕ_1 & ϕ_2 are (gravitational)
potentials at respective points.

$$\therefore J = -K \frac{\partial \phi}{\partial x} \quad (\text{specific conductivity or conductance})$$

$$J = k(E) \leftarrow \text{Electric field}$$

$$J = R \frac{(\Delta \phi)}{l} \rightarrow \text{Voltage / Potential Difference}$$

(2) (voltmeter)

from ① & ②

$$J = K \Delta \phi = I / R \quad \text{and} \quad A = \pi r^2$$

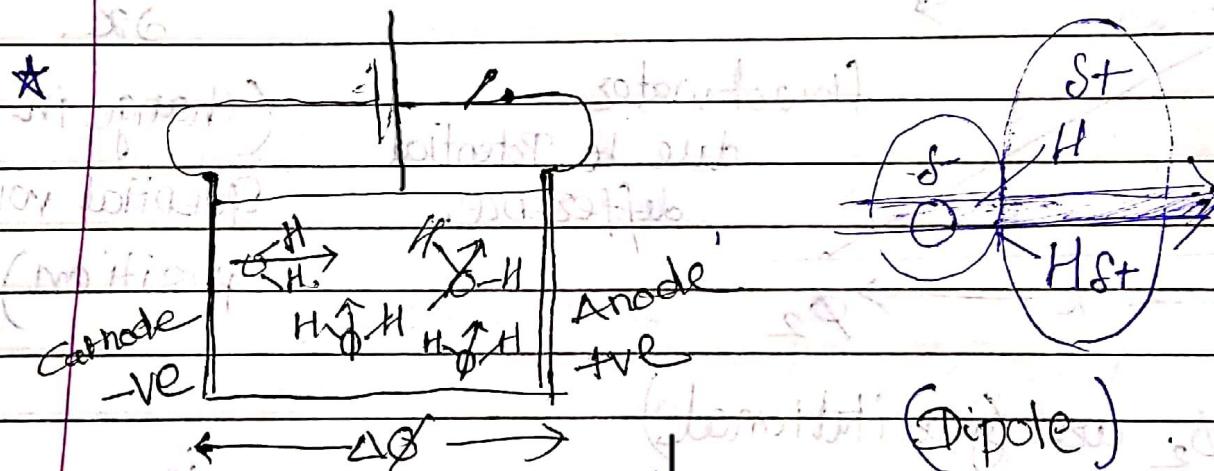
$$\Delta \phi = (I) \cdot l / (K \cdot A) = J \cdot l / R$$

\Rightarrow Resistivity.

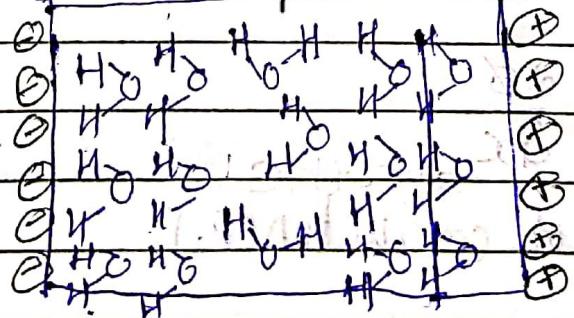
$$\Delta \phi = IR$$

$$I = \frac{\Delta \phi}{R}$$

R is the intrinsic property of the conductor



Switch
ON the
voltage



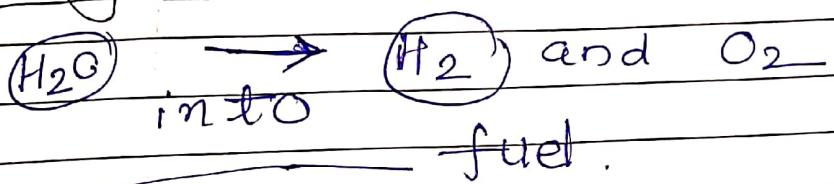
-ve side +ve side

As we move towards centre from the edges interactions get reduced due to screening. Therefore molecules away from the centre are more randomised and molecules at the edges get aligned according to Electric field.

* Autoionization of water

If we increase the E to a very large amount then water molecule gets ionized i.e. H^+ breaks away from water molecule.

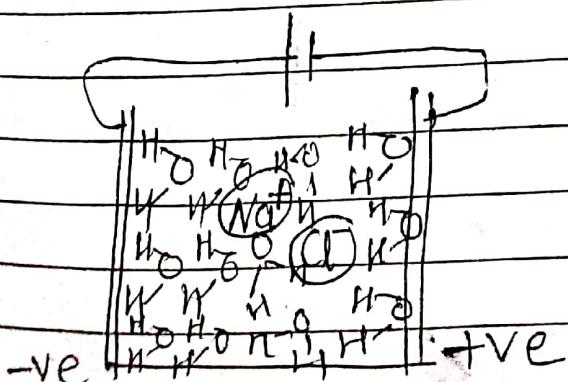
* Splitting of water



No pollution. as on combustion it only generates water.

* (Artificial Leaf). splitting of water by using solar energy. (catalysts are used)

* Pure water is bad conductor of electricity. So, to pass electric charge through water electrolytes are added (eg. $NaCl$).



Resistivity for electrolytic solutions is very high due to following factors

Solvent

① Friction of ion's movement.

(I) For +ve ion's solvent friction emanates from the water surrounding it.

(II) For -ve ion's \Rightarrow Hydrogen bonding, and other electrostatic interactions.

(2) Attraction between opposite charges.

(3) Friction because of Brownian Movement.
(Random Walk).

* Kohlrausch's Law of Independent Migration:

Total conductivity of the electrolyte solution is the sum of individual ions' conductance.

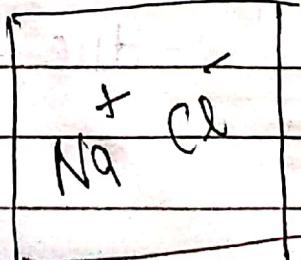
* Applicable for infinitely dilute solution.
Theoretically considered as $1/N_A$ dilution
 $N_A = 6.023 \times 10^{23}$ mol⁻¹.

Interactions between ions is negligible.

$$V = \frac{q_1 q_2}{C} = \frac{q_1 q_2}{4\pi \epsilon_0 r}$$

Coulombic
Interactions.

Considered to be 1.



Potentials: +ve repulsion
-ve attraction.

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Vanderwaals Interactions.
V \propto V_{LJ} (general interaction) Lennard-Jones Potential.

$$V_{LJ} = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

$$\text{Cation} \rightarrow 4\epsilon \left(\frac{\sigma}{r} \right)^{12} - 4\epsilon \left(\frac{\sigma}{r} \right)^6$$

Repulsion factor. attraction factor

$$V = \frac{q_1 q_2}{r}$$

$$V_{LJ} = 4\epsilon \left(\frac{1}{r} \right)^{12} - 4\epsilon \left(\frac{1}{r} \right)^6$$

$$(r = 2^{1/6} \sigma) = 4\epsilon \left(\frac{-1}{r} \right)^{12} = -\epsilon$$

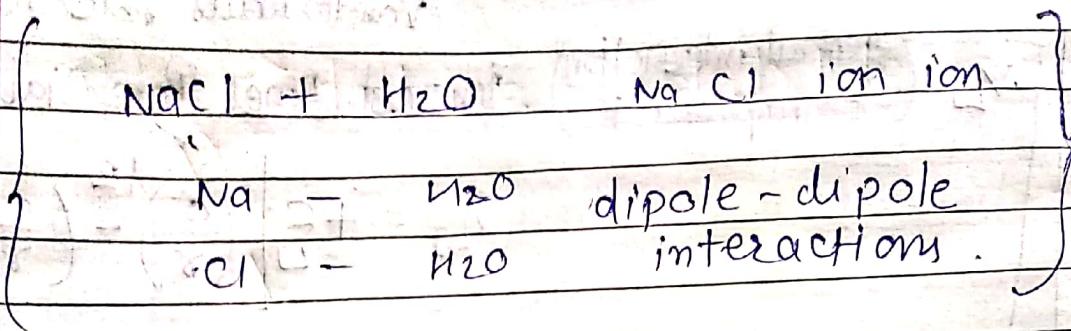
- For molecules having residual charges like ($\text{Na}^+ \text{Cl}^-$) .

Total for molecules like NaCl

$$(V_{\text{Total}})_{\text{vacuum}} = \frac{q_1 q_2}{r} + 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (\text{In vacuum})$$

$(V_{\text{Total}})_{\text{vacuum}}$ is more available at 00

bond length and equilibrium distance
of attraction and repulsion
Optimizing intermolecular forces



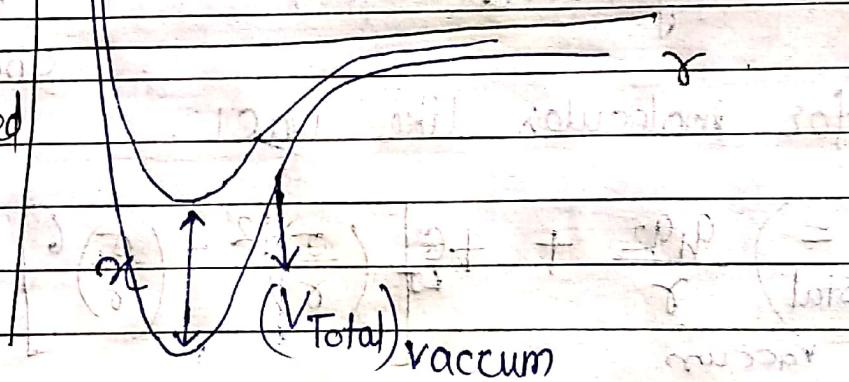
In a solvent, (Here water)

$$\left(\frac{V}{S} \right)_{\text{Total}} = 9.92 + 4\epsilon \left[\left(\frac{\alpha}{\delta} \right)^{12} - \left(\frac{\alpha}{\delta} \right)^6 \right]$$

$$V \quad \left(\frac{V}{S} \right)_{\text{Total}}$$

$S \rightarrow \text{water}$
 $\epsilon_0 = 80$

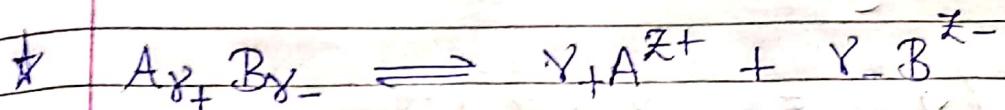
χ
 \rightarrow difference
in interactions
which will result
in difference
in energy required
for dissolution.



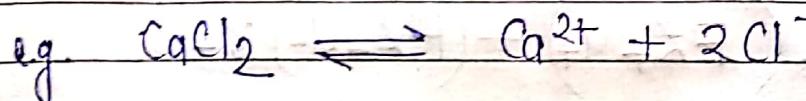
So, to dissolve NaCl in water much less amount of energy is required when compared with vacuum.

As interactions are considerably reduced in solvent like water due to ϵ_0
(change in permittivity)

→ If dipole-dipole interactions are also considered another factor $V_D = \frac{q_1 q_2}{r^3}$ will be added in (V_{Total}) expression (neglected here).



$$\boxed{\gamma_+ Z+ + \gamma_- Z- = 0} \Rightarrow \text{electroneutrality}$$



Validation: $(1)(2) + (2)(-1) = 0$

$$\boxed{K = N_+ u_+ Z_+ e + N_- u_- Z_- e} \quad \dots \quad (1)$$

number density = $\frac{\text{No. of cations}}{\text{Vol}}$ \downarrow velocity of cations. \downarrow charge \downarrow $\frac{\text{No. of anions}}{\text{Vol}}$

$$\boxed{N_+ = N_A \gamma_+ C} \quad \boxed{N_- = N_A \gamma_- C}$$

↓ Avagadro Number \downarrow Stockio.

$K \Rightarrow$ conductance of whole electrolyte solution.

$$\boxed{K = (\gamma_+ u_+ Z_+ + \gamma_- u_- Z_-) F \cdot C}$$

$F \Rightarrow$ Farad = 96500 coulombs

$C \Rightarrow$ concentration.

* Molar conductance of electrolyte solution

(Λ) :-

$$\Lambda = \frac{K}{C}$$

$$\therefore \Lambda = (\gamma_+ u_+ z_+ + \gamma_- u_- z_-) F$$

$$\Rightarrow \Lambda = \gamma_+ (Fz_+ u_+) + (Fz_- u_-) \gamma_-$$

molar conductance of cations molar conductance of anions

$$\boxed{\Lambda^\infty = \gamma_+ \lambda_+ + \gamma_- \lambda_-} = \Lambda_+^\infty + \Lambda_-^\infty$$

cation anion

* Transference Number :-

(t_k) :- $k \rightarrow +$ cation
 $\rightarrow -$ anion.

t_+ \rightarrow trans. no. for cation,

t_- \rightarrow trans. no. for anion.

Fraction of current carried by constituent ion is the transference number for that specific ion.

If Λ is the molar conductivity of the electrolyte solution. Then

$$t_+ = \frac{\lambda_+}{\Lambda}$$

$$; t_- = \frac{\lambda_-}{\Lambda}$$

(Here, stoichiometry is used (not in actual definition))

$$(t_+ = \frac{\gamma_+ \lambda_+}{\Lambda}; t_- = \frac{\gamma_- \lambda_-}{\Lambda})$$

$$\lambda_+ = F z_+ u_+$$

$$t_+ = \frac{\gamma_+ \cdot z_+ F u_+}{F(\gamma_+ z_+ u_+ + \gamma_- z_- u_-)}$$

$$t_- = \frac{\gamma_- \cdot z_- u_+}{\gamma_+ z_+ u_+ + \gamma_- z_- u_-}$$

$$t_+ = \frac{\gamma_+ z_+ u_+}{\gamma_+ z_+ u_+ + \gamma_- z_- u_-}$$

$$t_+ + t_- = 1$$

in many cases (where electroneutrality is maintained).

$$|\gamma_+ z_+| = |\gamma_- z_-|$$

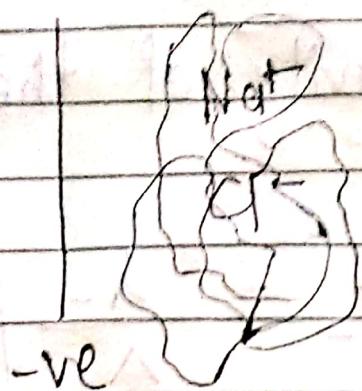
$$\Rightarrow t_+ = \frac{u_+}{u_+ + u_-}$$

$$t_- = \frac{u_-}{u_+ + u_-}$$

$$t_+ = \frac{\text{velocity of cation}}{\text{total velocity}}$$

$$t_- = \frac{\text{velocity of anion}}{\text{total velocity}}$$

$$\frac{t_+}{t_-} = \frac{u_+}{u_-}$$



velocity || to electrodes
does not contribute to
transference number.

-ve +ve

Brownian movement.

* Stokes Einstein Equation :-

$$\text{D} = \frac{K_B T}{6\pi\eta r}$$

\Downarrow size of particle (radius)

Diffusion coefficient

\Downarrow viscosity