

## THERMODYNAMICS :-

Heat & Temp

One is cause & other is effect.

Heat loss from body - Temp ↓

Heat is absorbed by body - Temp ↑

$$\frac{1}{2} m V^2 = \frac{3}{2} k_B T \quad \text{Equipartition principle.}$$

Single Property related to large number of molecules.

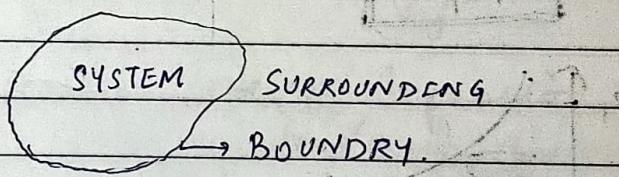
Thermodynamic - is property of large number of molecules  
 ↳ collective property.

Statistical Thermodynamics - Connects molecule and thermodynamic property.

Part of universe under investigation.

Everything outside the system is called surrounding.

A system is separated from the surrounding with the help of a boundary. A boundary has zero thickness so it does not contain any matter.



- \* Open System - Allows both matter and energy movement.
- \* Closed System - Does not allow flow of matter.
- \* Isolated System - Does not allow any flow of mass and energy.

→ It is a myth.

If whole universe is considered - then a isolated body is possible.

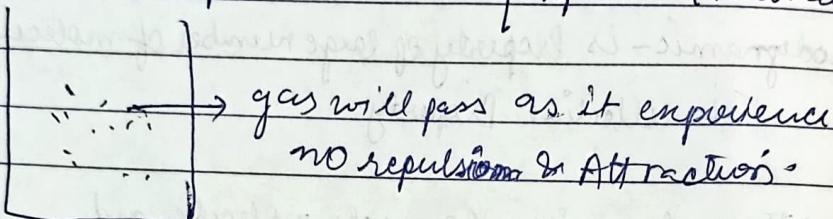
- (1) Isothermal Process.
- (2) Isochoric Process.
- (3) Isobaric Process.
- (4) Adiabatic Process.

A Process that can be reversed back without any extra work.

Ideal gas can be kept in cylinder or not?

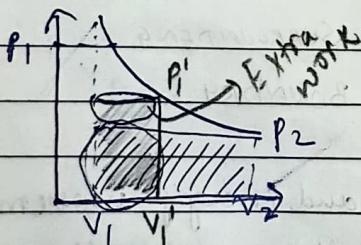
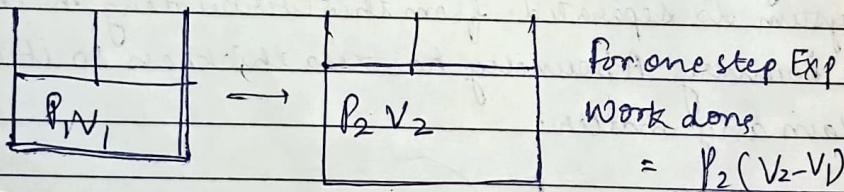
↳ zero volume

Interactive particle attraction / Repulsion (Interaction)

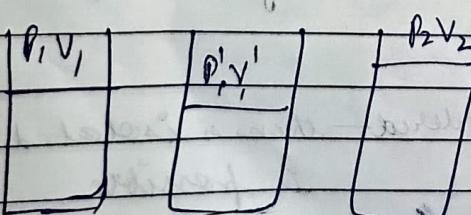


Isothermal Expansion of Ideal gas:-

Expanding the Ideal gas in just one step. (One step Expansion).



2 Step Expansion-



$$W = P_1'(V_1' - V_1)$$

$$W = P_2(V_2 - V_1')$$

$$\text{Extra work done will be} \\ = \underline{(P_1' - P_2)(V_1' - V_1)}$$

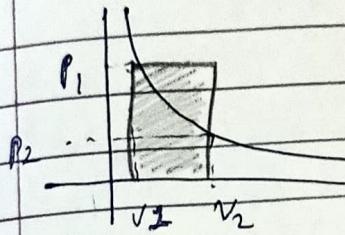
$$w = nRT \ln(V_2/V_1)$$

$$\int dW = \int P dV$$

$$w = \int (P - dP) dV \Rightarrow nRT \ln(V_2/V_1) \rightarrow \text{Maximum work done possible.}$$

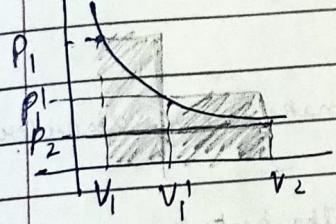
Compression of ideal gas:-

① one step Process:  $w = P_{\text{out}}(V_1 - V_2)$  (+ve value),  
 $= P_1(V_1 - V_2)$  (-ve value).



② Two step process.

Infinite step compression is minimum work required for compression.



③ Infinite step:  $dW = \int_P V dV = nRT \ln\left(\frac{V_f}{V_i}\right)$ ,

For infinite step process: work for expansion is equal to work for compression.  
 Process is reversible

for finite step process:  
 $\downarrow$  work for comp > work for Exp  
 Irreversible process

Expansion of gas = +ve

Compression of gas = -ve

Zeroth law of thermodynamics -

Two system is thermal equilibrium with a third system are also in thermal equilibrium with each other.

Thermal equilibrium - There is no heat flow or heat flow is in mutually opposite sign.

Chemical equilibrium - with time chemical composition does not change.

Quasi / fake equilibrium.

First law of thermodynamics -

Linear -  $3n-5$  Degree of Freedom

Non linear -  $3n-6$  Degree of Freedom

heating is the transfer of energy that make use of disorderly molecular motion.

If a system is under cyclic process then the heat change will be equal to work done.

$$\oint dq = \oint dw$$

$$\oint d(q-w) = 0 = \oint dU = \oint d(\text{state function}) = \oint dU$$

$$dq = dU + dw$$

Heat capacity: heat required to raise temp of substance by 1 degree

$$H_2O > H_{2Se} > H_{2Te} \rightarrow$$

$$H_2O > H_2Po > H_2Te > H_2Se > H_2S,$$

Boiling Point Order.

Ion-Ion > Dipole-Dipole > Vander-waal interactions

Strong tetrahedral 3-dimensional hydrogen bond network  
 So, water has highest heat capacity among II group.

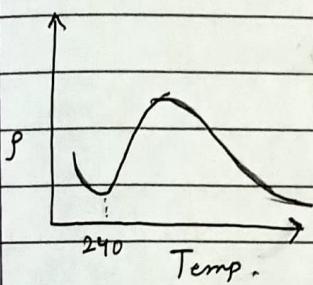
In liquid water tetrahedral structure is not possible because it has translational kinetic energy & due to tetrahedral structure moment will be restricted. Symmetrical forces so no net force applied on central molecule & structure is not tetrahedral.

In liquid phase, water has distorted tetrahedral geometry.

Temperature fluctuation is maintained on earth, because of water having high heat capacity.

(110) Anomalous behaviour of water - high heat capacity

density of water highest at  $4^{\circ}\text{C}$ .



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

$$C_V = \left( \frac{dq}{dT} \right)$$

at constant volume.

$$C_P = \left( \frac{dq}{dT} \right)_P \quad \text{at constant pressure.}$$

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

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad \text{at constant volume.}$$

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

Also,  $dU = dq_V$

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

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

$$\underline{d(U+PV) = dq_V = dU}$$

Enthalpy:

$$dU = dq_V - pdV$$

$$dU = pdV + Vdp = dq_H + Vdp \quad \text{at constant pressure}$$

$$d(U+PV) = dq_H + Vdp \quad \text{State function}$$

$$\downarrow H(\text{enthalpy}) \rightarrow \text{State function}$$

unit of enthalpy - Joules

Extensive property - depends on size of matter.

Enthalpy - is heat exchange with the system at constant pressure

$$dH = dq + Vdp$$

$$H = U + PV$$

heat cap at constant pressure

$$C_p = \left( \frac{dq}{dt} \right)_P$$

$$dH = C_p dt$$

$$\Delta H = \int_{T_1}^{T_2} C_p dt$$

$\rightarrow$  If independent of temp

$$\Delta H = C_p \int_{T_1}^{T_2} dt = C_p (T_2 - T_1)$$

$$C_p = a + bT + cT^2 \rightarrow \text{dependent on temp.}$$

$$\Delta H = \int_{T_1}^{T_2} (a + bT + cT^2) (dT)$$

### Second law of thermodynamics :-

why was 1<sup>st</sup> law not sufficient -

Our primary interest in thermo is to use it to establish the criterion for the feasibility of a given chemical or physical transformation under specific condition. First law of thermodynamics does not provide information as it deals with only conservation of energy. This law has to be satisfied whether reaction is spontaneous or not. It cannot explain naturally occurring process.

### Carnot Cycle :-

#### (i) Reversible Isothermal Expansion.

Slope of Adia > Slope of Isothermal.

$$PV^\gamma = \text{const}$$

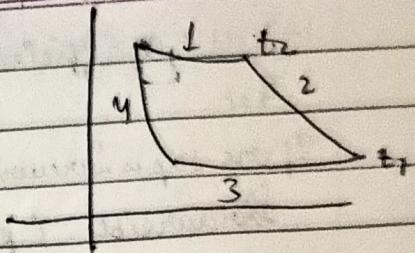
$$PV = \text{const}$$

$$\frac{P}{V^\gamma} = \text{const}$$

$$\frac{P}{V} = \text{const}$$

V

- (2) Reversible Adiabatic Expansion.
- (3) Isothermal Reversible compression
- (4) Adiabatic reversible compression.



Step 1:  $q_1 = \Delta U + w_1 \quad (\Delta U = nC_V \Delta T = 0)$

Step 2: temp change from  $t_2$  to  $t_1$

Adiabatic Expansion is a cooling Process.

temp  $t_2 > \text{temp } t_1$

Step 1: work done =  $w_1 = \int_{V_1}^{V_2} p_2 dV = nRT_2 \ln \frac{V_2}{V_1} = q_1$  (only step in which heat is absorbed)

Step 2:  $\Delta U = -w$   
 $\Delta U = -nC_V(T_1 - T_2)$        $q_2 = 0$   
 $= nC_V(T_1 - T_2)$

Step 3:  $\Delta U_3 = 0$

$$q_3 = w_3 = nRT_1 \ln \frac{V_4}{V_3}$$

Step 4: Adiabatic compression  $\rightarrow$  heating process.

$$q_{42} = \Delta U_4 = nC_V(T_2 - T_1) = w_4$$

Total work done by system

$$= nR \left[ \frac{T_2 \ln V_2}{V_1} + \frac{T_1 \ln V_4}{V_3} \right]$$

$$\text{Heat absorbed} = nRT_2 \ln \frac{V_2}{V_1}$$

$$\text{efficiency} = \frac{\text{Total workdone}}{\text{heat absorbed}} = \frac{nR \left[ T_2 \ln V_2 (V_1 + T_1 \ln V_4) / V_3 \right]}{nRT_2 \ln V_2 / V_1}$$

for Adiabatic process:  $VT^{\gamma-1} = \text{constant}$ .

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

$$V_3 T_1^{\gamma-1} = V_1 T_2^{\gamma-1}$$

$$\frac{V_1}{V_3} = \frac{T_1^{\gamma-1}}{T_2^{\gamma-1}} = \frac{V_2}{V_3}$$

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

$$T_2$$

$$1 - \frac{T_{cold}}{T_{hot}} = \eta = \text{efficiency}$$

That

If one step is irreversible whole cycle will become irreversible. (process is reversible when extra work is applied).

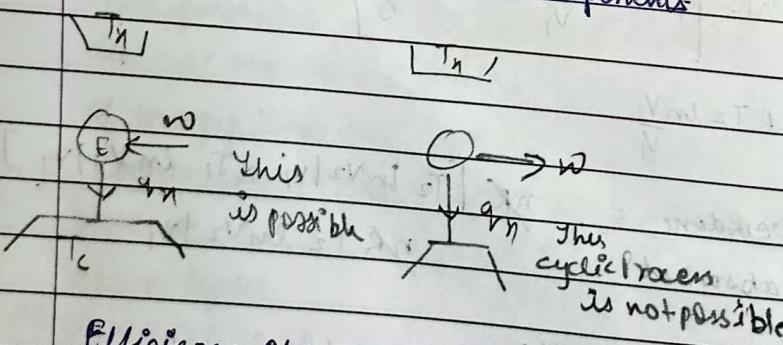
Two special case of interest are:

- (1) If  $T_1 = T_2$  then work done will be zero. Therefore there can't be net conversion of heat into work in an isothermal cycle alone.
- (2) For efficiency = 1, either  $T_1 = 0$  or  $T_2 = \infty$ , These are not possible. Therefore  $\eta = 1$ . Only a fraction. Efficiency can be zero - Yes.

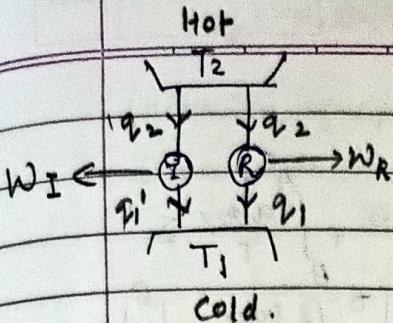
Kelvin Planck statement - It is impossible for a system operating in a cycle and connected to single heat reservoir to produce a positive amount of work in the surroundings.

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

Carnot engine will have = 3 components



Efficiency of reversible engine is more than irreversible engine, because R.E have maximum work done by the system and minimum work for compression on the system.



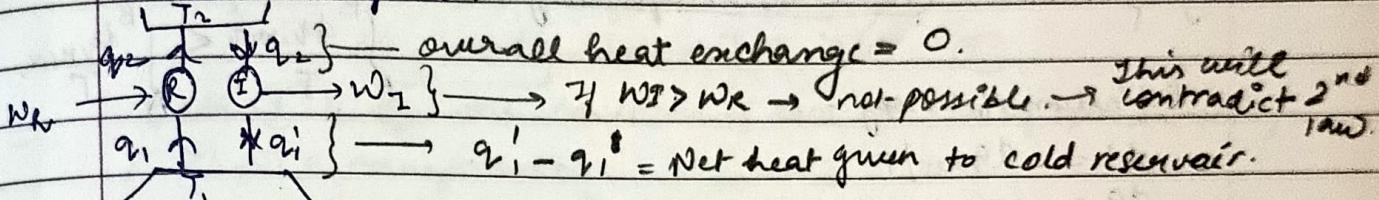
when engines are connected.

$$W = W_R + W_I$$

$$q_R = 2q_2$$

$$q_R = q_1' + q_1$$

combined engine.



so,  $W_I < W_R \rightarrow$  only possible case ]

This does not violate

2<sup>nd</sup> law of thermodynamics.

$W_I = W_R \rightarrow$  Not possible because no network. No engine

$$\eta(\text{reversible}) = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2} \quad \&$$

$$1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2} \Rightarrow \left[ \frac{T_1 - q_1}{T_2 - q_2} \right]$$

$$q_1/T_1 - q_2/T_2 = 0 \quad \text{or} \quad q_2/T_2 - q_1/T_1 = 0$$

$$\frac{q_2}{T_2} + \left( \frac{-q_1}{T_2} \right) = 0 \rightarrow \text{no sign resp heat rejected by system.}$$

$$\sum_{i=1}^{n/2} q_i/T_0 = 0 \quad (\text{n no. of steps in carnot cycle}).$$

This means sum of efficiencies of  $n$

$\oint dq/T = 0$  Thus  $q$  is a state function as cyclic reversible carnot cycle. integral is zero.

$\oint ds = 0$  S → entropy. unit = Joules/kelvin  
extensive property.

For irreversible carnot cycle :-

$$W/q_2 < \frac{T_2 - T_1}{T_2} \quad (\because \text{Work by irr is less than work by reversible})$$

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

If we divide Carnot cycle in 5 small Carnot cycles  
 sum of coefficients of four Carnot cycles is  
 $\sum \frac{q_i}{T_i} < 0$  equal to largest Carnot cycle

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For limiting case  $\oint d\varphi_{rev} < 0$

$$\text{Irreversible} \quad \text{reversible}$$

$$\oint \frac{d\varphi}{T} \leq 0 \rightarrow \text{Clausius inequality}$$

$$dS = \frac{d\varphi_{rev}}{T}$$

$$d\varphi = dU + pdV = dU + pdV$$

$$ds = \frac{dU}{T} + \frac{pdV}{T}$$

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} nR dV$$

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

Definition of entropy:-

$$ds = d\varphi_{rev}/T$$

$$d\varphi = dU + pdV = dU + pdV$$

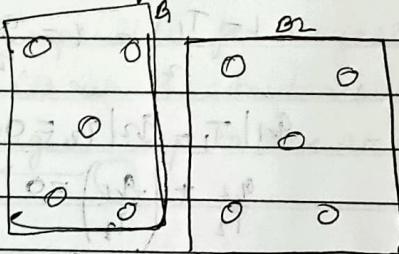
$$ds = \frac{dU}{T} + \frac{pdV}{T}$$

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} nR dV$$

$$\boxed{\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)}$$

We only know about change of entropy not absolute entropy.

Entropy - measure of order.



Both Boxes have same order but

entropy is different.

more entropy when it has more possibility of rearrangement.

$$\int_A^B \frac{d\varphi_{rev}}{T} < \Delta S_{A \rightarrow B}$$

For isolated system  $\boxed{dS_{A+B} > 0}$

Thus the condition of  $dS_{univ}$  in an isolated system is that entropy has a maximum value.

The energy of universe is constant but, no entropy always tends towards a maximum.

All spontaneous transformations is an irreversible process

Irreversible changes are Natural changes

Reversible means equilibrium,

e.g. water freezing at  $0^\circ\text{C}$  & 1 atm pressure.

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Criterion of spontaneity and equilibrium:

Irreversible change  $\leftrightarrow$  Natural change  $\leftrightarrow$  spontaneous change.

$$TdS > dq$$

$$TdS > dU + dW$$

$$-dU - dW + TdS \geq 0 \quad (1)$$

The work includes all type:

$$-dU_{ext} - dV_{ext} - dW_a + TdS \geq 0 \quad (2)$$

Both (1) & (2) are condition of eqm ( $\rightleftharpoons$ ) and of spontaneity  
( $>$ ) for a transformation.

cond'n of spontaneity & eqm in presence of ~~constraint~~ constraint:

(1) Transformations in an isolated system:

$$TdS \cdot dU = 0, dW = 0, dq = 0$$

$$\text{So, eqn (1) is } TdS \geq 0 \quad (3)$$

$$dS \geq 0 \quad (4)$$

From eqn (4) it follows that an isolated system at eqm must have same temp. in all parts

equality  $\rightarrow$  equilibrium  $\rightarrow$  spontaneous

(2) Transformation at constant temp and volume:

$$TdS = d(TS)$$

$$-dU - dW + TdS \geq 0 \quad -dU - dW + d(TS) \geq 0$$

$$TdS =$$

$$-d(U - TS) - dW \geq 0$$

$(U - TS) \rightarrow$  is state function as

U, T, S all of them are state function

$$-dA \geq dW$$

$$dA \leq -dW$$

If  $W \neq 0$ :  $dA \leq 0$   $\rightarrow$  criterion of spontaneity

$$\Delta A \leq 0$$

$\rightarrow$  criterion of equilibrium

$\rightarrow$  Helmholtz free energy

(3) Transformation at constant temp & pressure

$$-dU - dW + TdS \geq 0$$

$$= dU - PdV - dW_{\text{ext}} + TdS \geq 0$$

$$-du + g(\tau s) - d(\rho v) \geq dw$$

$$-d(V - TS + PV) \geq d\Delta w$$

$$-d(H - TS) \geq dW_{av}$$

$$-dG \geq 0$$

## Gibb's free energy

$\xrightarrow{\text{S.E.O.}}$  spontaneous

$$\underline{\Delta G \leq 0}$$

→ equilibrium,

(4) For constant-  $T$  &  $V$  condition.

$$-dV - pdV - dw + Tds \geq 0$$

$$-dV + T dS \geq dW$$

$$dW = 0 \quad \& \quad T \text{ const.}$$

$dA \geq 0$   $\rightarrow$  spontaneously

$\xrightarrow{\hspace{1cm}}$  equilibrium

⑤ For constant- P & entropy:-

$$-dU - pdV - dW \geq 0$$

$$-(dU + pdV) \geq dW$$

$$D - dH \geq d_{10}$$

## Properties of gibbs free energy:-

$$G = H - TS$$

$$\Delta G = \Delta H - T \Delta S - S \Delta T$$

$$dS = dU + pdV + \nu dP - TdS - SdT$$

$$dG = Ndp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right) = -S \quad \& \quad \left(\frac{\partial G}{\partial p}\right)_T = V \quad \rightarrow \text{Important.}$$

At cons. temp

$$\int dG = \int V dp \quad \text{et} \quad G - G_0 > \int V dp \Rightarrow G > G_0 +$$

\* Extensive quantity - depends on mass.

Gibbs free energy / mole - Intensive - chemical Potential.

For solid & liquid volume is almost constant.

$$G - G^0 = \int_{p_0}^p V dp = V \int_{p_0}^p dp = V(p - p_0)$$

for  $b = b_0$  ( $G_1 = G^*$ )

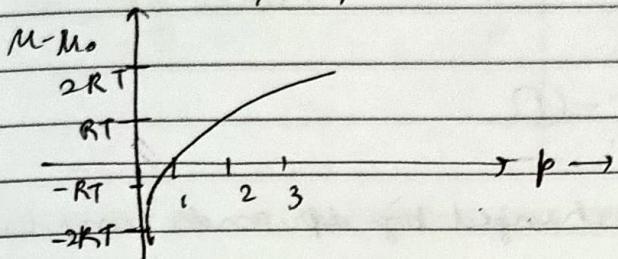
The volume of the gas is much higher. For ideal gas,

$$G = G^\circ(T) + \int_{p_0}^P \frac{nRT}{P} dp$$

$$\frac{G}{n} = \frac{G^\circ(T)}{n} + RT \ln\left(\frac{P}{P_0}\right)$$

If  $P_0 = 1 \text{ atm}$ :  $\rightarrow$  chemical Potential

$$\mu = \mu^\circ(T) + RT \ln(P)$$



Phase transition :-

$$dG = Vdp - SdT$$

$$d\bar{G} = d\mu = Vdp - \bar{S}dT$$

Gibbs free energy per mole

we as  $\bar{S}$   
will always be

+ve

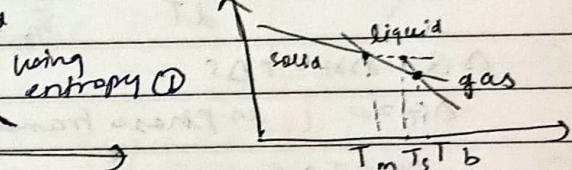
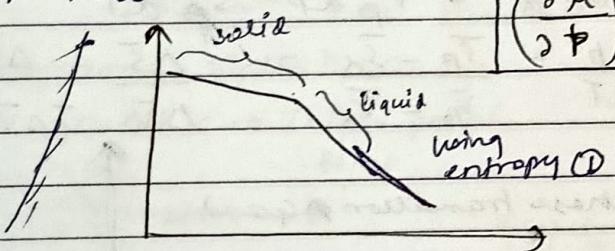
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}$$

(1)

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$$

(2)

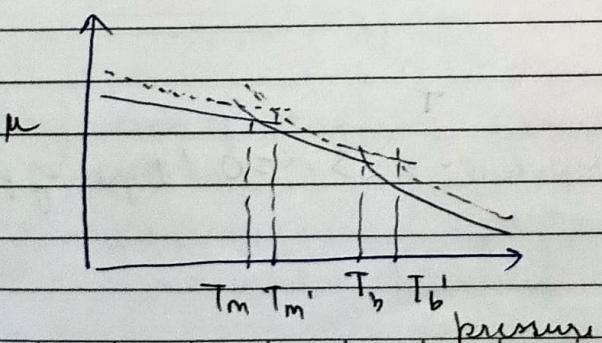
Plot ( $\mu$  vs  $T$ )  
keeping  
pressure  
constant



Two crossing point: Phase transition

chemical Pot for solid & liq is same at crossing point.

using (1) at a temp inc pressure, volume constant, chemical potential will ↑



inc in Boiling point > inc in melting point.

For same T inc temp:

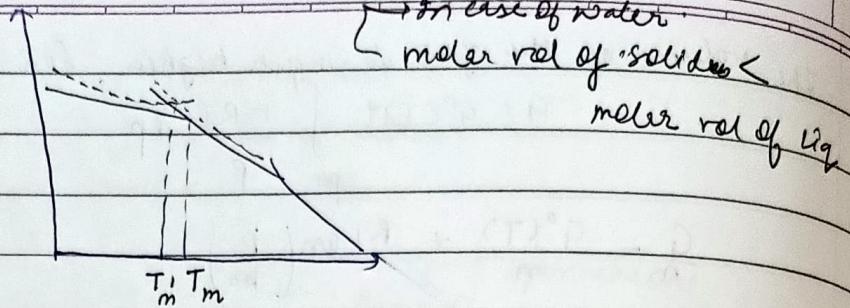
when we go from solid to liq,  
molar volume ~~decreases~~

at the time of phase transition temp &  
pressure remains  
constant.

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for water:



Claapeyron Equation:-



$$\mu_\alpha - \mu_\beta = \frac{p_\beta}{(T, p)} - \frac{p_\alpha}{(T, p)} \quad \text{--- (1)}$$

Let us assume pressure is changed by  $dp$ , and temp is changed by  $dT$ .

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

$$\text{From (1) & (2)} \quad [d\mu_\alpha = d\mu_\beta]$$

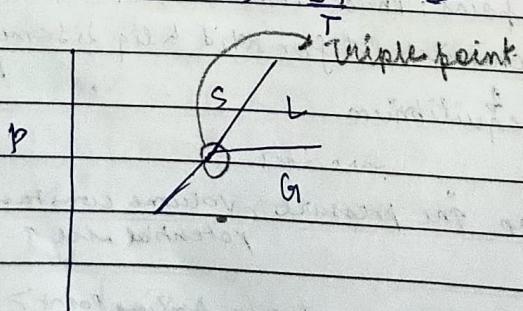
$$\bar{V}_\alpha dp - \bar{S}_\alpha dT = \bar{V}_\beta dp - \bar{S}_\beta dT$$

$$\frac{dp}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta S}{\Delta V} = \frac{\Delta n}{T \Delta V}$$

$$\therefore \Delta G = \Delta n - T \Delta S$$

$$\Delta G = 0 \quad (\text{as phase transition } \Delta G = 0)$$

$$\Delta n = T \Delta S \quad \Delta S = \Delta n / T$$



1 degree of freedom

$$F = C - f + 2 = 1$$

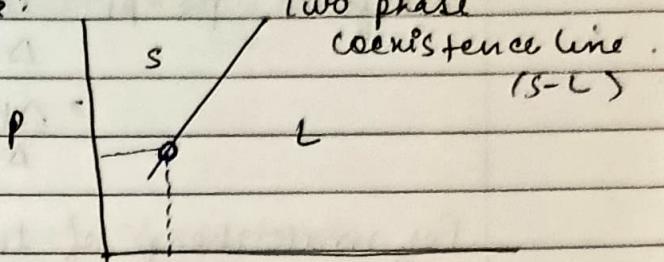
$\downarrow$   
No. of  
components

for triple point:  $1 - 3 + 2 = 0$ . (degree of freedom)

### Phase Diagram and Phase Rule:

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = \frac{\Delta S}{\Delta V}$$

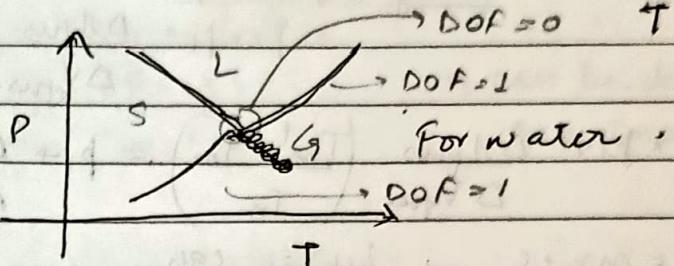
↳ Clapeyron's equation



For water  $\Delta S > 0$ ,  $\Delta V < 0$

so,  $\frac{dp}{dT}$  is negative.

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$



( $V_2 - V_{\text{ap}}$   $\Rightarrow$  co-existence line  $\Rightarrow$  slope is +ve.)

Both temp & pressure need to be taken care of at the triple point.

Phase Rule  $\leftarrow F = C - p + 2$  phase  $\rightarrow$  Line = 2  $\rightarrow$  Area = 1  
 ↳ 1 (type of liq)  $\rightarrow$  components

$$F = 1 - 2 + 2 = 1 \text{ (for line)}$$

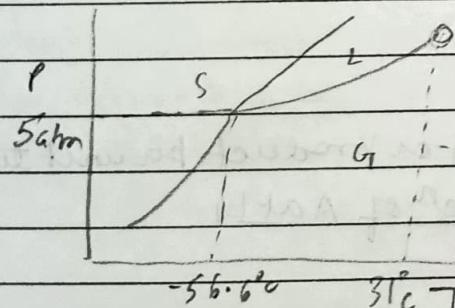
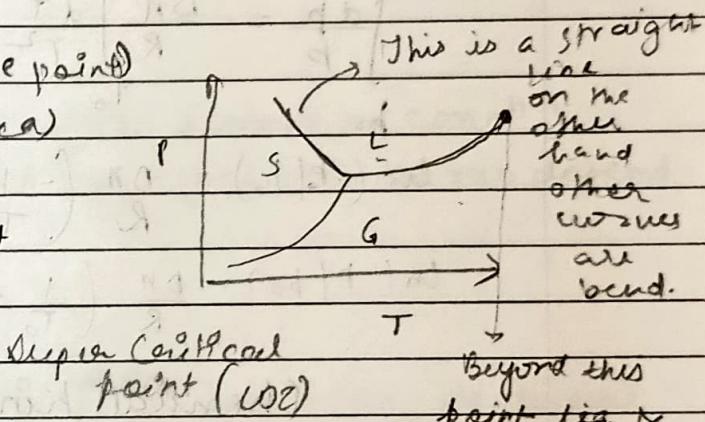
$$F = 1 - 3 + 2 = 0 \text{ (for triple point)}$$

$$F = 1 - 1 + 2 = 2 \text{ (for Area)}$$

Phase diagrams - Water &  $\text{CO}_2$ .

$0.01^\circ\text{C} \rightarrow$  triple point

$61 \text{ pascal} \rightarrow$  triple point  
 point of  $\text{Hg}$   $\rightarrow$   $1 \text{ atm} \rightarrow$  temp.



Integration of Clapeyron's equations:

$$S \rightleftharpoons L$$

$$p_2 \quad T_m'$$

( $\Delta H_{\text{fus}}$  &  $\Delta V_{\text{fus}}$  can be considered const)

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fusion}}}{T_m' \Delta V_{\text{fusion}}} \quad \int dp = \int \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \frac{dT}{T} \Rightarrow p_2 - p_1 = \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \int \frac{dT}{T}$$

$$= \frac{\Delta H_{\text{fusion}}}{\Delta V_{\text{fusion}}} \ln \left( \frac{T_m'}{T_1} \right)$$

Therefore,  $p_2 - p_1 = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \left( \frac{T_m + T_m' - T_m}{T_m} \right)$

$$= \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \left( 1 + \frac{T_m' - T_m}{T_m} \right) = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \left( 1 + \frac{\Delta T}{T_m} \right)$$

For small change of temp:

$$p_2 - p_1 = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\Delta T}{T_m} = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{(T_m' - T_m)}{T_m}$$

$$p_2 = p_1 + \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \left( \frac{T_m' - T_m}{T_m} \right) = p_1 + \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{T_m'}{T_m} - \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}}$$

$y = mx + c$  → Linear eqn

$$S/L \rightarrow G.$$

negligible compared to  $V_{\text{gas}}$ ,

$$\frac{dp}{dT} = \frac{\Delta n}{T \Delta V} = \frac{\Delta n}{T(V_{\text{gas}} - V_{\text{rigid}})} , \Delta n = \frac{\Delta H_p}{RT^2}$$

$$\frac{dp}{T} = \frac{\Delta n}{R} \int_{T_0}^T \frac{dT}{T^2}$$

ideal gas

considered.

(even though  
ideal gas can't be  
liquified)

$$\ln \left( \frac{p}{p_0} \right) = \frac{\Delta n}{R} \left( -\frac{1}{T} \right)_T = \frac{\Delta n}{R} \left( -\frac{1}{T} + \frac{1}{T_0} \right)$$

$$\ln \left( \frac{p}{p_0} \right) = \frac{\Delta n}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \cdot \Rightarrow p = p_0 e^{-\Delta n R \left( \frac{1}{T} - \frac{1}{T_0} \right)}$$

### Chemical Kinetics

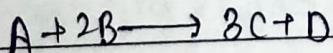
Rate Reaction:  $A \rightarrow P$

Change in concentration of reactant or product per unit time

Rate = concn of A at  $t_2$  - concn of A at  $t_1$

$$\text{Rate} = \frac{A A}{t_2 - t_1}$$

unit =  $(\text{mol L}^{-1} \text{s}^{-1})$  (mol dm $^{-3}$  s $^{-1}$ )



$$\text{Rates} = \frac{d[A]}{dt} = \frac{1}{3} \frac{d[B]}{dt}, \frac{1}{2} \frac{d[B]}{dt}, \frac{d[C]}{dt}$$

Rate of formation      Rate of consumption

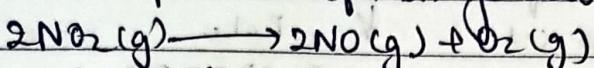
$$U = \frac{1}{r_j} \frac{d[C_j]}{dt}$$

$U$  = rate,  $r_j$  = stoichiometry of  $J$ .

### Rate Law:

Shows how rate depends on the conc<sup>n</sup> of reactants.

For the decomposition of nitrogendioxide.



$$\text{Rate} = k[\text{NO}_2]^n \quad k = \text{rate constant}$$

$n$  can be determined

experimentally.

- \* The order is number of molecules colliding.
- \* When order & stoichiometry doesn't match then that reaction is not a for single step reaction and elementary reaction.
- The conc<sup>n</sup> of the products do not appear in the rate law because the rate rxn is being studied under conditions.

### Types of Rate law:-

- ① Differential Rate law (show how rate of rxn depends on conc<sup>n</sup>)
- ② Integrated Rate law ( show how conc<sup>n</sup> of species in the rxn depend on the time )

### Determination of Rate law:-

- Isolated method:  $V = k[A][B]$  (B is taken in excess)  
when A is taken in excess we can approximate [B] by its initial value ( $B_0$ ).  
determining order w.r.t. B.  
 $V = k_{eff}[A]$  - pseudo first order rate.
- Method of Initials Rate: (used in conjugation with isolation method)

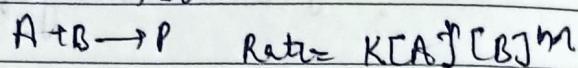
$$V = k_f [A]^a \quad (\text{rate law of rxn with isolated A})$$

$$\text{Initial rate of rxn} \Rightarrow V_0 = k_f [A]_0^a$$

$$\log V = \log k_{eff} + a \log [A_0].$$

This method doesn't work for complex rxn. (synthesis of HBr) where products affects the rates -

Overall Reaction Order:



Overall order =  $m+n$ .

Rate constant:  $\text{Rate} = k[A]^m[B]^n$

$\downarrow$  Rate constant.

Unit depends on order of rxn

For 1st order unit =  $s^{-1}$   $k = \frac{\text{Rate}}{[A]^n[B]^m}$

$$[A]^n[B]^m$$

→ Some Rxn have no order

e.g.: Rxn with catalyst.

1st Order Reaction :-

$$\frac{dn}{dt} = k_n (a_0 - n)$$

$k_n$  = first order constant rate

$$\text{at } t=0 \quad \text{conc of A} = a_0$$

$$\text{at } t=t \quad n \quad " " = a_0 - n ; \text{ conc of product} = n$$

$$\frac{dn}{dt} = k_n dt$$

$$a_0 - n$$

$$-\ln(a_0 - n) = k_n t + I$$

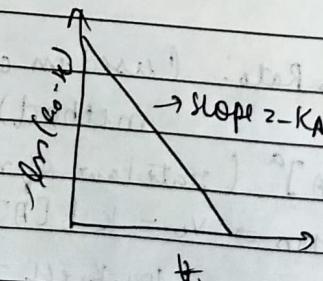
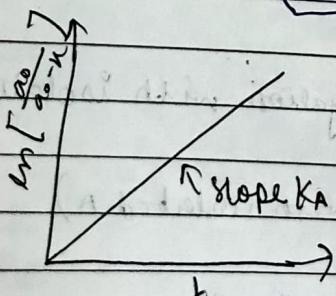
$$\text{at } t=0, n=0 \Rightarrow I = \ln(a_0)$$

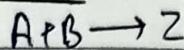
$$-\ln(a_0 - n) = k_n t - \ln(a_0)$$

$$k_n t = \ln \left[ \frac{a_0}{a_0 - n} \right] \quad \text{unit of } k_n = s^{-1}$$

$$\text{at } t=t \quad k_n t = \ln \left[ \frac{a_0}{a_0 - n} \right] \quad \begin{array}{l} \text{Initial concn of A at } t=0 \\ \text{concn of A at } t=t \end{array}$$

$$a_0 - n = a_0 e^{-k_n t}$$



2nd Order Reaction :-

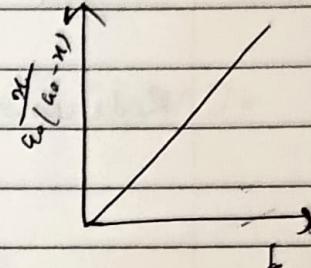
$$\frac{dx}{dt} = k_A (a_0 - x)^2$$

$b^{2b}$   
 $n =$  amount of A that has reacted in  $t = b$   
 $t^{20}$  concn of A =  $a_0$

$$\frac{dx}{(a_0 - x)^2} = k_A dt \quad \frac{1}{a_0 - x} = k_A t + I$$

$$\text{at } t^{20}, n^{20} \quad I = \frac{1}{a_0}$$

$$k_A b = \frac{n}{a_0(a_0 - x)}$$



$$\text{units of } k_A = \text{L mol}^{-1} \text{s}^{-1}$$

Reaction of  $n^{\text{th}}$  order

$$V_A = \frac{dx}{dt} = k_A (a_0 - x)^n$$

$$K_A = \frac{1}{b(n+1)} \left[ \frac{1}{(a_0 - x)^{n+1}} - \frac{1}{a_0^{n+1}} \right] \quad n > 1$$

Half life :-

$$\text{For first order Rxn: } \ln \left( \frac{a_0}{a_0 - a_{1/2}} \right) = k_A b_{1/2} \quad b_{1/2} = \frac{\ln 2}{k_A}$$

It is independent

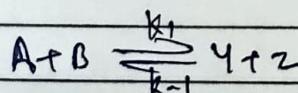
of initial concn.

$$\text{for 2nd order: } \frac{1}{a_0 - a_0} \quad \text{for 3rd order: } \frac{3}{2k_A a_0^2}$$

Empirical eqn for temperature dependence of Rxn rate constant -

$$\left( \frac{\partial \ln k_A}{\partial T} \right)_P = \frac{\Delta U^\circ}{RT^2}$$

where  $k_C = \text{eqm constant}$   $\Delta U^\circ = \text{standard internal energy}$



$$\text{Rate from left} \rightarrow \text{Right} = k_1 [A][B]$$

$$\text{Rate from right} \rightarrow \text{Left} = k_{-1} [Y][Z]$$

$$\text{At eqm: } k_1 [A][B] = k_{-1} [Y][Z]$$

$$\frac{[Y][Z]}{[A][B]} = k_2 \frac{k_L}{k_1}$$

$$\frac{d\ln k_1}{dT} = \frac{d\ln k_2}{dT} = \frac{\Delta U^\circ}{RT^2}$$

Rate constant  $k_1$  &  $k_2$  will be influenced by 2 diff energy factors:

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2}$$

$$\frac{d\ln k_2}{dT} = \frac{E_2}{RT^2}$$

Two energy  $E_1$  &  $E_2$

must be such that  $E_1 - E_2 = \Delta U^\circ$

Internal Energy change

$E_1$  is independent of temp:

$$\ln k = \text{const} - \frac{E}{RT} \quad \text{or} \quad k = A e^{-E/RT}$$

Pre exponential factor

Arrhenius Equation:-

$$\ln k_r = \ln A - \frac{E_a}{RT} \rightarrow \text{Activation energy}$$

Frequency Factor

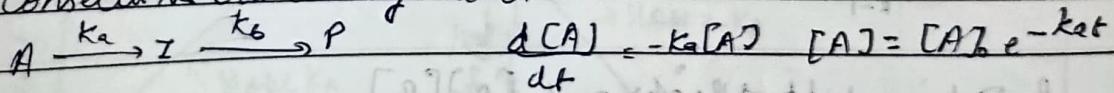
$$\ln k_r(T') - \ln k_r(T) = -\frac{E_a}{RT'} + \frac{E_a}{RT}$$

$$\ln \frac{k_r(T')}{k_r(T)} = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T'} \right)$$

Activation Energy is the minimum KE the reactant must have in order to form products.

The fraction of collisions with a KE  $\omega$  in excess of given by the Boltzmann distribution is  $e^{-E_a/RT}$ .

Consecutive Elementary Reaction.



$$\frac{d[P]}{dt} = k_b [I]$$

Net Rate of formation of I :

$$\frac{d[I]}{dt} = k_a[A] - k_b[I]$$

$$\frac{d[I]}{dt} + k_b[I] = k_a[A_0] e^{-k_a t}$$

Solving the DE gives:  $[I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A_0]$

$$[A] + [I] + [P] = [A_0] \quad \xrightarrow{\text{initial conc'g A.}}$$

$$[P] = \left\{ 1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a} \right\} [A_0] \quad \star$$

At Max<sup>m</sup> I can be obtained by setting slope to zero.

$$\frac{d[I]}{dt} = 0$$

$$-k_b [A_0] \frac{(k_a e^{-k_a t} - k_b e^{-k_b t})}{k_b - k_a} = 0 \quad k_a e^{-k_a t} = k_b e^{-k_b t}$$

$$t_{\max} = \frac{1}{k_a - k_b} \ln \frac{k_a}{k_b} \rightarrow \text{At this time } I \text{ will be Max}^m$$