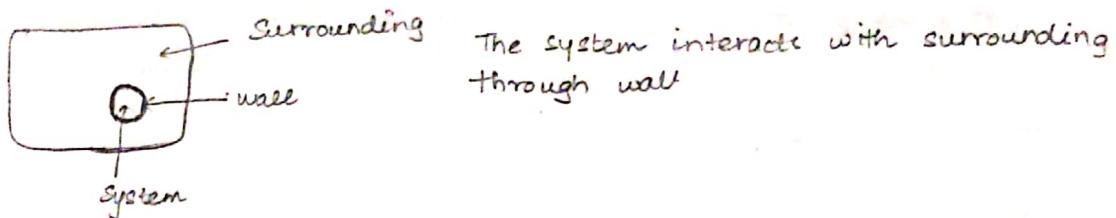


## Thermodynamics

## System

A part of the universe whose properties are being investigated

Surrounding - Rest of the universe

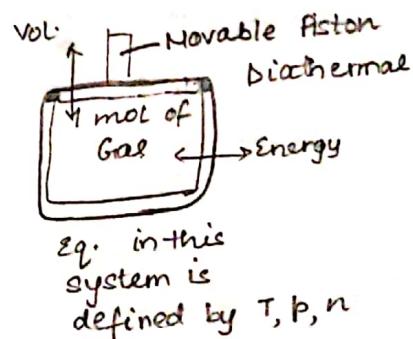
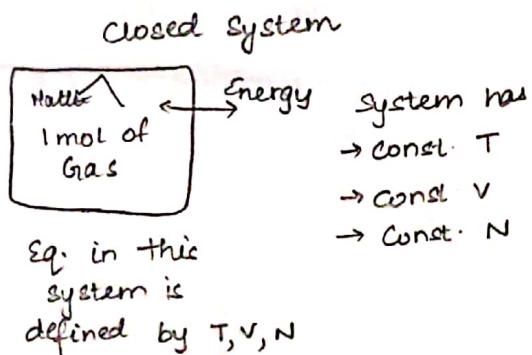


It deals with equilibrium properties of macroscopic systems  
There exist particular states of simple macroscopic system that are characterized by "three variables"

**Macroscopic properties** - The properties which govern the state of system. They remain constant with time.

In an isolated system, the equilibrium state is defined in terms of

- Internal Energy ( $U$ )
  - Volume ( $V$ )
  - No. of particles ( $N$ )



System	Wall	Eq. state
open	Diathermic, Rigid, Permeable	T, V, $\mu$
closed	Diathermic, Rigid, Permeable	T, V, N
Closed	Diathermic, <del>Rigid</del> Flexible, Impermeable	T, P, N
Isolated	Adiabatic, Rigid, Impermeable	U, V, N

Properties of partial derivatives

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

chain Rule

$$\frac{df}{ds} = \left(\frac{\partial f}{\partial x}\right)_y \frac{dx}{ds} + \left(\frac{\partial f}{\partial y}\right)_x \frac{dy}{ds} \quad x, y \text{ are fn. of } s$$

Cyclic rule

$$z = z(x, y)$$

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -1$$

Exact Differential

$$df = M(x, y)dx + N(x, y)dy$$

represent exact differential iff  $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

The expression  $Mdx + Ndy$  doesn't represent an exact diff if

$$\left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y$$

→ The sum of two inexact differentials can be equal to an exact diff.

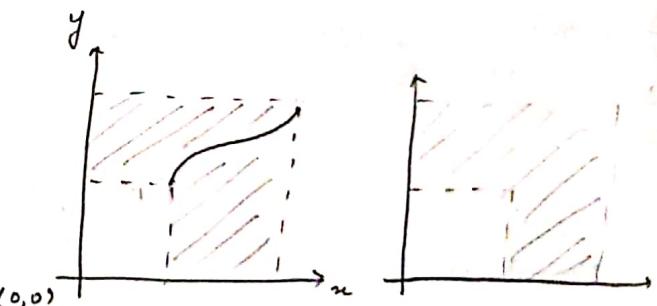
Case 1:  $\oint dz' = ydx$  is inexact

$$\int_1^2 dz' = \int_{x_1}^{x_2} y dx = A_1$$

Case 2:  $\oint dz'' = xdy$  is inexact

$$\int_1^2 dz'' = \int_{x_1}^{x_2} x dy = A_2$$

$$dz = dz' + dz''$$



→ Multiplication of an inexact diff by "Integrating Factor" can be equal to exact diff.

$$\begin{matrix} I.F \\ \uparrow \\ \text{Inexact} \end{matrix} \quad \begin{matrix} \oint dz = df \\ \uparrow \\ \text{Exact diff} \end{matrix}$$

Using the properties of inexact differential

The sum of two inexact differentials  
can be equal to an exact differential

$$dU = \partial q + \partial w$$

1<sup>st</sup> Law of Thermodynamics

Multiplication of an inexact differential  
by an integrating factor can be equal  
to exact differential

$$dS = \frac{\partial q_{rev}}{T}$$

2<sup>nd</sup> Law of Thermodynamics

### Work

$$W = - \int_{V_i}^{V_f} P \, dV$$

Only for reversible process

### Heat

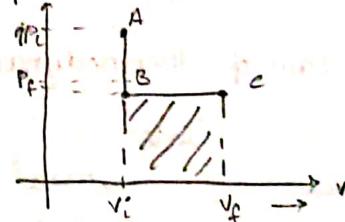
- Heat is transferred between a system and surrounding by virtue of temp. diff. only
- It isn't a state fn.
- Heat can be transferred reversibly or irreversibly. A reversible transfer of heat requires the temperature difference b/w two bodies to be infinitesimal when the system is expanded under constant pressure (BC)

$$\text{Work done} = - P_{ext} \Delta V$$

Free expansion (AB):

Expansion against zero force

$$W = 0$$



Expansion, i.e.,  $V_f > V_i$ ,  $W < 0$  (work is done by system on surrounding)

Compression, i.e.,  $V_i > V_f$ ,  $W > 0$  (work is done on system by surrounding)

For an ideal gas,  $PV = nRT$

### Isothermal expansion

For rev. isothermal expansion of an ideal gas

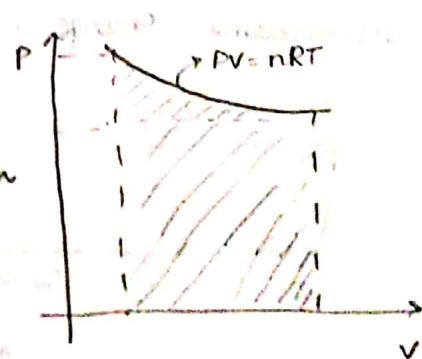
$$P_{ext} = P$$

At higher T, more work is done for same expansion of volume.

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

$$W_{irrev} = -P_f(V_2 - V_1)$$

$$|W_{rev}| > |W_{irrev}|$$



## Adiabatic Expansion

$$dU = \partial q + \partial w, \quad \partial q = 0$$

$$\Rightarrow \partial w = dU$$

$$\Rightarrow dU = n C_V dT$$

$$\partial w = n C_V dT \Rightarrow \boxed{w = n C_V \Delta T}$$

Rev. adiabatic expansion

To obtain  $T_2$

$$\boxed{PV^{\gamma} = \text{const.}}, \quad \boxed{TV^{\gamma-1} = \text{const.}}, \quad \boxed{T^{\gamma} P^{1-\gamma} = \text{const.}}$$

Irrev. adiabatic expansion

To obtain  $T_2$

$$n C_V \Delta T = - P_2 \left( \frac{n R T_2}{P_2} - \frac{n R T_1}{P_1} \right)$$

$$\Rightarrow \boxed{T_2 = T_1 \left( \frac{\frac{C_V}{R} + \frac{P_2}{P_1}}{\frac{C_V}{R} + 1} \right)}$$

→ Work done is a path dependent fn:

→  $|W_{\text{rev, comp}}| = |W_{\text{irrev, expansion}}|$

## First Law of Thermodynamics

→ Introduces Internal Energy ( $U$ )

→  $U$  can't be measured

→ Change in  $U$  can be measured

→ For an infinitesimal change in state

$$\boxed{dU = \partial q + \partial w}$$

→ For a finite change

$$\boxed{\Delta U = q + w}$$

## Infinitesimal change in Internal Energy

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

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

$$\text{Response fn: } C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad \pi_V = \left( \frac{\partial U}{\partial V} \right)_T$$

$\uparrow$   
specific heat  
at const. vol.

Internal  
pressure

$$dU = C_V dT + \kappa_T dV$$

$$\boxed{\Delta U = C_V \Delta T + \kappa_T \Delta V}$$

$$\int dU = \int (C_V dT + \kappa_T dV)$$

Measuring change in Internal Energy

$$\boxed{\Delta U = q + w}$$

Const. Vol. process  $\Delta U = q_V$ ,  $w = 0$

Using  
calorimeter

Adiabatic process  $\Delta U = w$ ,  $q = 0$

Variation of  $U$  with  $V$

$$\left(\frac{\partial U}{\partial V}\right)_T = \kappa_T$$

$$\text{let } U = U(T, V) \Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V = -1}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = - \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\kappa_T = - \mu_J C_V}$$

Joule Thomson Experiment



"Isothermal expansion of an ideal gas against zero pressure"

Observation:  $dT = 0$

$$\frac{\partial W}{\partial T} = 0, \quad \frac{\partial q}{\partial T} = 0 \quad \Rightarrow \quad dU = 0$$

$$dU = C_V dT + \kappa_T dV = 0$$

$$\Rightarrow \kappa_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$$

For an ideal gas

For free expansion of "real" gas against zero pressure

$$\partial W = 0, \partial q = 0 \Rightarrow dU = 0$$

$$dU = C_V dT + \pi_V dV$$

$$\Rightarrow dN\pi_V = -C_V dT$$

$$\Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = \pi_T = -u_J C_V$$

$$\Rightarrow -u_J = \pi_T / C_V$$
$$\Delta T = - \int_{V_1}^{V_2} u_J dV$$

→ Variation of <sup>temp.</sup> pressure at const' pressure

$$dU = C_V dT + \pi_T dV$$

$$\left( \frac{\partial U}{\partial T} \right)_P = C_V + \pi_T \left( \frac{\partial V}{\partial T} \right)_P \quad \pi_T = -u_J C_V$$

$$\Rightarrow \left( \frac{\partial U}{\partial T} \right)_P = C_V \left[ 1 - u_J \left( \frac{\partial V}{\partial T} \right)_P \right]$$

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

$$\left( \frac{\partial U}{\partial T} \right)_P = C_V [1 - \alpha u_J V]$$

## Variation of Internal Energy $U$ with temp.

→ Heating at const. volume

$$\Delta U = q_v = Q = m C_V \Delta T$$

→ Heating at const. pressure

$$q_p = Q = m C_p \Delta T$$

## Enthalpy and heat

$$\rightarrow H = U + PV$$

$$\rightarrow \Delta H = H_2 - H_1, \Delta H \text{ is a state fn.}$$

→ exact differential

$$dH = d(U + PV) = dU + PdV + VdP$$

→ For const. pressure process,

$$dP = 0 \Rightarrow dH = dU + PdV = \partial q \quad (\text{Using 1st law})$$

For a finite process

$$\int_1^2 dH = \Delta H = \int_1^2 \partial q_p = Q_p \Rightarrow \Delta H = Q_p$$

Molar specific heat at const. pressure,

$$C_{p,m} = \left( \frac{\partial H}{\partial T} \right)_P$$

$$\therefore dH = C_{p,m} dT$$

$$C_{p,m} = f(T) = a + bT + \frac{c}{T^2} \Rightarrow \Delta H = Q_p = n \int_{T_1}^{T_2} C_{p,m} dT$$

For ideal gases,

$$PV = nRT$$

$$\Rightarrow dH = dU + Rdn$$

For an ideal gas undergoing isothermal change in state

$$dH = dU + RT dn \Rightarrow \Delta H = \Delta U + RT \Delta n$$

For a non-reactive ideal gas undergoing heating/cooling in a closed vessel

$$dH = dU + nRdT \Rightarrow \Delta H = \Delta U + nR\Delta T = (C_V + nR)\Delta T$$

$$\Delta H = C_p \Delta T$$

## Variation of Enthalpy with System Variables

→ Variation with temp at const. pressure

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad dH_P = C_P dT \quad \Delta H_P = \theta_P = C_P \Delta T$$

In general, for a closed system

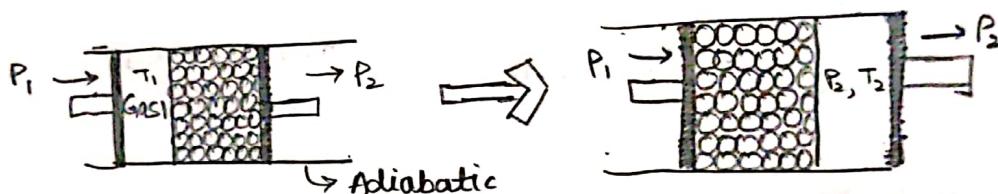
$$H = H(C_P, T)$$

$$dH = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

$$\left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_H \left( \frac{\partial T}{\partial H} \right)_P = -1$$

$$\therefore \left( \frac{\partial H}{\partial P} \right)_T = - \left( \frac{\partial T}{\partial P} \right)_H \left( \frac{\partial H}{\partial T} \right)_P = - \mu_{JT} C_P$$

## Joule Thomson Experiment



For this exp,  $q=0 \Rightarrow \Delta U = W$

Total work done =  $W_L + W_R$

$$W_L = -P_{ext}(\Delta V) = -P_1(0 - V_1) = P_1 V_1$$

$$W_R = -P_{ext}(\Delta V) = -P_2(V_2 - 0) = -P_2 V_2$$

$$\Rightarrow W = P_1 V_1 - P_2 V_2$$

$$\Rightarrow V_2 - V_1 = P_1 V_1 - P_2 V_2 \Rightarrow V_1 + P_1 V_1 = V_2 + P_2 V_2$$

$$\therefore H_2 = H_1$$

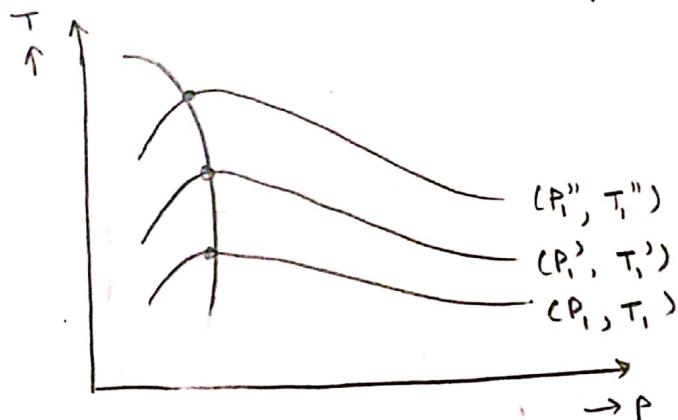
- The gas in compartment 1 is compressed isothermally under const. pressure  $P_1$  such that its vol. changes from  $V_1$  to 0
- After crossing the plug, the gas in compartment 2 expands against a const. pressure  $P_2$  ( $P_1 > P_2$ ) so that its volume increase from 0 to  $V_2$
- Boundary of system moves with gas and encloses same mass of

Thus,

Joule Thomson Experiment is

"Isenthalpic expansion of a gas from a region of constant high pressure to a region of constant low pressure through porous plug"

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H \approx \frac{\Delta T}{\Delta P} \text{ under isenthalpic conditions}$$

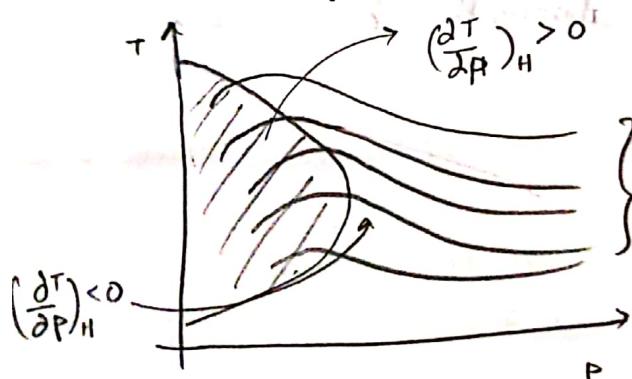


As we move from higher pressure to lower pressure, the gas gets heated up as slope is -ve

In this exp,  $\Delta P < 0$

On a (T, P) isoenthalpic plot this is the point where  $\mu_{JT}$  changes sign from + to -

For a real gas  $\mu_{JT} \neq 0$  (Except at max Inversion temp)



The "Inversion Temperature"

$\mu_{JT}$

+ve

$\Delta T$

-ve

Remarks

Gas cools on expansion

-ve

+ve

Gas heats on expansion

$$\mu_{JT} = \frac{1}{C_P} \left( \frac{2a}{RT} - b \right)$$

→ AS  $\Delta P < 0$  in JT exp.

$N_2, O_2$  will cool upon expansion at room temp. whereas  $He, H_2, Ne$  will warm upon expansion at room temp.

### Response Fn:

Specific heat at const. v

Specific heat at const. P

Isobaric expansion co-eff

Joule w-eff

Joule Thomson co-eff

### Definition

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

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

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

$$\mu_J = \left( \frac{\partial T}{\partial V} \right)_U$$

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H$$

**Change in U = U(T, V)**

→ Const. volume process  $\Delta U = Q_V = C_V \Delta T$

→ Const. temp. process  $\Delta U = -\mu_J C_V \Delta V$

→ With change in both T & V.  $\Delta U = C_V \Delta T - \mu_J C_V \Delta V$

**Change in H = H(T, P)**

→ Const. pressure process  $\Delta H = Q_p = C_P \Delta T$

→ Const. temp. process  $\Delta H = -\mu_{JT} C_P \Delta P$

→ With change in both T and p  $\Delta H = C_P \Delta T - \mu_{JT} C_P \Delta P$

### Response Function

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

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

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

$$\mu_J = \left( \frac{\partial T}{\partial V} \right)_U$$

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H$$

### Ideal gas behaviour

$$\frac{3}{2} R$$

$$\frac{5}{2} R$$

$$1/T$$

$$0$$

$$0$$

For  $p = p(V, T)$

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

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

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

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\nu} \left(\frac{\partial V}{\partial T}\right)_P \times -V \left(\frac{\partial P}{\partial V}\right)_T$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\kappa}{\nu}$$

$\kappa \rightarrow$  Isobaric expansion co-eff  $\kappa = \frac{1}{\nu} \left(\frac{\partial V}{\partial T}\right)_P$

$\kappa \rightarrow$  Isothermal compressibility  $\kappa = -\frac{1}{\nu} \left(\frac{\partial V}{\partial P}\right)_T$

### 1<sup>st</sup> Law of Thermodynamics

→ Concept of internal energy,  $U$  and enthalpy,  $H$

→ Assumption: system plus surrounding is isolated

→ During any change in state of system

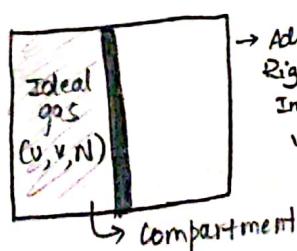
$$dU_{\text{universe}} = dU_{\text{system}} + dU_{\text{surrounding}} = 0$$

→ A system needs to undergo a change in state

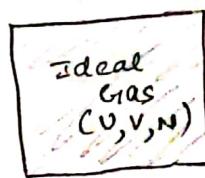
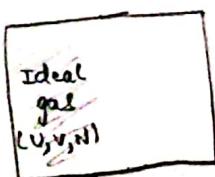
### Limitations of 1<sup>st</sup> Law

- Will the change in state take place?
- If change is happening, will it be a spontaneous change happen?  
In the sense  
no external  
supp. req.
- What will new eq. state be? under what condition will the change stop?

Initial Eq. state  $\longrightarrow$  Final eq. state



→ Adiabatic,  
Rigid,  
Impermeable  
wall  $\rightarrow$



→ First law of Thermodynamics  
Doesn't say anything  
abt the final state

## Second Law of Thermodynamics

- A spontaneous process occurs naturally and needs no ext. source of  $w_o$ .
- A non-spontaneous process, although allowed by 1st law, req. external force.
- This law tells us
  - The direction of a spontaneous change in state
  - The new eq. state achieved at the end of change

### Converting Heat to Work

- From 1<sup>st</sup> law,  $\Delta U = 0$ ,  $q = -w$ . So heat supplied to a system can be completely converted to work.
- Such possibility is tested by construction of heat engine.
- First law shows such construction is possible whose efficiency  $\eta = 1$

An engine is a device (system) that converts energy to work

### A heat engine

- Draws heat from a hot reservoir,
- Converts some heat to work.
- Releases some heat to a cold reservoir.

The engine itself is a system that undergoes cyclic process

### Efficiency of heat engine

$$\eta = \frac{|W|}{Q_h}$$

### Kelvin's statement of 2<sup>nd</sup> law

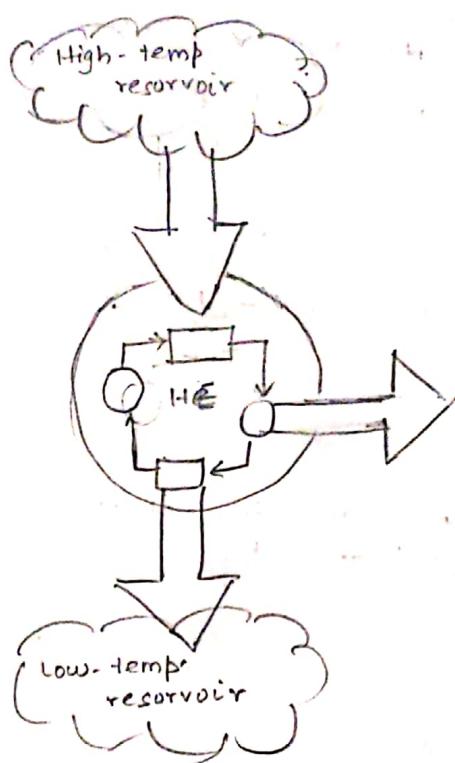
It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in surroundings without at the same time transferring some heat to a cold reservoir.

For a cyclic process,

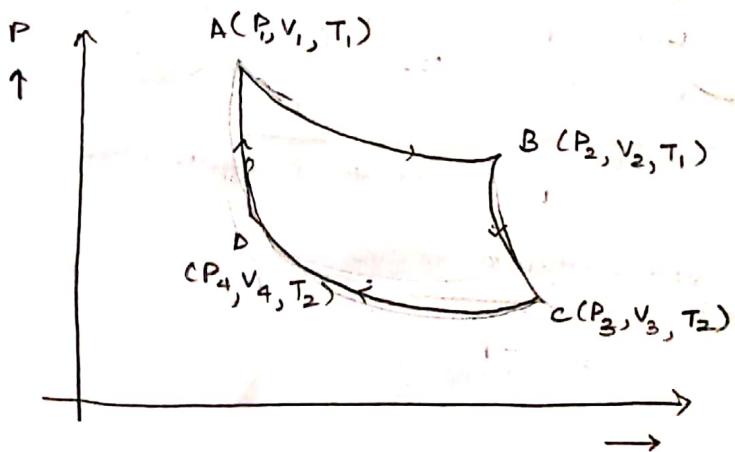
$$\Delta U = 0$$

$$\Rightarrow W = -Q = -(Q_h + Q_c)$$

$$\eta = \frac{|W|}{Q_h} = \frac{Q_h + Q_c}{Q_h} = 1 + \frac{Q_c}{Q_h} \quad \because Q_c < 0 \Rightarrow \eta < 1$$



### Carnot Engine



$A \rightarrow B$  : Isothermal Expansion  
 $B \rightarrow C$  : Adiabatic Expansion  
 $C \rightarrow D$  : Isothermal Compression  
 $D \rightarrow A$  : Adiabatic Compression

Reversible processes

Step 1 :-

$$W = -nRT_1 \ln \frac{V_2}{V_1} \Rightarrow Q = +nRT_1 \ln \frac{V_2}{V_1}$$

$$\Delta U = 0$$

Step 2 :-

$$W = CV(T_2 - T_1)$$

$$Q = 0$$

$$\Delta U = CV\Delta T$$

Step 3 :-

$$\Delta U = 0$$

$$W = -nRT_2 \ln \frac{V_4}{V_3}$$

$$Q = nRT_2 \ln \frac{V_4}{V_3}$$

Step 4 :-

$$W = CV(T_1 - T_2)$$

$$\Delta U = CV(T_1 - T_2)$$

$$Q = 0$$

$$\text{Total Work done} = -nR(T_2 - T_1) \ln \frac{V_2}{V_1}$$

$$\text{Total } Q = nR(T_2 - T_1) \ln \frac{V_2}{V_1}$$

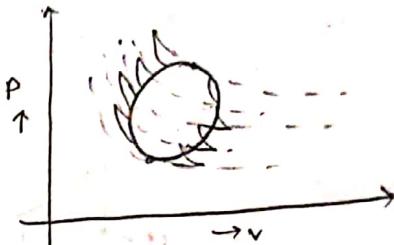
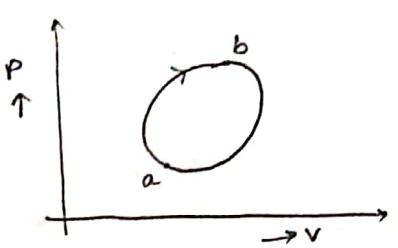
$$(\Delta U)_{\text{total}} = 0$$

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

$$\eta = 1 + \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

$$1 + \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \Rightarrow \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

### Entropy



→ Over one cycle of carnot engine

$$\oint \frac{\partial q_{\text{rev}}}{T} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

→ Any reversible cycle can be approximated by a series of carnot cycles

→  $\oint \frac{\partial q_{\text{rev}}}{T} = 0$  along any reversible cyclic path

→ A state fn: called entropy,  $S$  is identified

→  $dS = \frac{\partial q_{\text{rev}}}{T}$  is an exact differential

$$\rightarrow \underline{\underline{\Delta S}} = S_b - S_a = \int_a^b dS = \int_a^b \frac{\partial q_{\text{rev}}}{T} \text{ is a state fn:}$$

For an adiabatic process

$$\frac{\partial q_{rev}}{\partial T} = 0 \Rightarrow dS = 0 \text{ for non-zero temperature}$$

$$\Rightarrow \int_1^2 dS = 0 \Rightarrow S_2 - S_1 = 0$$

$\therefore S_2 = S_1$

→ An adiabatic process is isoentropic process

For an isothermal process

$$\Delta S = \int_1^2 \frac{\partial q_{rev}}{T} = \frac{1}{T} \int_1^2 \partial q_{rev}$$

$$\Delta S_{\text{isothermal}} = \frac{q_{rev}}{T}$$

For expansion of an ideal gas in an isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For an isochoric rev. process

$$\frac{\partial w_{rev}}{\partial T} = 0 \Rightarrow dU = \frac{\partial q_{rev}}{\partial T} = C_V dT$$

$$\Delta S = \int_1^2 C_V \frac{dT}{T} = C_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{rev, isochoric}} = C_V \ln \frac{T_2}{T_1}$$

→ For a reversible process involving changes in T and V of 1 mole of an ideal gas

$$\frac{\partial q_{rev}}{\partial T} = dU + PdV \Rightarrow \frac{\partial q_{rev}}{T} = \frac{dU}{T} + \frac{P}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

$$\Rightarrow \int_1^2 dS = S_2 - S_1 = \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For reversible process  $(T_1, V_1, N) \rightarrow (T_2, V_2, N)$

$$\Delta S_{\text{rev}} = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For an irreversible process  $(T_1, V_1, N) \rightarrow (T_2, V_2, N)$

$$\Delta S_{\text{irrev}} = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Reversible heating at constant pressure (no phase change)

$$\partial q_{\text{rev}} = \partial q = Cp dT \Rightarrow \Delta S = Cp \int_{T_1}^{T_2} \frac{dT}{T}$$

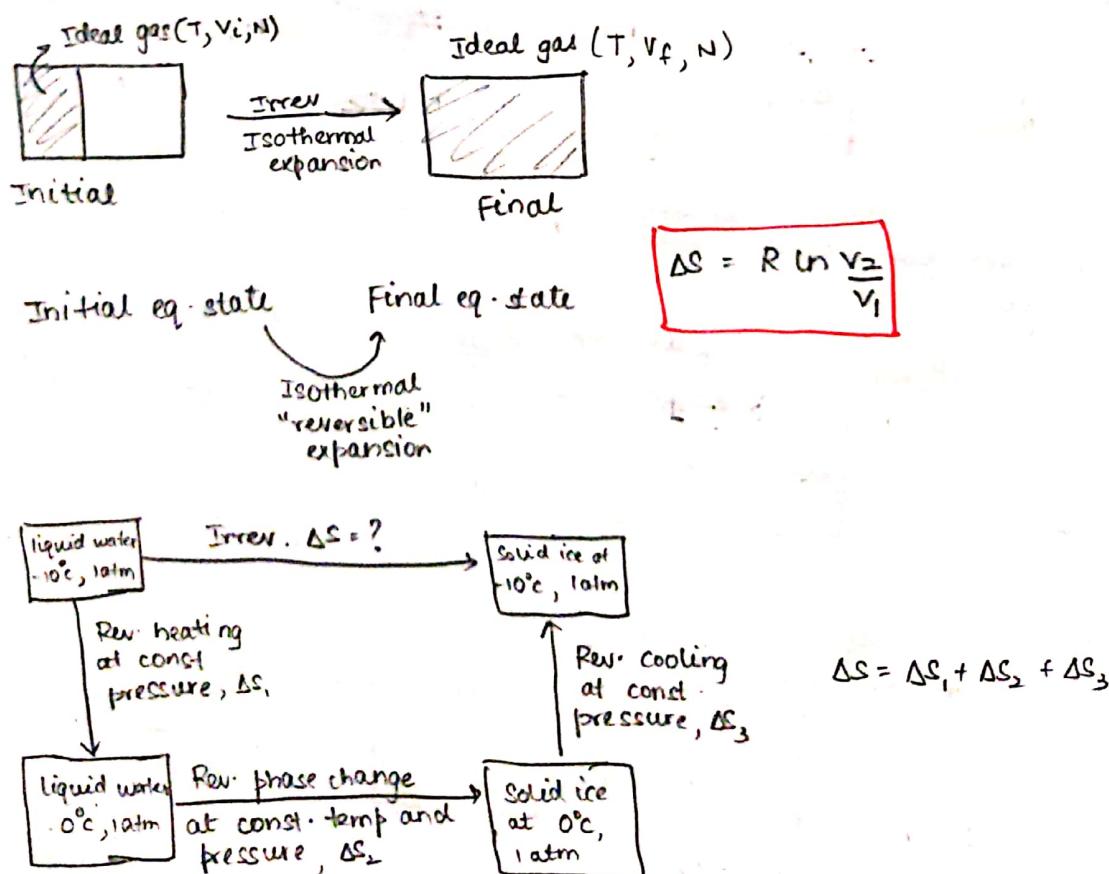
$$\therefore \Delta S_{\text{isobar, rev}} = Cp \ln \frac{T_2}{T_1}$$

Reversible heating at constant pressure (with phase change)

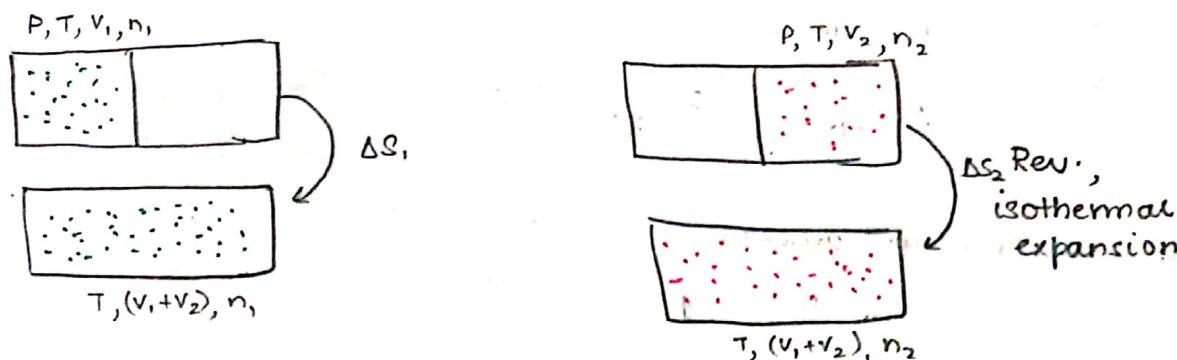
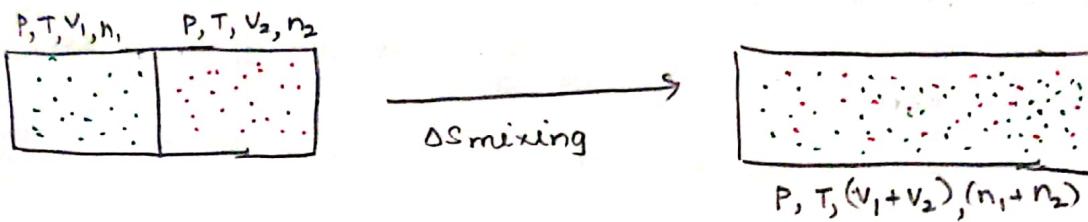
$$\Delta S = \frac{\Delta H}{T}$$

$\Delta H$  is enthalpy of phase change at transition temp.

Estimating  $\Delta S$  in irrev processes



## Entropy of mixing of two ideal gases



$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1} \quad \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$\Delta S_{\text{mixing}} = \Delta S_1 + \Delta S_2$$

$$\frac{V_1}{V_1 + V_2} = \frac{\frac{n_1 RT}{P}}{\frac{n_1 RT}{P} + \frac{n_2 RT}{P}} = \frac{n_1}{n_1 + n_2} = x_1$$

$$\frac{V_2}{V_1 + V_2} = x_2$$

$$\Rightarrow \Delta S_{\text{mixing}} = -n_1 R \ln x_1 - n_2 R \ln x_2$$

$$\Rightarrow \Delta S_{\text{mixing}} = -nR(x_1 \ln x_1 + x_2 \ln x_2) \quad , \quad n = n_1 + n_2$$

$\Delta S_{\text{mixing}}$  is max. for  $x_1 = x_2 = 1/2$

## Measurement of entropy at any temp

$$S(T) = S(0) + \int_0^T \frac{C_p(s)}{T} dT + \Delta H_{\text{fus}} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^T \frac{C_p(g)}{T} dT$$

$$T = 0 \xrightarrow{\text{solid}} T_f \xrightarrow{\text{liquid}} T_b \xrightarrow{\text{Gas}} T$$

→ At low T for the solid,  $C_p(s) = \alpha T^3$

→ For most liquids, the standard entropy of vaporization

$$\Delta S_{\text{vap}}^\circ \approx 85.0 \text{ J K}^{-1} \text{ mol}^{-1} \rightarrow \text{Trouton's Std. enthalpy of vapourization}$$

$$\Delta H_{\text{vap}}^\circ = T_b \Delta S_{\text{vap}}^\circ$$

## Entropy at very low Temperature

The  $\Delta S$  for any chemical or physical transformation approaches zero as  $T$  approaches zero.

As  $T \rightarrow 0$ ,  $S \rightarrow 0$  if all the substances involved are perfectly ordered

$$\Rightarrow S(T) = \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{\text{fus}}}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{\text{trap}}}{T_b} + \int_{T_b}^T \frac{C_p(g)}{T} dT$$

## Third law of Thermodynamics

The entropy of all perfect crystalline substances is zero at  $T=0$

## → Boltzman Hypothesis

The eq. thermodynamic state of an isolated system is the most probable state

$$S = k_B \ln W$$

$k_B$  is Boltzmann's const.

$W$  is no. of diff. ways

## Entropy and Clausius Inequality

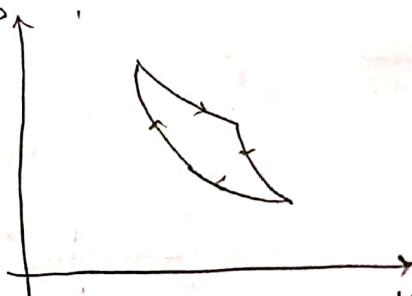
For any reversible engine, operating cycle between two temp.  $T_h$  and  $T_c$

$$\eta_{\text{rev}} = \frac{W_{\text{rev}}}{Q_h}$$

$$\eta_{\text{rev}} = 1 + \frac{Q_c}{Q_h} \quad \eta_{\text{rev}} = 1 - \frac{T_c}{T_h}$$

$$\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

$$\int_A^B \frac{\partial q}{T} + \int_B^C \frac{\partial q}{T} + \int_C^D \frac{\partial q}{T} + \int_D^A \frac{\partial q}{T} = 0 \Rightarrow \oint \frac{\partial q}{T} = 0$$



$$\oint \frac{\partial q}{T} = 0$$

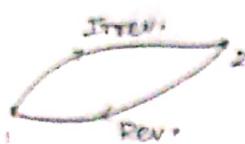
For any irreversible engine, operating in cycle b/w temperatures  $T_h$  and  $T_c$

$$\eta_{irrev} = \frac{W_{irrev}}{Q_h} = 1 + \frac{Q_c}{Q_h}$$

$$\Rightarrow \frac{Q_h}{T_h} + \frac{Q_c}{T_c} < 0$$

$$W_{irrev} < W_{rev} \quad \therefore 1 + \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h}$$
$$\eta_{irrev} < \eta_{rev}$$

$$\oint \frac{\partial Q}{T} < 0$$



for any irreversible cycle

$$\oint \frac{\partial Q}{T} < 0$$

state 1  $\xrightarrow{\text{Irrev}}$  state 2  $\xrightarrow{\text{Rev}}$  state 1

so as a whole the process is irrev

$$\int_1^2 \frac{\partial q_{rev}}{T} + \int_2^1 \frac{\partial q_{rev}}{T} < 0$$

$$\Rightarrow \int_1^2 \frac{\partial q_{rev}}{T} - \int_1^2 ds < 0 \Rightarrow \int_1^2 \frac{\partial q_{rev} + s_1 - s_2}{T} < 0$$

$$s_2 - s_1 > \int_1^2 \frac{\partial q_{irr}}{T} \Rightarrow \Delta s > \int_1^2 \frac{\partial q_{irr}}{T}$$

For a reversible change in state from state 1 to state 2

$$\int_1^2 ds = \int_1^2 \frac{\partial q_{rev}}{T} \Rightarrow ds = \frac{\partial q_{rev}}{T}$$

For an irreversible change in state from state 1 to state 2

$$\int_1^2 ds > \int_1^2 \frac{\partial q_{irr}}{T} \Rightarrow ds > \frac{\partial q_{irr}}{T}$$

For any change in state from state 1 to state 2

$$ds > \frac{\partial q}{T}$$

E → Mathematical

$$dS \geq \frac{\partial q}{T}$$

T

If  $dS > \frac{\partial q}{T}$

Irreversible and Spontaneous change in state

If  $dS = \frac{\partial q}{T}$

Reversible process

If  $dS < \frac{\partial q}{T}$

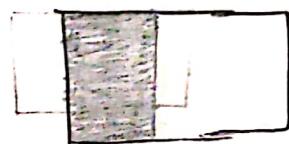
Process associated with the change in state isn't permitted.

In an isolated system, during irrev. process,

$$\partial q_{\text{irrev}} = 0 \Rightarrow dS > 0$$

For real transformation in an isolated system, upon withdrawal of an internal constraint, the system spontaneously changes towards that direction that increases entropy

Initial ( $V_i, T, N$ )



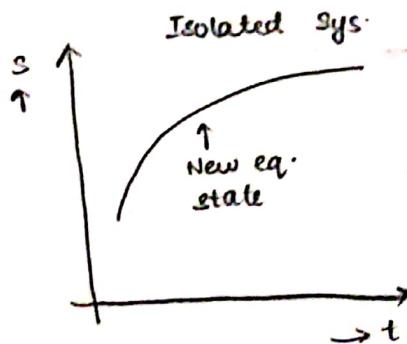
Final ( $V_f, T, N$ )

of all possibilities  
This is final  
state as:

$$\Delta S = R \ln \left( \frac{V_f}{V_i} \right)$$

$\Delta S$  reaches a maxm when  $V_f$  is maxm  
 $\Rightarrow S_{\text{final}}$  is maxm in the above case

The ideal gas will spontaneously expand till it fills up the entire available volume.



→ Any natural change within an isolated system is accompanied by increase in entropy.

→ The entropy continues to increase as long as the change occurs within the system.

→ When entropy attains its max value, system reaches a new eq. state.

## Maximization of Entropy in a closed system

$$S = S(U, V)$$

At equilibrium,  $\left(\frac{\partial S}{\partial V}\right)_U = 0$  and  $\left(\frac{\partial^2 S}{\partial V^2}\right)_U < 0$

Since  $V = V(S, U)$

$$\left(\frac{\partial V}{\partial S}\right)_U \left(\frac{\partial S}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_S = -1$$

$$\Rightarrow \left(\frac{\partial V}{\partial U}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_U \left(\frac{\partial S}{\partial V}\right)_U$$

w.k.t.,  $dU = TdS - pdV$ ,  $T = \left(\frac{\partial U}{\partial S}\right)_V$

$$\left(\frac{\partial U}{\partial V}\right)_S = -T \left(\frac{\partial S}{\partial V}\right)_U$$

At equilibrium,  $\left(\frac{\partial U}{\partial V}\right)_S = 0$  as  $\left(\frac{\partial S}{\partial V}\right)_U = 0$

To know its nature we find  $\left(\frac{\partial^2 U}{\partial V^2}\right)_S$

$$\Rightarrow \left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0$$

when system exhibits maxm w.r.t S, it also exhibits a minimum w.r.t U

$$dS > 0$$

$$dU < 0$$

Irreversible and spontaneous change in state

$$dS = 0$$

$$dU = 0$$

No further change, a new eq has reached.

$$dS < 0$$

$$dU > 0$$

Process associated with change in state isn't permitted

## Thermodynamic Potential

→ Energy, state fn. of the system

→ If the eq. state of a closed system is given by

$$x_1, x_2$$

its thermodynamic potential, E is given by

$$E = E(x_1, x_2)$$

such that  $dE = M_1 dx_1 + M_2 dx_2$

## Forms of energy in a closed system

Internal energy  $U = U(S, V, N)$

$$dU = TdS - pdV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, N} \quad - p = \left(\frac{\partial U}{\partial V}\right)_{S, N}$$

Enthalpy

$$H = U + PV$$

$$dH = TdS + Vdp$$

$$H = H(S, P, N)$$

Helmholtz free energy,  $F = U - TS$

$$dF = -SdT - pdV$$

$$F = F(T, V, N)$$

Gibbs free energy,  $G = U - TS + PV$

$$dG = -SdT + Vdp$$

$$G = G(T, P, N)$$

System

Equilibrium state

Thermodynamic potential

Thermodynamic eqn. of state

Isolated

$S, V, N$

$$U = U(S, V, N)$$

$$dU = TdS - pdV$$

System + Thermostat

$T, V, N$

$$F = U - TS$$

$$F = F(T, V, N)$$

$$dF = -SdT - pdV$$

System + Barostat

$S, P, N$

$$H = U + PV$$

$$H = H(S, P, N)$$

$$dH = TdS + Vdp$$

System + Thermostat + Barostat

$T, P, N$

$$G = U - TS + PV$$

$$G = G(T, P, N)$$

$$dG = -SdT + Vdp$$

For an isothermal process

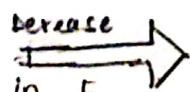
$$-dW + TdS \geq -\delta w \Rightarrow -d(U - TS) \geq -\delta w$$

defining  $F = U - TS$ ,  $\delta w = 0$  at const.  $V$

$$-\delta F \geq \delta w$$

$$-\delta F_{T,V} \geq 0$$

Initial eq. state



Final eq. state

$$dU = \partial q + \partial w, \quad TdS \geq \partial q$$

$$\Rightarrow -\partial w \leq -dU + TdS$$

$$-\partial w_{max} = -dF_{T,V}$$

$$\Rightarrow w_{max} = \Delta F_{T,V}$$

For an isothermal work

$$\partial w = -p_{ext} dV + \partial w_{add}$$

$$-dU + TdS \geq -\partial w \Rightarrow -\partial w_{add} \leq dF_T$$

**Free Energy:** Amount of energy that is available freely to do work.

$$A = U - TS \quad G = H - TS$$

conditions of Eq.

in terms of

Reservoir  
Properties

System  
Properties

Minimization of U

Direction of  
spontaneous  
change in state

Decrease in U

Decrease in F

$$T_{sys} = T_{res}$$

Minimization of F

$$T_{sys} = T_{res}$$

$$P_{sys} = P_{res}$$

Minimization of G

Decrease in G

**Maxwell's Relations**

$$\left( \frac{\partial T}{\partial V} \right)_{S,N} = - \left( \frac{\partial P}{\partial S} \right)_{V,N}$$

$$\left( \frac{\partial T}{\partial P} \right)_{S,N} = \left( \frac{\partial V}{\partial S} \right)_{P,N}$$

$$\left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial P}{\partial T} \right)_{V,N}$$

$$\left( \frac{\partial S}{\partial P} \right)_{T,N} = - \left( \frac{\partial V}{\partial T} \right)_{P,N}$$

For a state  $f_n: A(x, y)$   $dA$  is an exact differential

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy \quad dA = M dx + N dy$$

For it to be exact,  $\left(\frac{\partial N}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy \quad M = \left(\frac{\partial A}{\partial x}\right)_y \quad N = \left(\frac{\partial A}{\partial y}\right)_x \quad \left(\frac{\partial N}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

$$dU = Tds - pdv \quad T = \left(\frac{\partial U}{\partial s}\right)_v \quad -P = \left(\frac{\partial U}{\partial v}\right)_T \quad \left(\frac{\partial T}{\partial v}\right)_{s,N} = -\left(\frac{\partial P}{\partial s}\right)_T$$

$$dH = Tds + vdp \quad T = \left(\frac{\partial H}{\partial s}\right)_p \quad V = \left(\frac{\partial H}{\partial p}\right)_s \quad \left(\frac{\partial T}{\partial p}\right)_{s,N} = \left(\frac{\partial V}{\partial s}\right)_p$$

$$dF = -SdT - pdV \quad -S = \left(\frac{\partial F}{\partial T}\right)_V \quad -P = \left(\frac{\partial F}{\partial V}\right)_T \quad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + Vdp \quad -S = \left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T \quad \left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_p$$

Application of Maxwell's Eqns:

$$C_p - C_V = ??$$

$$dU = C_V dT + \pi_T dv$$

$$\left(\frac{\partial U}{\partial T}\right)_p - C_V = \pi_T \propto V \Rightarrow C_p - C_V = \alpha V (\pi_T + P)$$

$$C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p - C_V + P \propto V$$

$$\left(\frac{\partial U}{\partial T}\right)_p : C_V + \pi_T \left(\frac{\partial V}{\partial T}\right)_p \quad \left(\left(\frac{\partial V}{\partial T}\right)_p = \alpha V\right)$$

$$\text{Isothermal Compressibility} \quad K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\pi_T + P = \frac{KT}{K}$$

$$\therefore \boxed{C_p - C_V = \frac{\alpha^2 TV}{K}}$$

→ To estimate Joule Thomson coefficient.

$$u_{JT} = -\frac{1}{c_p} \left( \frac{\partial H}{\partial P} \right)_T$$

$$dH = T dS + V dP \quad \left( \frac{\partial H}{\partial P} \right)_T = T \left( \frac{\partial S}{\partial P} \right)_T + V$$

$$\left( \frac{\partial H}{\partial P} \right)_T = -T \left( \frac{\partial V}{\partial T} \right)_P + V \quad \left( \frac{\partial V}{\partial T} \right)_P = \alpha V$$

$$\Rightarrow \left( \frac{\partial H}{\partial P} \right)_T = -V(\alpha_T - 1) \quad \Rightarrow \boxed{u_{JT} = \frac{V}{c_p} (\alpha_T - 1)}$$

$$dV = c_V dT + \frac{\alpha T - k_P}{k} dP$$

$$dH = c_p dT + V(1 - \alpha_T) dP$$

$$dS(T, V) = c_V \frac{dT}{T} + \frac{\alpha}{k} dV$$

$$dS(T, P) = c_p \frac{dT}{T} - \alpha V dP$$

Variation of Gibbs Free Energy in closed systems

$$dG = -SdT + VdP$$

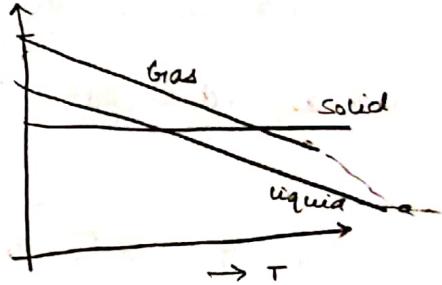
$$\text{where } \left( \frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

System stable in a single phase

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

(As  $S$  is a measure of disorderedness)

$G_f$  decreases with increasing temp. at a given pressure  $P$



### Gibb's Helmholtz equation

$$\left( \frac{\partial G_f}{\partial T} \right)_P = -S$$

$$[G_f = H - TS]$$

$$\Rightarrow -S = \frac{G_f - H}{T}$$

$$\Rightarrow \boxed{\left( \frac{\partial G_f}{\partial T} \right)_P = \frac{G_f - H}{T}}$$

$$\left[ \frac{\partial \left( \frac{G_f}{T} \right)}{\partial T} \right]_P = \frac{1}{T} \left( \frac{\partial G_f}{\partial T} \right)_P - \frac{G_f}{T^2} = -\left( \frac{G_f + TS}{T^2} \right)$$

$$\Rightarrow \boxed{\left[ \frac{\partial \left( \frac{G_f}{T} \right)}{\partial T} \right]_P = -\frac{H}{T^2}}$$

and

$$\boxed{\left[ \frac{\partial \left( \frac{G_f}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right]_P = H}$$

$$\Rightarrow \left( \frac{\partial (\Delta G/T)}{\partial (1/T)} \right)_P = -\frac{\Delta H}{T^2}$$

Variation of Gibbs Free Energy with pressure in closed system

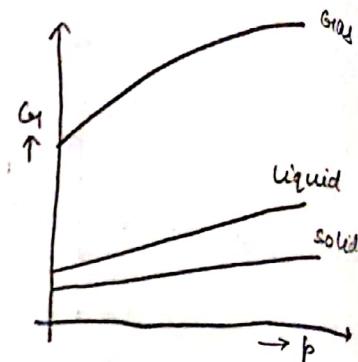
$$dG = -SdT + Vdp$$

$$\text{For an isothermal process } \int_i^f dG = \int_i^f V dp$$

$$\Rightarrow G_f(T, P_f) = G_i(T, P_i) + \int_i^f V dp$$

For 1 mole of substance

$$G_m(T, P_f) = G_m(T, P_i) + \int_i^f V_m dp$$



$$\text{In condensed phase? } G_m(T, P_f) = G_m(T, P_i) + (P_f - P_i) V_m$$

$$\text{For an ideal gas } G_m(T, P_f) = G_m(T, P_i) + RT \int_{P_i}^{P_f} \frac{dp}{P}$$

$$\Rightarrow G_m(T, P_f) = G_m(T, P_i) + RT \ln \left( \frac{P_f}{P_i} \right)$$

$$dG = -SdT + Vdp$$

This eqn. isn't applicable when

→ System composition is changing due to exchange of matter with surrounding (open system)

→ An irreversible chemical reaction takes place

→ An irreversible inter phase transport of matter takes place

Closed System  $dG = -SdT + Vdp$

Open System  $dG = -SdT + Vdp + \sum_{i=1}^M \mu_i dN_i$

$\mu_i \rightarrow$  chemical potential (Intensive)

↳ Material eq.

System	Wall	Wall	Equilibrium state
Open	Diathermal, Rigid, Permeable " Flexible "		$T, V, \mu$ $T, P, \mu$
Closed	Diathermal, Rigid, Permeable Flexible		$T, V, \mu$ $T, P, N$
Isolated	Adiabatic, Rigid, Impermeable		$U, V, N$ (OR) $S, V, N$

### Chemical Potential

→ It is defined as rate of change of thermodynamic potential w.r.t change in no. of particles,  $n_i$  of type  $i$  ( $i = 1 \dots M$ )

$$dU = Tds - pdv + \sum_{i=1}^M \mu_i dn_i \Rightarrow \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, \text{all } j \neq i}$$

$$dH = Tds + Vdp + \sum_{i=1}^M \mu_i dn_i \Rightarrow \mu_i = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, \text{all } j \neq i}$$

$$dF = -SdT - pdV + \sum_{i=1}^M \mu_i dn_i \Rightarrow \mu_i = \left( \frac{\partial F}{\partial n_i} \right)_{T, V, \text{all } j \neq i}$$

$$dG = -SdT + Vdp + \sum_{i=1}^M \mu_i dn_i \Rightarrow \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, \text{all } j \neq i}$$

For a pure substance,  $M = 1$

$$dG(T, P, n) = -SdT + Vdp + \mu dn$$

For 1 mole of substance

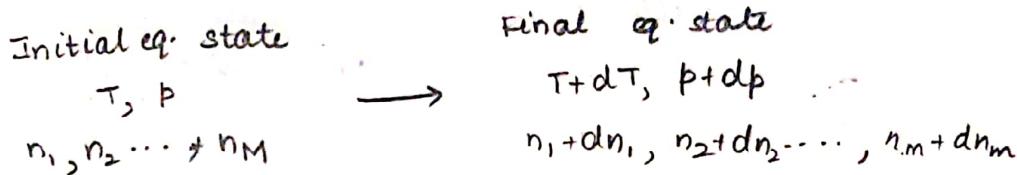
$$dG_m(T, P, n) = -S_m dT + V_m dp$$

$$d\mu = -SdT + V_m dp$$

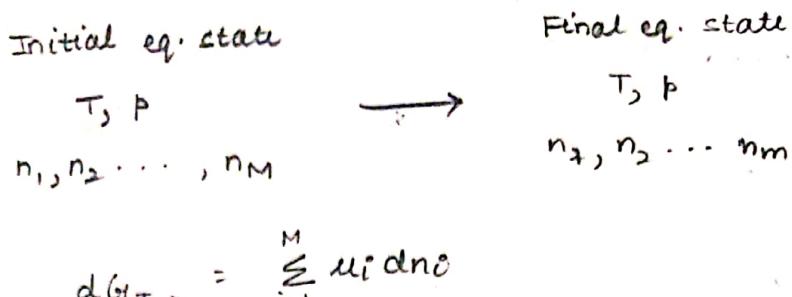
For an ideal gas,  $d\mu = -SdT + \frac{RT}{P} dp$

For an isothermal change from  $(T, p^*)$  to  $(T, p)$

$$\mu(T, p) = \mu^*(T) + RT \ln\left(\frac{p}{p^*}\right)$$



At const. temp and pressure



Assumption: Mixture behaves ideally

$x_i \rightarrow$  Mole fraction of  $i$ -th component

$p_i = x_i p \rightarrow$  partial pressure

$$\mu_i = \mu_i^\circ + RT \ln \left( \frac{p_i}{p_0} \right)$$

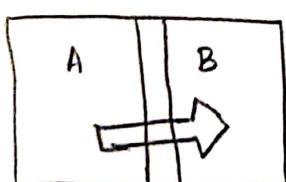
$$\Rightarrow \mu_i = \mu_i^\circ + RT \ln \left( \frac{x_i p}{p_0} \right)$$

$$\Rightarrow \mu_i = \mu_i^\circ + RT \ln \left( \frac{p}{p_0} \right) + RT \ln x_i$$

$$\mu_i^* (T, p) = \mu_i^\circ + RT \ln (P/p_0)$$

$$\mu_i = \mu_i^* (T, p) + RT \ln x_i$$

Since  $x_i < 1 \Rightarrow \mu_i (T, p)$  in the mixture  $< \mu_i (T, p)$  in pure phase



$$dG_A = \mu_{i,A} (-dn_i)$$

$$dG_B = \mu_{i,B} (+dn_i)$$

Net change

$$\begin{aligned} dG_i &= dG_A + dG_B \\ &= (\mu_{i,B} - \mu_{i,A}) dn_i \end{aligned}$$

Case 1:  $\mu_{i,A} > \mu_{i,B}$

$$\Rightarrow dG_i < 0$$

Case 2:  $\mu_{i,A} < \mu_{i,B}$

$$\Rightarrow dG_i > 0$$

Case 3:  $\mu_{i,A} = \mu_{i,B}$

$$\Rightarrow dG_i = 0$$

Spontaneous transfer of matter occurs from region of high to low  $\mu$ .

At eq. the chemical potential  $\mu$  is same everywhere.

## Chemical potential and composition of system

$$dG(T, P, n_1, n_2 \dots n_M) = -SdT + VdP + \sum_{i=1}^M \mu_i dn_i$$

Assumption:

At const. T and P, let  $dn_i = n_i dn$

Consequence:

$$dG_{T,P} = \left( \sum_{i=1}^M \mu_i n_i \right) dn$$

$$dG_{T,P} = G_1 dn \quad (\text{AS } G_1 \text{ is extensive})$$

$$dG_{T,P} = \sum_{i=1}^M (\mu_i dn_i + n_i d\mu_i)$$

$$G_1 = \sum_{i=1}^M \mu_i n_i \quad \sum_{i=1}^M n_i d\mu_i = 0$$

Gibbs  
Duhem  
Relations

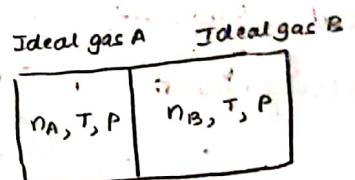
## Applications of Fundamental Concepts of Thermodynamics

### Thermodynamic mixing of ideal gases

Before mixing, all components are in their respective pure phase at same time T and p

$$\mu_A^*(T, P) = \mu_A^\circ + RT \ln \left( \frac{P}{P^\circ} \right)$$

$$\mu_B^*(T, P) = \mu_B^\circ + RT \ln \left( \frac{P}{P^\circ} \right)$$



$T, P_A, P_B$  with  
 $P_A + P_B = P$

Before mixing

$$G_{li} = \sum_{i=1}^M \mu_i dn_i$$

$$G_{li} = n_A \mu_A^* + n_B \mu_B^*$$

After mixing

$$\text{at } T, P = P_A + P_B$$

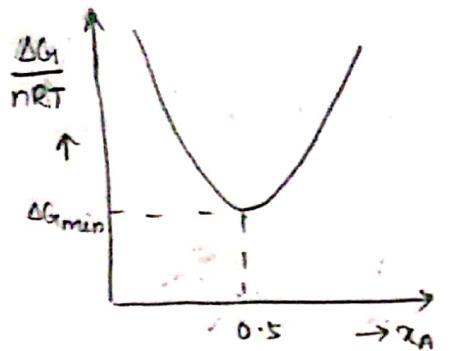
$$G_{lf} = n_A \left[ \mu_A^\circ + RT \ln \left( \frac{P_A}{P^\circ} \right) \right] + n_B \left[ \mu_B^\circ + RT \ln \left( \frac{P_B}{P^\circ} \right) \right]$$

$$= n_A \left[ \mu_A^\circ + RT \ln \left( \frac{x_A P}{P^\circ} \right) \right] + n_B \left[ \mu_B^\circ + RT \ln \left( \frac{x_B P}{P^\circ} \right) \right]$$

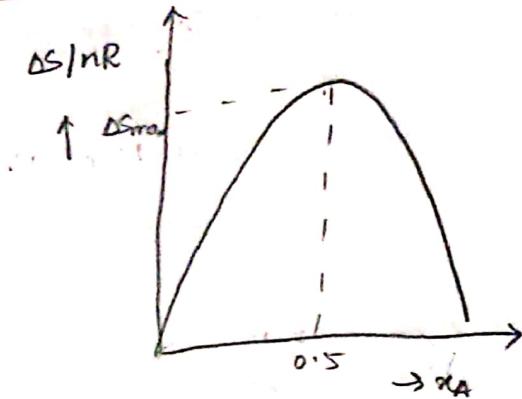
$$\Rightarrow G_{lf} = n_A \mu_A^* + n_B \mu_B^* + nRT [x_A \ln x_A + x_B \ln x_B]$$

$$G_{lf} = G_{li} + nRT [x_A \ln x_A + x_B \ln x_B]$$

$$\therefore \Delta G_f = nRT [x_A \ln x_A + x_B \ln x_B]$$



$$\Delta G_{\text{mix}} = nRT \sum_{i=1}^M x_i \ln x_i$$



$$\Delta S_{\text{mix}} = nR \sum_{i=1}^M x_i \ln x_i$$

### Phase stability

$$d\mu = -S_m dT + V_m dp$$

$$S_m(\text{solid}) < S_m(\text{liquid}) \ll S_m(\text{gas})$$

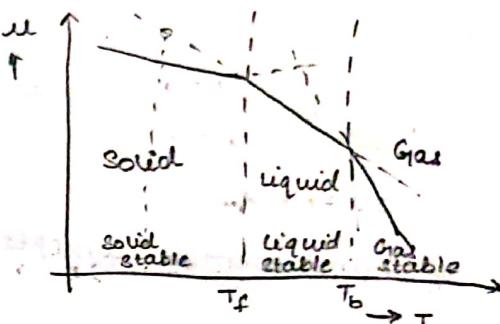
At temp  $T < T_f$

$$\mu_{\text{solid}} < \mu_{\text{liq}} < \mu_{\text{gas}}$$

At melting point  $T = T_f$

$$\mu_{\text{solid}} = \mu_{\text{liquid}}$$

$$\left( \frac{\partial \mu}{\partial T} \right)_P = -S_m$$



At temp  $T_f < T < T_b$

$$\mu_{\text{liq}} < \mu_{\text{solid}} < \mu_{\text{gas}}$$

At boiling pt,  $T = T_b$

$$\mu_{\text{liq}} = \mu_{\text{gas}}$$

### Phase Equilibrium

$$\mu(T, P) = G_m(T, P) = \frac{G(T, P)}{N}$$

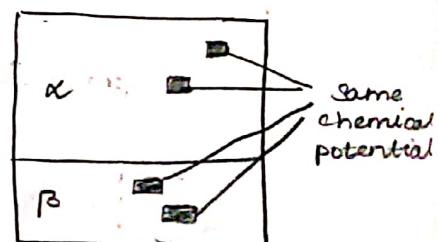
Chemical potential for a pure substance in the phases that are in equilibrium

$$\mu^{\alpha}(T, P) = \mu^{\beta}(T, P)$$

At eq., the chemical potential of a substance is same throughout a sample regardless of how many phases are present

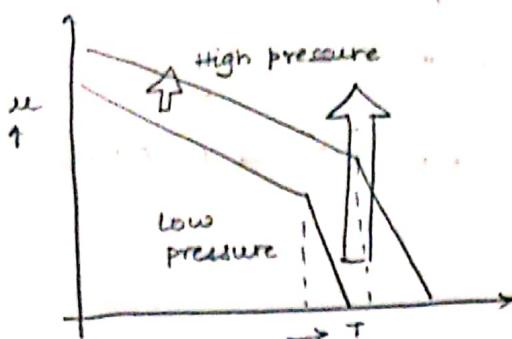
$$\mu_i(T, P) = \left( \frac{\partial G_i}{\partial n_i} \right)_{T, P, n_j \neq i}$$

$$\mu_i^{\alpha}(T, P) = \mu_i^{\beta}(T, P)$$

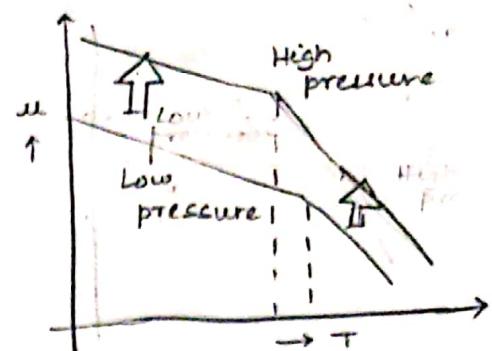


$$dG = -SdT + VdP, \quad dU = -C_v dT + V_m dP$$

$$\left(\frac{\partial U}{\partial P}\right)_T = V_m \quad V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$



Melting point increases with pressure ↑ when  
 $V_m(s) < V_m(l)$



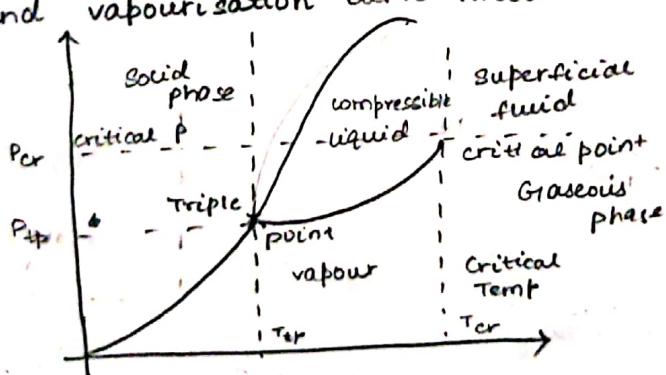
Melting point decreases with pressure ↑ when  
 $V_m(s) > V_m(l)$

$V_m(g) \gg V_m(l) \rightarrow$  Resulting in large increase in  $T_b$  with increasing Pressure  
 Vapourization:

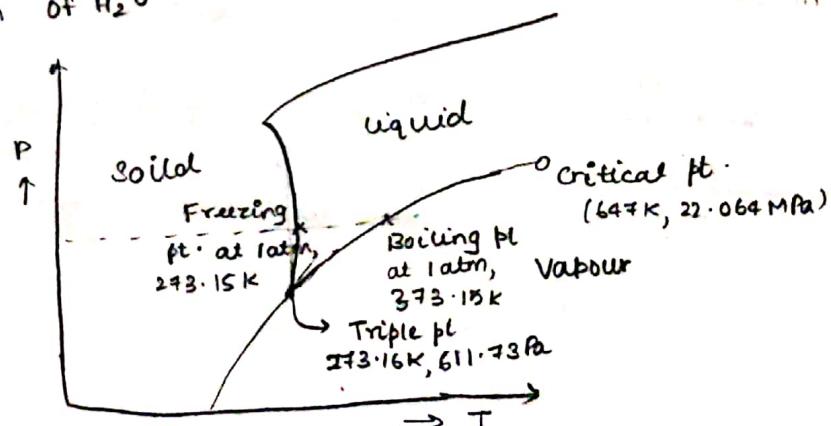
### Triple Point

- Triple point of a substance is temp., pressure at which the three phases (gas, liq., solid) of that of substance co-exist in thermodynamic eq.

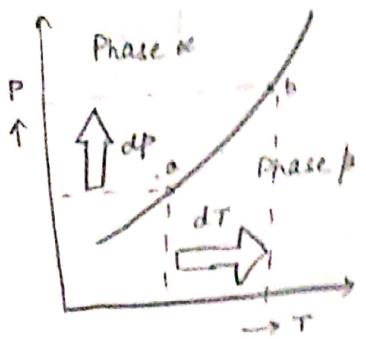
It is that temp. and pressure at which the sublimation curve, fusion curve and vapourisation curve meet.



### Phase Diagram of $H_2O$



## Location and Shape of Phase Boundary



$$\text{At point (a)} \\ \mu^\alpha(T, P) = \mu^\beta(T, P)$$

At point (b)

$$\mu^\alpha(T+dT, P+dP) \\ = \mu^\beta(T+dT, P+dP)$$

$$\Rightarrow \mu^\alpha(T, P) + d\mu^\alpha = \mu^\beta(T, P) + d\mu^\beta \\ \Rightarrow d\mu^\alpha = d\mu^\beta$$

$$\therefore \frac{dP}{dT} = \frac{s_m^\alpha - s_m^\beta}{v_m^\alpha - v_m^\beta}$$

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

$$\therefore \frac{dP}{dT} = \frac{\Delta S_{trans}}{\Delta V_{trans}} \rightarrow \begin{array}{l} \text{Applies to any} \\ \text{phase eq. of} \\ \text{any pure substance} \end{array}$$

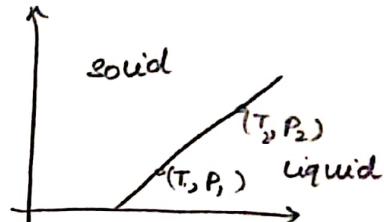
## Solid to Liquid Phase Boundary

$$\frac{dP}{dT} = \frac{\Delta H_f}{T \Delta V_f}$$

$$\Rightarrow \Delta P = \frac{\Delta H_f}{\Delta V_f} \ln \frac{T_2}{T_1}$$

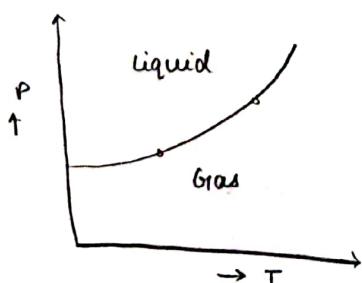
for  $T_2 \approx T_1$

$$\Rightarrow \Delta P = \frac{\Delta H_f}{T_1 \Delta V} \Delta T \Rightarrow \Delta T = \frac{T_1 \Delta V}{\Delta H_f} \Delta P$$



Melting point varies linearly with pressure

## Liquid to Vapour Boundary



$$\frac{d \ln P}{dT} = \frac{\Delta V_H}{RT^2}$$

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_V}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Claussius Clapeyron Eqn:

## Solid to Vapour Phase Boundary

$$\Delta V_{\text{sub}} = v_m(g) - v_m(s) \approx v_m(g) = RT/P$$

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_{\text{f}}}{RT^2}$$

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_{\text{f}}}{RT^2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$P_2 = P_1 e^{-\frac{\Delta H_{\text{f}}}{RT^2}}$$

$$\xi_1 = \frac{\Delta H_{\text{f}}}{RT^2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= \frac{\Delta H_f + \Delta H_v}{RT^2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Clapeyron Eqn:  $\frac{dP}{dT} = \frac{\Delta S_{\text{trs}}}{\Delta V_{\text{trs}}}$

Solid  $\rightarrow$  Liquid Phase Boundary  $\Delta T = \frac{\Delta V \cdot T_1}{\Delta f H} \Delta P$

Liquid  $\rightarrow$  Vapour Phase Boundary  $\ln \frac{P_2}{P_1} = - \frac{\Delta f H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

Clausius Clapeyron Eqn:  $\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}$

Solid  $\rightarrow$  Vapour Phase Boundary  $\frac{d \ln P}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2} = \frac{\Delta f H + \Delta f f}{RT^2}$

## Chemical Equilibrium

consider  $A \rightleftharpoons B$

let  $d\xi_1$  of A change into B such that  $d n_A = -d\xi_1$ ,  $d n_B = d\xi_1$   
 $\xi_1$  is extent of reaction

$$\Delta r G_1 = \left( \frac{\partial G_1}{\partial \xi_1} \right)_{T, P} = \mu_B - \mu_A$$

The reaction Gibbs energy is the difference b/w the chemical potential of product and reactant at the composition of reaction mixture

For  $v_1 A_1 \rightleftharpoons v_2 A_2$

$$\Delta r G_1 = \left( \frac{\partial G_1}{\partial \xi_1} \right)_{T, P} = \mu_2 v_2 - \mu_1 v_1 = \sum_i \mu_i v_i$$



$$\Delta G_r = \left( \frac{\partial G}{\partial \varepsilon_i} \right)_{T, P}$$

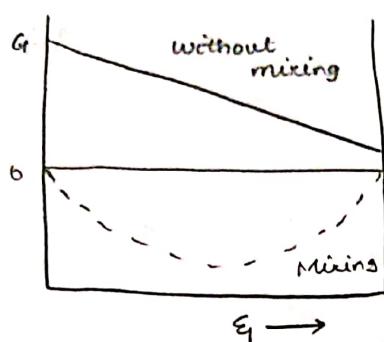
$$G_i = \sum_i n_i (\mu_i^* + \mu_i - \mu_i^*)$$

$\mu_i^*(T, P)$  → chemical potential of pure species i

$$G_i = \sum_i n_i \mu_i + \sum_i n_i (\mu_i - \mu_i^*)$$

$G_{\text{pure}}$                        $\Delta G_{\text{mix}}$

$$G(T, P, \varepsilon_i) = G_{\text{pure}}(T, P, \varepsilon_i) + \Delta G_{\text{mix}}(T, P, \varepsilon_i)$$



$$G_{\text{pure}} = \sum_i n_i \mu_i^*$$

$$n_i = n_{i, \text{initial}} + v_i \varepsilon_i$$

$$\Delta G_{\text{mix}} = nRT \sum_i n_i \ln x_i$$

$$\Delta_r G = \left( \frac{\partial G}{\partial \varepsilon_i} \right)_{T, P} = \mu_B - \mu_A$$

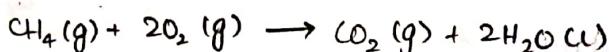
↑ work producing

The forward rxn is spontaneous if  $\mu_A > \mu_B$ . ( $\Delta_r G < 0$ )

The reverse rxn is spontaneous if  $\mu_B > \mu_A$  ( $\Delta_r G > 0$ )

The rxn reaches equilibrium when  $\mu_A = \mu_B$  ( $\Delta_r G = 0$ )

Eg :-



Cond. for eq.

$$\left[ 2\mu_{\text{H}_2\text{O}(l)} + \mu_{\text{CO}_2(g)} - \mu_{\text{CH}_4(g)} - 2\mu_{\text{O}_2(g)} \right]_{\text{eq}} = 0$$

### Ideal Gas equilibrium

$$\Delta_r G = \mu_B - \mu_A = \mu_B^\circ - \mu_A^\circ + RT \ln \left( \frac{P_B}{P_A} \right)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\text{Let } K = \left( \frac{P_B}{P_A} \right)_{\text{eq}}, \quad \Delta_r G^\circ = -RT \ln K$$

$\Delta_r G^\circ > 0 \Rightarrow K < 1, \quad P_A > P_B, \quad \text{Eq. is towards A}$

$\Delta_r G^\circ < 0 \Rightarrow K > 1, \quad P_B > P_A, \quad \text{Eq. is towards B}$

$$\mu_j = \mu_j^\circ + RT \ln(\alpha_j) \quad \alpha_j \rightarrow \text{Activity of } j\text{-th species}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q, \quad \Delta_r G^\circ = \sum_j \mu_j^\circ \alpha_j; \quad Q = \prod_j \alpha_j^{\nu_j}$$

$$\text{At eq.} \quad \Delta_r G = -RT \ln K, \quad K = (\prod_j \alpha_j^{\nu_j})_{\text{eq}}$$

Temperature Dependence of Eq. constant

$$\rightarrow \Delta_r G^\circ = -RT \ln K$$

$$\rightarrow \frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^\circ / T)}{dT}$$

$$\rightarrow \frac{d(\Delta_r G^\circ / T)}{dT} = -\frac{\Delta_r H^\circ}{T^2} \quad (\text{Gibbs Helmholz Eqn.})$$

$$\rightarrow \frac{d(\ln K)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad (\text{Vant Hoff Eqn.})$$

$$\rightarrow \ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\rightarrow \left( \frac{dK}{dP} \right)_T = 0$$

$$A \rightleftharpoons 2B(g)$$

As pressure  $\uparrow$ ,  $\alpha$  should decrease

$$\begin{array}{ccc} A & \rightleftharpoons & 2B \\ 1 & & 0 \\ 1-\varepsilon_1 & & 2\varepsilon_1 \end{array} \quad \begin{array}{l} x_A = \frac{1-\varepsilon_1}{1+\varepsilon_1} \quad x_B = \frac{2\varepsilon_1}{1+\varepsilon_1} \\ P_A = P \left( \frac{1-\varepsilon_1}{1+\varepsilon_1} \right) \quad P_B = \left( \frac{2\varepsilon_1}{1+\varepsilon_1} \right)^P \end{array}$$

$$Q = \frac{4\varepsilon_1^2 P}{1-\varepsilon_1^2} \quad \Delta G_{rT} = \Delta G_{rT}^\circ + RT \ln Q$$

If  $Q > K$ , reverse rxn must occur to reach eq.  
If  $K > Q$ , forward rxn must occur to reach eq.