

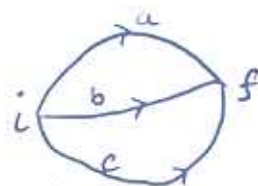
Thermodynamics

- Quantitative study of energy transformations associated with physical or chemical processes
- Based on few fundamental laws/concepts
- Work concept: Work is done when an object is moved against an opposing force (e.g. change in height of a weight)
- System + Surroundings \rightarrow Universe
 - (a) Isolated system: no exchange of energy or matter
 - (b) closed system: Exchange of energy allowed
 - (c) Open system: Both energy & matter can transfer

• First law: $\boxed{\Delta U = q + w}$ OR, $\boxed{dU = dq + dw}$

- Internal energy (u): Total energy of a system (KE + PE)
 $U = f(V, T)$ or $f(P, T)$ or $f(P, V)$

- extensive property
- state function
- ΔU is independent of path
- for cyclic process; $\oint dU = 0$
- dU is a perfect differential (exact)



$$\Delta U = \int_i^f dU = U_f - U_i$$

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

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

Partial derivatives

$$Z = f(x, y)$$

partial derivative of the function Z is the slope of the function w.r.t. one of the variables, the other one held constant

$$\left(\frac{\partial Z}{\partial x}\right)_y ; \left(\frac{\partial Z}{\partial y}\right)_x$$

$$\left(\frac{\partial Z}{\partial x}\right)_y = \lim_{h \rightarrow 0} \frac{f(x+h, y) - f(x, y)}{h}$$

$$\left(\frac{\partial Z}{\partial y}\right)_x = \lim_{k \rightarrow 0} \frac{f(x, y+k) - f(x, y)}{k}$$

If x and y change by dx and dy , then Z changes by:

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy \quad dZ \text{ is a perfect differential}$$

Important properties:

$$(i) \frac{\partial^2 Z}{\partial x \partial y} = \frac{\partial^2 Z}{\partial y \partial x}$$

$$(ii) \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad \text{Euler chain relation}$$

Example: $T = f(P, V)$; ideal gas: $PV = RT$

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

$$\frac{\partial^2 T}{\partial P \partial V} = \frac{\partial^2 T}{\partial V \partial P} = \frac{1}{R} \quad (dT \text{ is a perfect differential})$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} ; \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R} ; \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

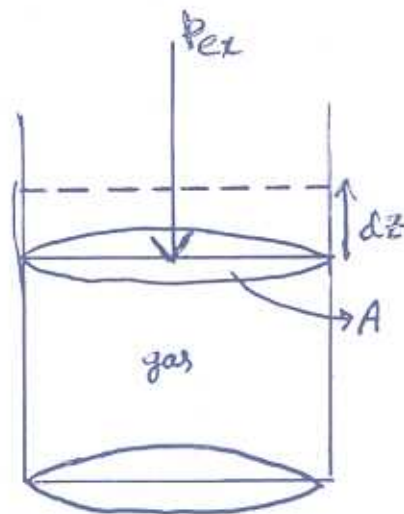
$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

Expansion/Compression Work

Work done to move the piston a distance dZ against an opposing force:

$$dW = -F dZ = -p_{ex} A dZ = -p_{ex} dV$$

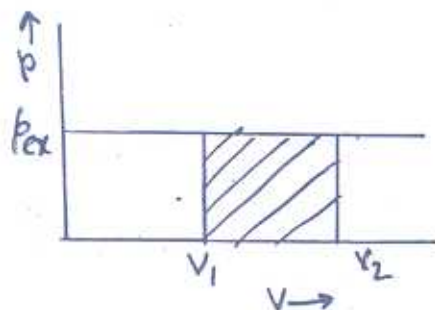
$$\text{total work, } W = - \int_{V_1}^{V_2} p_{ex} dV$$



- (a) Free expansion: $p_{ex} = 0$ (system expands in vacuum)
 $W = 0$ (no work is done)

- (b) Expansion against constant pressure (irreversible process)

$$W = -p_{ex} \int_{V_1}^{V_2} dV = -p_{ex} (V_2 - V_1) \\ = -p_{ex} \Delta V$$



- (c) Reversible expansion:

- changes occur in successive stages of infinitesimal amounts
- changes can be reversed

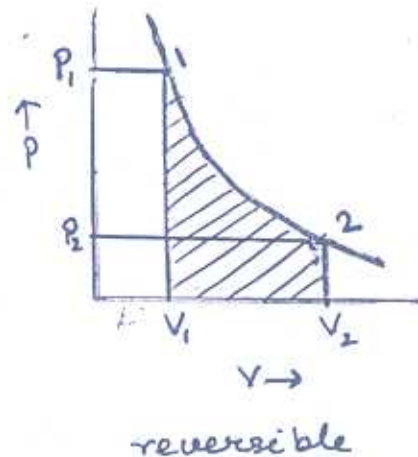
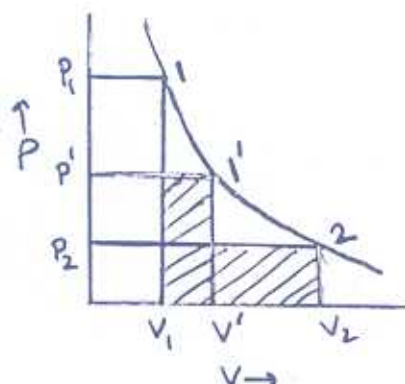
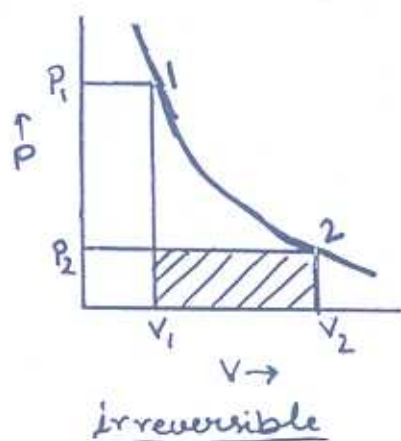
$$W = - \int_{V_1}^{V_2} (p - dp) dV = - \int_{V_1}^{V_2} p dV + \int_{V_1}^{V_2} dp dV = - \int_{V_1}^{V_2} p dV$$

Consider isothermal reversible expansion of an ideal gas
 $(pV = nRT)$

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

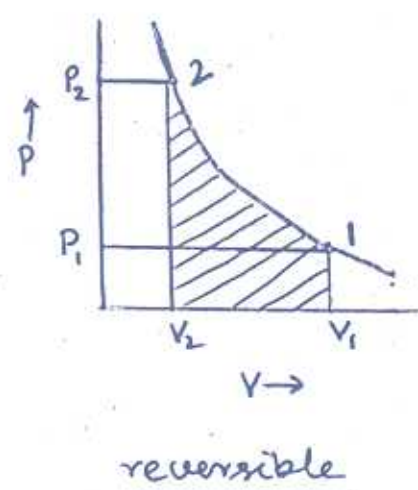
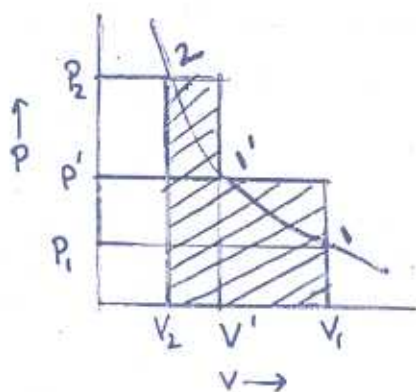
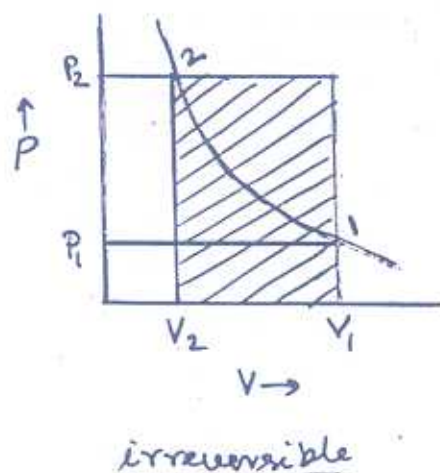
For expansion, $V_2 > V_1 \Rightarrow W < 0$
 compression, $V_2 < V_1 \Rightarrow W > 0$ } Sign convention

Expansion



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

Compression



reversible process → work obtained in the surroundings is exactly same as that required to compress the gas back to initial state

irreversible process → work obtained in the surroundings is less than that required to compress the gas back to initial state.

Enthalpy (H)

First law: $du = dq + dw$

$$= dq - p dv \text{ (no additional work)}$$

If the change occurs at constant volume,

$$\underline{du = dq_v} \text{ or } \underline{\Delta u = q_v}$$

- At constant V , the energy supplied to a system as heat ($q > 0$) or obtained from it as heat ($q < 0$) is same as the change in the internal energy of the system.
- However, if the process is carried out at constant P , the system changes its volume.
- Part of the energy supplied as heat will be utilized for doing expansion work. So, $\underline{du < dq}$ (at constant P)
(compression)

Define another thermodynamic property of the system, Enthalpy (H), useful for processes at constant P .

$$H = u + pV$$

- H is a state function
- dH is an exact differential
- ΔH is independent of path

Enthalpy (H)

* H is a state fn: $H = f(P, T)$

Defined as: $H = U + PV$

$$dH = dU + PdV + VdP = dq + dw + PdV + VdP$$

at constant Pressure

$$dH = dq_p + dw + PdV$$

if the system performs only mechanical work (expansion)
($dw = -PdV$)

$$\boxed{dH = dq_p}$$

change in enthalpy is the heat absorbed by the system
at constant P (no additional work)

Heat capacity (C_v, C_p)

$$C_v = \frac{dq_v}{dT} ; C_p = \frac{dq_p}{dT}$$

Amount of heat required to raise the temperature of 1 mol
of a substance at constant V or constant P.

$$dU = dq_v \Rightarrow C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

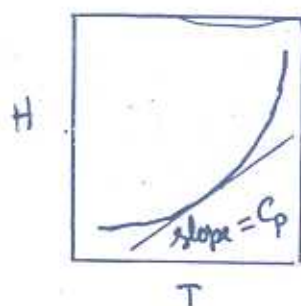
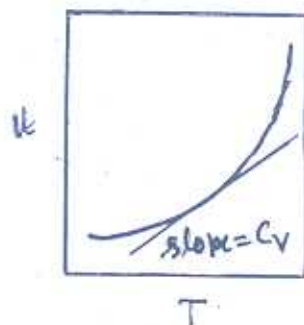
$$dU = n C_v dT$$

$$\boxed{\Delta U = n \int_{T_1}^{T_2} C_v dT}$$

$$dH = dq_p \Rightarrow C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$dH = n C_p dT$$

$$\boxed{\Delta H = n \int_{T_1}^{T_2} C_p dT}$$



Variation with T: $C_p = a + bT + \frac{c}{T^2} + \dots$

For ideal gas: $C_p - C_v = R$

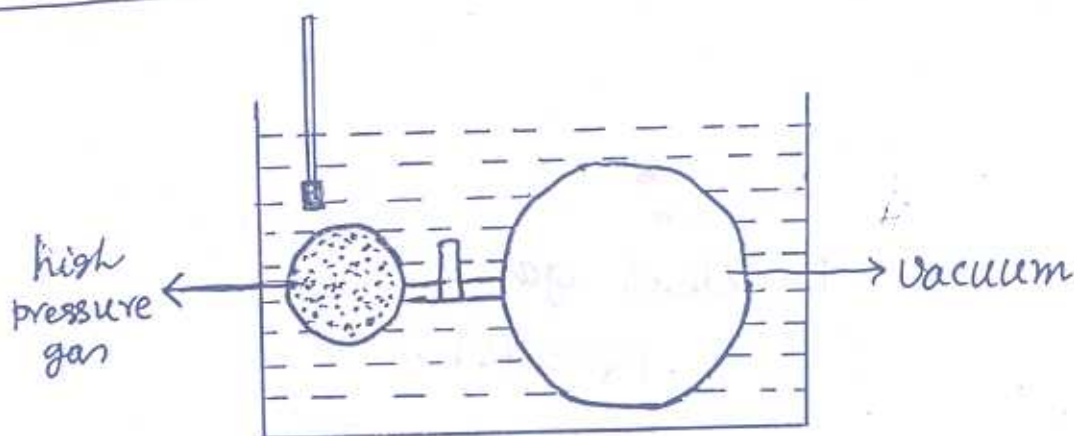
Variation of U with system variables: $U = f(V, T)$

① w.r.t. T at constant V : $du_v = \left(\frac{\partial u}{\partial T}\right)_v dT$

$$\left(\frac{\partial u}{\partial T}\right)_v = C_v \Rightarrow \Delta U = C_v \Delta T$$

② w.r.t. V at constant T : $du_T = \left(\frac{\partial u}{\partial V}\right)_T dV$

Joule's Expt.



expansion against $p_{ex} = 0 \Rightarrow dw = 0$

no change in $T \rightarrow$ isothermal expansion $\Rightarrow du_T = 0 (\because dq = 0)$

$$U = f(V, T) \Rightarrow du = \left(\frac{\partial u}{\partial V}\right)_T dV + \left(\frac{\partial u}{\partial T}\right)_V dT = \left(\frac{\partial u}{\partial V}\right)_T dV + C_v dT$$

$$du_T = \left(\frac{\partial u}{\partial V}\right)_T dV = 0 \Rightarrow \left(\frac{\partial u}{\partial V}\right)_T = 0 \quad \text{valid for an ideal gas ONLY}$$

$$\left(\frac{\partial u}{\partial P}\right)_T = \left(\frac{\partial u}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = 0 \Rightarrow \left(\frac{\partial u}{\partial P}\right)_T = 0$$

③ w.r.t. T at constant P :

$$du = C_v dT + \left(\frac{\partial u}{\partial V}\right)_T dV$$

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

$$= C_v + \alpha V \left(\frac{\partial u}{\partial V}\right)_T$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P : \text{isobaric expansion coeff.}$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T : \text{isothermal compressibility}$$

Ideal gas: $\left(\frac{\partial u}{\partial T}\right)_P = C_v (\because \left(\frac{\partial u}{\partial V}\right)_T = 0)$

Variation of H with system variables

$$H = f(P, T) ; dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

1. w.r.t. T at constant P :

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

$$\underline{\Delta H = C_P \Delta T = \int_P}$$

2. w.r.t. P at constant T : $\left(\frac{\partial H}{\partial P}\right)_T$

$$H = U + PV$$

$$dH = du + PdV + VdP$$

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

For ideal gas : $\left(\frac{\partial U}{\partial P}\right)_T = 0$ and $P\left(\frac{\partial V}{\partial P}\right)_T = -V$

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 ; \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = 0$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = 0} \text{ valid for ideal gases}$$

In general, $H = f(P, T)$

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

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

$$\mu_{JT} \rightarrow \text{Joule Thomson coeff} = \left(\frac{\partial T}{\partial P}\right)_H$$

Adiabatic processes

Isolated system ; no heat exchange with surroundings ($dq=0$)

$$du = dw = -p_{ex} dv \quad (\text{only mechanical work})$$

$$\Delta U = \int_{u_1}^{u_2} du = u_2 - u_1 = w = - \int_{V_1}^{V_2} p_{ex} dV$$

For ideal gas : $du = C_v dT$

$$\Delta U = \int_{u_1}^{u_2} du = C_v \int_{T_1}^{T_2} dT = C_v (T_2 - T_1)$$

$$\boxed{w = \Delta U = C_v (T_2 - T_1)} \quad \text{adiabatic work (ideal gas)}$$

Work in an adiabatic process when C_v is independent of T .

→ For expansion : ΔU decreases ; $T_2 < T_1$

→ For compression : ΔU increases ; $T_2 > T_1$

For adiabatic reversible processes with an ideal gas :

$$du = C_v dT = -p dv = - \frac{RT}{V} dV$$

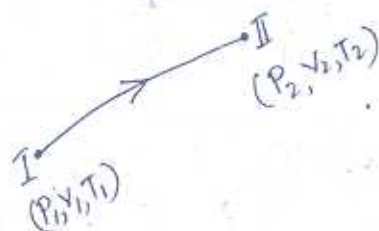
$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

$$\text{or, } \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{R/C_v} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \left[\begin{array}{l} C_p - C_v = R \\ \text{and } \gamma = \frac{C_p}{C_v} \end{array} \right]$$

$$\Rightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

$$\text{So, } \boxed{TV^{\gamma-1} = \text{constant}}$$



$$\underline{\gamma > 1}$$

Similarly,

$$\left(\frac{T_2}{T_1}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{1-\gamma}$$

or

$$T^\gamma P^{1-\gamma} = \text{constant}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma$$

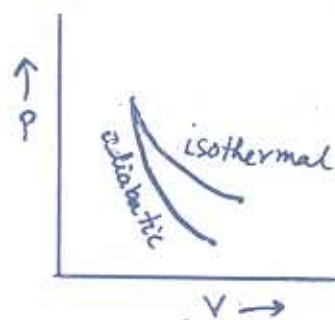
or

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

For isothermal expansion of ideal gas: $PV = K$ ($P \propto \frac{1}{V}$)

adiabatic " " " : $PV^\gamma = K'$ ($P \propto \frac{1}{V^\gamma}$)

$\gamma > 1$; adiabatics fall more sharply



Physically; fall in pressure is more
for a given volume expansion
in an adiabatic expansion

Alternatively,

$$\text{slope, } \frac{dP}{dV} = -\frac{P}{V} \text{ (isothermal)}$$

$$= -\gamma \frac{P}{V} \text{ (adiabatic)}$$

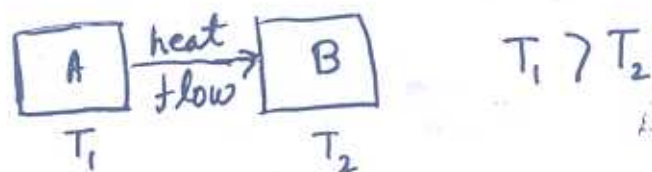
as $\gamma > 1$; adiabatic slope is more negative

2nd Law of Thermodynamics

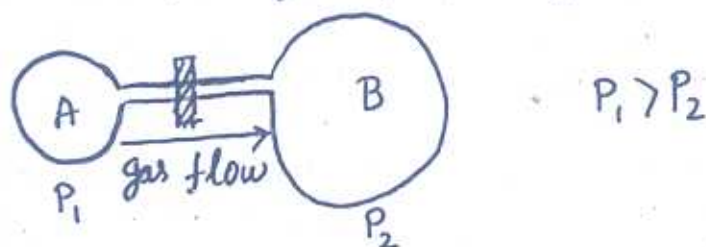
1st law → Different forms of energy are interconvertible;
total energy is conserved

Incomplete picture: No information on the extent and
direction of change/spontaneity of a process

Example: (1) Two objects at different 'T's are in contact



(2) Expansion of a gas from high to low P



Spontaneous processes: changes that take place automatically
in a system without the aid of an external device (engine)

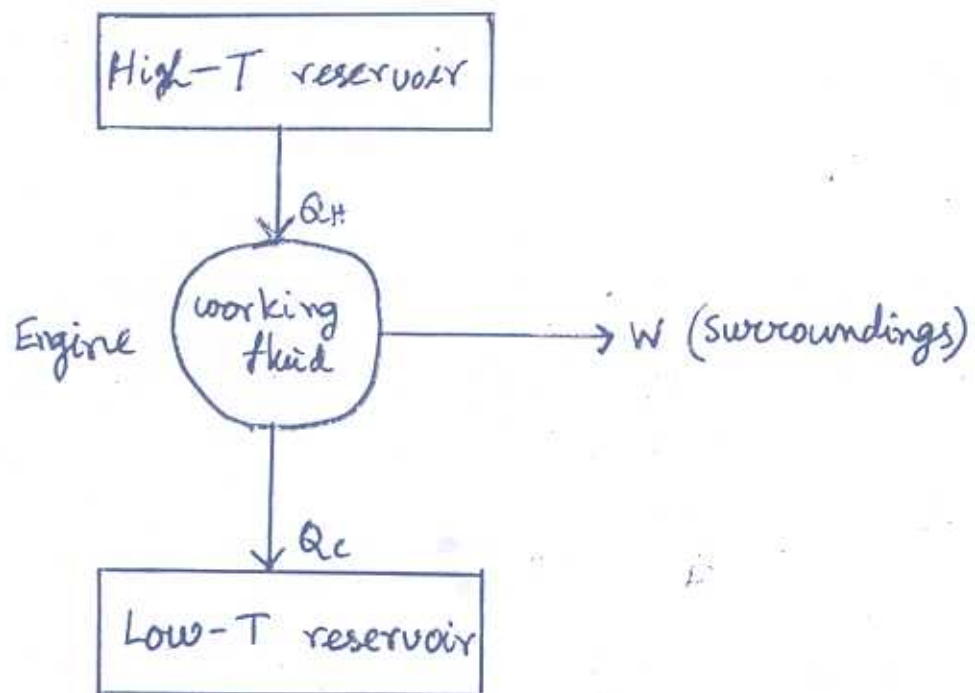
- Spontaneous processes are irreversible and
tend to equilibrium

Interconversion of heat and work (an engine is required)

Heat engine: A device that can convert heat into
mechanical work by carrying a 'working substance'
through a cyclic process.

Example: Carnot engine

Heat engine



Statement of 2nd law : (Kelvin-Planck)

It is impossible to construct an engine, that operating in a cycle will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

$$\text{Efficiency of the engine: } \eta = \frac{W}{Q_H}$$

$$\text{as } W < Q_H ; \eta < 1$$

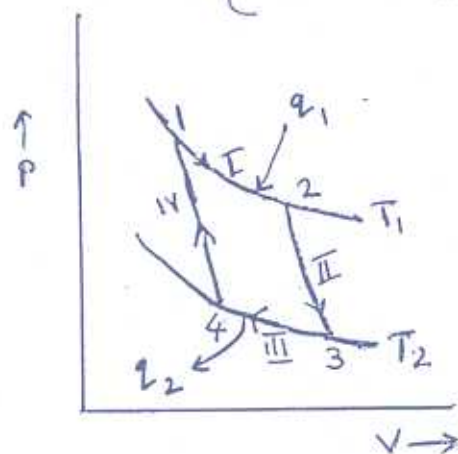
$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

For a given Q_H , higher the work (W), greater the efficiency (η)

Carnot Cycle

(Carnot, 1824)

(How and to what extent work can be obtained from heat)



Engine: ① Ideal gas in a cylinder with a frictionless piston

② Works in a cycle (4 steps)

③ All the steps are reversible

Step I : Isothermal expansion : $1 \rightarrow 2$ ($T_1, P_1, V_1 \rightarrow T_1, P_2, V_2$)

heat absorbed $= q_1$; work done $= w_1$

So, $\Delta U_I = q_1 + w_1$

Step II : Adiabatic expansion : $2 \rightarrow 3$ ($T_1, P_2, V_2 \rightarrow T_2, P_3, V_3$)

heat absorbed, $q'_2 = 0$; work done $= w_2$

So, $\Delta U_{II} = w_2$

Step III : Isothermal compression : $3 \rightarrow 4$ ($T_2, P_3, V_3 \rightarrow T_2, P_4, V_4$)

heat released $= q_2$; work done $= w_3$

So, $\Delta U_{III} = q_2 + w_3$

Step IV : Adiabatic compression : $4 \rightarrow 1$ ($T_2, P_4, V_4 \rightarrow T_1, P_1, V_1$)

heat released $= 0$; work done $= w_4$

So, $\Delta U_{IV} = w_4$

The cycle is completed. So, $\Delta U_{cy} = 0$

$$\Delta U_{CY} = 0 = \Delta U_I + \Delta U_{II} + \Delta U_{III} + \Delta U_{IV}$$

$$\Rightarrow (q_1 + q_2) + (w_1 + w_2 + w_3 + w_4) = 0$$

$$\text{or, } q_{CY} + w_{CY} = 0 \Rightarrow \boxed{w_{CY} = -q_{CY} = -(q_1 + q_2)}$$

Work involved in 4 steps:

$$w_1 = - \int_{V_1}^{V_2} p dV = -RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$w_2 = \int_{T_1}^{T_2} C_V dT \quad ; \quad w_3 = - \int_{V_3}^{V_4} p dV = -RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$w_4 = \int_{T_2}^{T_1} C_V dT$$

$$w_{CY} = w_1 + w_2 + w_3 + w_4 = -RT_1 \ln\left(\frac{V_2}{V_1}\right) - RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

Consider the adiabatics II & IV:

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \text{and} \quad T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\boxed{w_{CY} = -R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)}$$

$$\text{Efficiency of the engine : } \eta = \frac{|w_{CY}|}{q_1}$$

$$\text{Step I} \rightarrow \Delta T = 0 \quad ; \quad \Delta U_I = 0 \Rightarrow q_1 = -w_1$$

(ideal gas)

$$\eta = \frac{R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)} = \frac{T_1 - T_2}{T_1} = \frac{\Delta T}{T_1}$$

Also, $|W_{cy}| = |Q_1 + Q_2|$

so, $\eta = \frac{|Q_1 + Q_2|}{Q_1} = \frac{T_1 - T_2}{T_1} \left[\frac{\Delta T}{T_1} \right]$ (i) $0 < \eta < 1$
 (ii) if $T_2 = 0$; $\eta = 1$; Impossible
 (iii) if $T_1 = T_2$; $\eta = 0$; no work

$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$ (for reversible cycle)

- IMPORTANT: for a reversible cyclic process; $\oint \frac{dQ_{rev}}{T} = 0$
- A new state function S (entropy), whose change is given by $ds = \frac{dQ_{rev}}{T}$ and $\oint ds = 0$
- dq is an inexact differential; but $\frac{dQ_{rev}}{T}$ is an exact differential
- If heat is absorbed; $dQ_{rev} > 0$; entropy of the system increases
- If heat is rejected; $dQ_{rev} < 0$; entropy decreases
- If $dq = 0$; $ds = 0$. Adiabatic changes are isentropic

Entropy (S) is a new thermodynamic ~~var~~ variable which is introduced through 2nd law

Clausius Theorem (criterion for spontaneous change)

Carnot theorem: No engine operating between two heat reservoirs can be more efficient than a reversible engine operating between the same two reservoirs

$$\text{So, } \eta \leq \eta_{\text{rev}} \quad (\because w \leq w_{\text{rev}})$$

$$1 + \frac{q_2}{q_1} \leq 1 + \frac{q_{2,\text{rev}}}{q_{1,\text{rev}}} = 1 - \frac{T_2}{T_1} \quad (\text{Carnot cycle})$$

$$\Rightarrow 1 + \frac{q_2}{q_1} \leq 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \boxed{\frac{q_2}{T_2} + \frac{q_1}{T_1} \leq 0} \quad \text{or} \quad \boxed{\oint \frac{dq}{T} \leq 0}$$

This is Clausius theorem

$\oint \frac{dq}{T} < 0$: if any part of the cyclic process is irreversible

$\oint \frac{dq}{T} = 0$: if the cyclic process is reversible

$\oint \frac{dq}{T} > 0$: Impossible

We apply Clausius theorem for an irreversible cyclic process

$$\oint \frac{dq}{T} \leq 0$$

$$\text{So, } \int_1^2 \frac{dq_{\text{irr}}}{T} + \int_2^1 \frac{dq_{\text{rev}}}{T} \leq 0$$

$$\Rightarrow \int_1^2 \frac{dq_{\text{irr}}}{T} - \int_1^2 \frac{dq_{\text{rev}}}{T} \leq 0$$

$$\Rightarrow \underline{\Delta S = S_2 - S_1 = \int_1^2 dS \geq \int_1^2 \frac{dq_{\text{irr}}}{T}}$$



$$\Delta S = S_2 - S_1 = \int_1^2 ds \geq \int_1^2 \frac{dq}{T}$$

Clausius inequality

We have a criterion for spontaneous process:

$ds > \frac{dq}{T}$: spontaneous/irreversible process

$ds = \frac{dq}{T}$: reversible process

$ds < \frac{dq}{T}$: impossible

Consider an isolated system

$$dq = 0$$

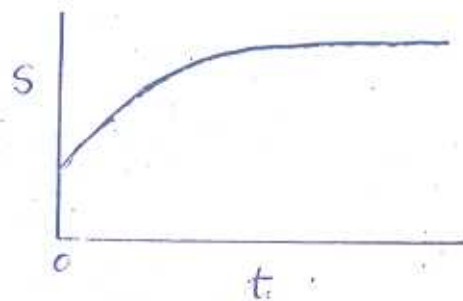
3 possibilities :

$\Delta S > 0$: spontaneous/irreversible process

$\Delta S = 0$: reversible process

$\Delta S < 0$: impossible

- Entropy increases for a spontaneous (natural) process in an isolated system : maximum at equilibrium.



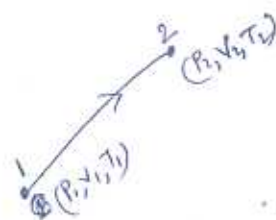
Entropy changes of an ideal gas (reversible processes)

$$du = dq + dw = dq - pdv$$

$$\Rightarrow dq = du + pdv = C_v dT + \frac{RT}{v} dv$$

$$\frac{dq}{T} = dS = C_v \frac{dT}{T} + R \frac{dv}{v}$$

$$\Delta S = S_2 - S_1 = \int_1^2 dS = \int_1^2 C_v \frac{dT}{T} + R \int_1^2 \frac{dv}{v}$$



$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

$$\text{Or } \Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\left. \begin{aligned} \therefore C_v &= C_p - R \\ &\& \\ v &= \frac{RT}{P} \end{aligned} \right\}$$

Special cases

(a) At constant v ; $\Delta S_v = C_v \ln \frac{T_2}{T_1}$

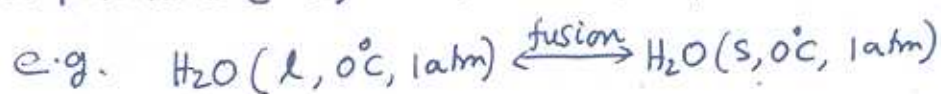
(b) At constant P ; $\Delta S_P = C_p \ln \frac{T_2}{T_1}$

(c) At constant T ; $\Delta S_T = R \ln \frac{v_2}{v_1} = R \ln \frac{P_1}{P_2}$

Entropy at phase transitions

Isothermal and reversible process

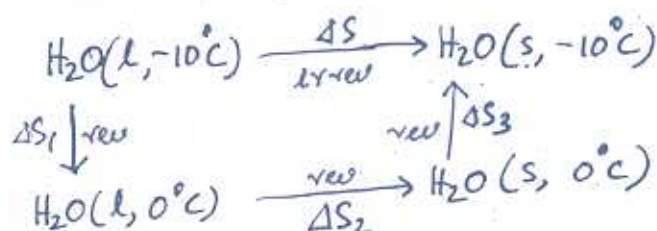
At transition temperature (T_{tr}) two phases are in eq/m.



transition occurs at constant P : $q_{rev} = \Delta H_{tr}$

$$\therefore \Delta S = \frac{q_{rev}}{T_{tr}} = \frac{\Delta H_{tr}}{T_{tr}}$$

transition	ΔH_{tr}	ΔS_{tr}
vaporization	> 0	> 0
melting	> 0	> 0
freezing	< 0	< 0



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

Entropy of mixing (ideal gases)

n_1 moles of gas 1 is mixed with n_2 moles of gas 2 at constant T and P .

Final volume, $V = V_1 + V_2$

Entropy changes for the two gases,

$$\Delta S_1 = n_1 R \ln \frac{V}{V_1} = -n_1 R \ln \frac{V_1}{V} = -n_1 R \ln \frac{n_1}{n_1+n_2} = -n_1 R \ln x_1$$

$$\Delta S_2 = n_2 R \ln \frac{V}{V_2} = -n_2 R \ln \frac{V_2}{V} = -n_2 R \ln \frac{n_2}{n_1+n_2} = -n_2 R \ln x_2$$

Total entropy change: $\Delta S_m = \Delta S_1 + \Delta S_2$

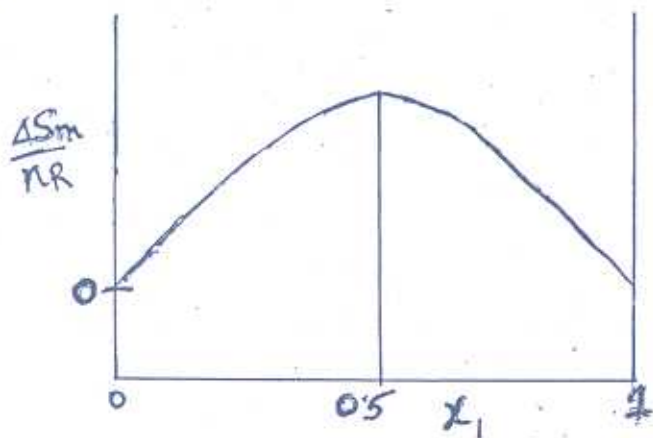
$$(n=n_1+n_2) \quad = -R [n_1 \ln x_1 + n_2 \ln x_2]$$

$$= -nR [x_1 \ln x_1 + x_2 \ln x_2]$$

In general, $\Delta S_m = -nR \sum_{i=1}^N x_i \ln x_i$

As $x_i < 1$, $\ln x_i < 0$; ΔS_m is always positive

Entropy increases on mixing



mixing of 2 gases:

ΔS_m is maximum when

$$\frac{d(\Delta S_m)}{dx_1} = 0$$

$$\Rightarrow \underline{x_1 = x_2 = 0.5}$$

Helmholtz and Gibbs energies

For any process : $dS \geq \frac{dq}{T}$ (Clausius inequality)

$TdS \geq dq$ $\begin{cases} \rightarrow \text{Equality for reversible processes} \\ \rightarrow \text{Inequality for Spontaneous (irreversible) processes} \end{cases}$

From 1st law : $du = dq + dw$

$$du \leq TdS + dw \Rightarrow dw \geq du - TdS$$

dw is $\ominus ve \rightarrow$ energy obtained from the system as work

The maximum work obtained from the system

$$dw_{\max} = du - TdS$$

possible for reversible processes (Clausius equality applies)

For isothermal change : $du - TdS = d(u - Ts) = dA$

New state function : Helmholtz energy (A)

$$A = U - TS$$

So, $\boxed{dw_{\max} = dA}$ or $\boxed{W_{\max} = \Delta A}$

A is such a thermodynamic property, whose change for an isothermal reversible process gives maximum work available during the process.

$$H = U + PV$$

$$dH = dU + d(PV) = dq + dw + d(PV)$$

We know, $TdS \geq dq$ (Clausius inequality)

$$\text{So, } dH \leq TdS + dw + d(PV)$$

$$\Rightarrow dw \geq dH - TdS - d(PV)$$

Again dw is $\ominus ue$.

Maximum work obtained from the system

$$dw_{\max} = dH - TdS - d(PV) \quad (\text{Reversible processes})$$

$$\text{total work, } dw = dw_{p-v} + dw_e = -pdV + dw_e$$

$$\text{So, } -pdV + dw_{e,\max} = dH - TdS - pdV + Vdp$$

$$\text{at constant } P; dw_{e,\max} = dH - TdS$$

$$\text{for isothermal change; } dH - TdS = d(H - TS) = dG$$

New state function: Gibbs energy (G)

$$\boxed{G = H - TS}$$

$$\text{So, } \boxed{dw_{e,\max} = dG} \quad \text{or} \quad \boxed{w_{e,\max} = \Delta G}$$

G is such a thermodynamic property of the system, whose change at constant T and P provides the maximum external (non-pv) work available during the process.

Fundamental Equations

1st law : $du = dq + dw$

Reversible process and only p-V work : $dq = Tds$; $dw = -pdv$

$$\boxed{du = Tds - pdv}$$

du is path independent. The eqn. applies for any change (reversible or irreversible) for a closed system

$$H = U + pV ; dH = du + pdv + vdp = Tds - pdv + pdv + vdp$$

$$\boxed{dH = Tds + vdp}$$

$$A = U - TS ; dA = du - Tds - sdT = Tds - pdv - Tds - sdT$$

$$\boxed{dA = -pdv - sdT}$$

$$G = H - TS ; dG = dH - Tds - sdT = Tds + vdp - Tds - sdT$$

$$\boxed{dG = vdp - sdT}$$

Four fundamental equations.

Valid for : (1) closed systems

(2) only p-V work

(3) reversible/irreversible change

Maxwell relations

Fundamental equation: $du = Tds - pdv$

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -p$$

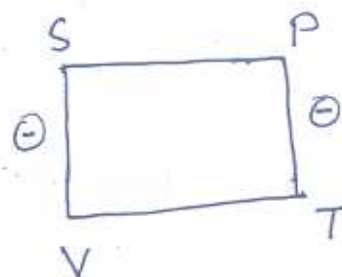
$$\frac{\partial^2 u}{\partial v \partial s} = \left(\frac{\partial T}{\partial v}\right)_s \quad \text{and} \quad \frac{\partial^2 u}{\partial s \partial v} = -\left(\frac{\partial p}{\partial s}\right)_v$$

As du is an exact differential

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial p}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial p}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_p \\ \left(\frac{\partial p}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T \\ \left(\frac{\partial v}{\partial T}\right)_p &= -\left(\frac{\partial s}{\partial p}\right)_T \end{aligned}$$

Maxwell relations



Important relations; can be used to express any thermodynamic property of a system in terms of measurable quantities (P, T, V etc.).

Thermodynamic Equations of state

$$du = Tds - pdv$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad (\text{using Maxwell relation})$$

$$\text{And, } \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = - \left(\frac{\partial v}{\partial T}\right)_p / \left(\frac{\partial v}{\partial p}\right)_T = \frac{\alpha}{\kappa}$$

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p : \text{expansion coefficient}$$

$$\kappa = - \frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T : \text{isothermal compressibility}$$

$$\boxed{\left(\frac{\partial u}{\partial v}\right)_T = \frac{T\alpha}{\kappa} - p = \frac{\alpha T - \kappa p}{\kappa}} \quad \text{Thermodynamic eqn. of state}$$

$\left(\frac{\partial u}{\partial v}\right)_T$ is called internal pressure; due to intermolecular interactions

$$\text{For ideal gas: } \alpha = \frac{1}{T}; \kappa = \frac{1}{p} \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = 0 \quad (\text{Joule's expt.})$$

Similarly,

$$\boxed{\left(\frac{\partial h}{\partial p}\right)_T = v(1 - \alpha T)}$$

$$\text{For ideal gas, } \alpha = \frac{1}{T} \Rightarrow \left(\frac{\partial h}{\partial p}\right)_T = 0$$

Temperature dependence of Gibbs energy

Fundamental eqn: $dG = Vdp - SdT$

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

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

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

$$\text{Now, } \left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

$$= -\frac{G}{T^2} + \frac{G-H}{T^2} = -\frac{H}{T^2}$$

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2} = H \left[\frac{\partial(1/T)}{\partial T}\right]_P \quad \text{or, } \boxed{\left[\frac{\partial(G/T)}{\partial T}\right]_P = \Delta H \left[\frac{\partial(1/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}}$$

$$\text{So, } \boxed{\left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P = H} \quad \text{or, } \boxed{\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H}$$

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

Gibbs-Helmholtz eqn.

Temperature dependence of ΔG .

This equation is important for the calculation of ΔG at another temperature if it is known at one temperature and ΔH is known. (assume that ΔH is independent of temp.)

Pressure dependence of Gibbs energy

Fundamental eqn: $dG = Vdp - SdT \Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dp \Rightarrow G_2 = G_1 + \int_{P_1}^{P_2} V dp$$

Case-I: liquid or solid ; V constant

$$G_2 = G_1 + V(P_2 - P_1) ; G = G^\circ + V(P - P^\circ)$$

\downarrow Standard Gibbs energy

Case-II: for gases ; V depends on P

for ideal gas : $\int_{G^\circ}^G dG = nRT \int_{P^\circ}^P \frac{dP}{P} \quad (T \text{ constant})$

$$G = G^\circ + nRT \ln \frac{P}{P^\circ}$$

Alternatively, $\Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$

Spontaneity of a change

Compute Gibbs energy change (ΔG) \rightarrow direction of any transformation

$$dU = dq_r + dw_r = dq_{ir} + dw_{ir}$$

$$dw_r > dw_{ir} \Rightarrow dq_r > dq_{ir} ; \text{ i.e. } dq_{ir} + dq_r < 0 \quad \left[\begin{array}{l} \text{Clausius} \\ \text{inequality} \end{array} \right]$$

$$G = H - TS = U + pV - TS$$

$$dG = dU + p dV + V dp - T dS - S dT = dq + V dp - T dS - S dT \quad (\text{only } p\text{-}V \text{ work})$$

at constant T and P : $dG_{P,T} = dq - T dS$

for a spontaneous (irreversible) process: $dG_{P,T} = dq_{ir} - dq_r < 0$

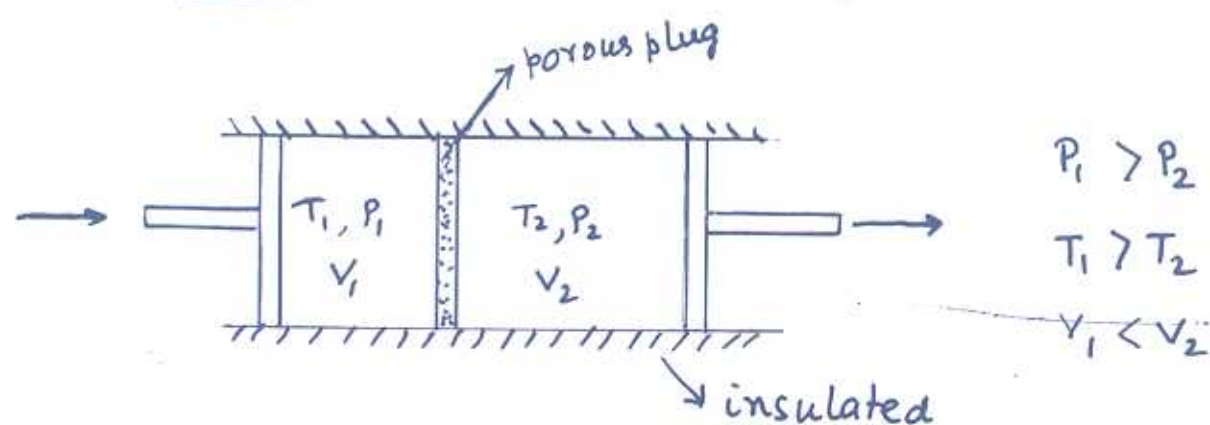
$$\boxed{\Delta G_{P,T} < 0} \quad \text{For a spontaneous change}$$

To check whether a process would be spontaneous at fixed T & P :

calculate ΔG :

- (1) $\Delta G < 0$: the change is spontaneous
- (2) $\Delta G = 0$: the system is in equilibrium
- (3) $\Delta G > 0$: the change is not spontaneous

Joule Thomson effect



Experiment: Passage of a fixed amount of gas at volume V_1 and temperature T_1 through a porous plug from high pressure P_1 to low pressure P_2 . The volume and temperature becomes V_2 & T_2 . Whole system is insulated \rightarrow changes occur adiabatically ($q=0$)

$$\text{work done on the gas in left} = P_1 V_1 = \cancel{P_1 \Delta V} = \cancel{P_1 (0 - V_1)}$$

$$\text{work done by the gas in right} = -P_2 V_2 = \cancel{-P_2 \Delta V} = \cancel{-P_2 (V_2 - 0)}$$

$$\text{Net work} : W = P_1 V_1 - P_2 V_2$$

$$\Delta U = U_2 - U_1 = W = P_1 V_1 - P_2 V_2 \quad (\because q=0)$$

$$\Rightarrow U_1 + P_1 V_1 = U_2 + P_2 V_2 \Rightarrow H_1 = H_2 \quad \text{i.e.} \quad \boxed{\Delta H = 0}$$

isoenthalpic expansion

In general, temperature of outgoing gas drops ($T_2 < T_1$)

→ Joule Thomson effect (cooling of a gas)

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

As, $P_2 < P_1$; dP is $\ominus ve$

$\left[\begin{array}{l} \text{if } \mu_{JT} \text{ is } \oplus ve ; \text{ then } dT \text{ is } \ominus ve \rightarrow \text{temp. drops (cooling effect)} \\ \text{if } \mu_{JT} \text{ is } \ominus ve ; \text{ then } dT \text{ is } \oplus ve \rightarrow \text{temp increases (heating effect)} \end{array} \right]$

Most gases (except H_2, He) cool down at room temp. ($\mu_{JT} \oplus ve$).

$$H = f(T, P) \Rightarrow dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT$$

Joule Thomson expt : $dH = 0$

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

$$\text{or, } \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial H}{\partial P} \right)_T / \left(\frac{\partial H}{\partial T} \right)_P = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\boxed{\mu_{JT} = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T}$$

Ideal gas : $\left(\frac{\partial H}{\partial P} \right)_T = 0 \Rightarrow \boxed{\mu_{JT} = 0}$ No effect

Real gas : $\left(\frac{\partial H}{\partial P} \right)_T \neq 0 \Rightarrow \boxed{\mu_{JT} \neq 0}$ cooling/heating effect

Fundamental eqn: $dH = TdS + vdP$

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

$$= -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad \left[\because \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P : \text{Maxwell relation}\right]$$

$$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

$\mu_{JT} \neq 0$ for real gas

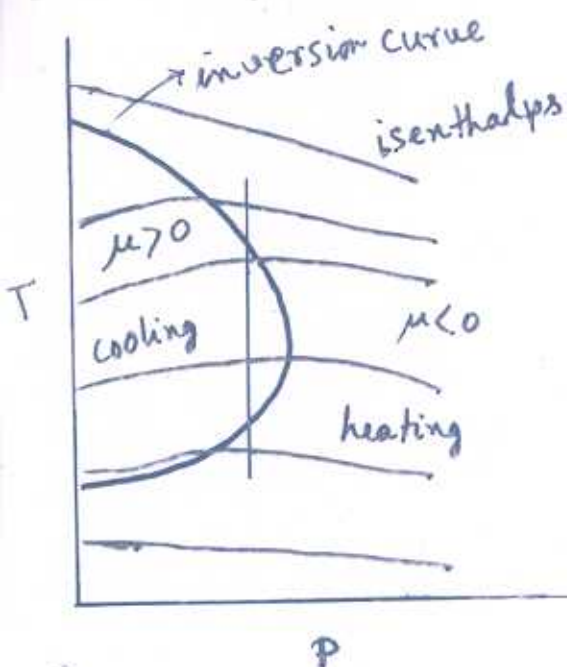
μ_{JT} can be calculated knowing the eqn of state of a gas.

Ideal gas: $T \left(\frac{\partial V}{\partial T} \right)_P = V \Rightarrow \mu_{JT} = 0$

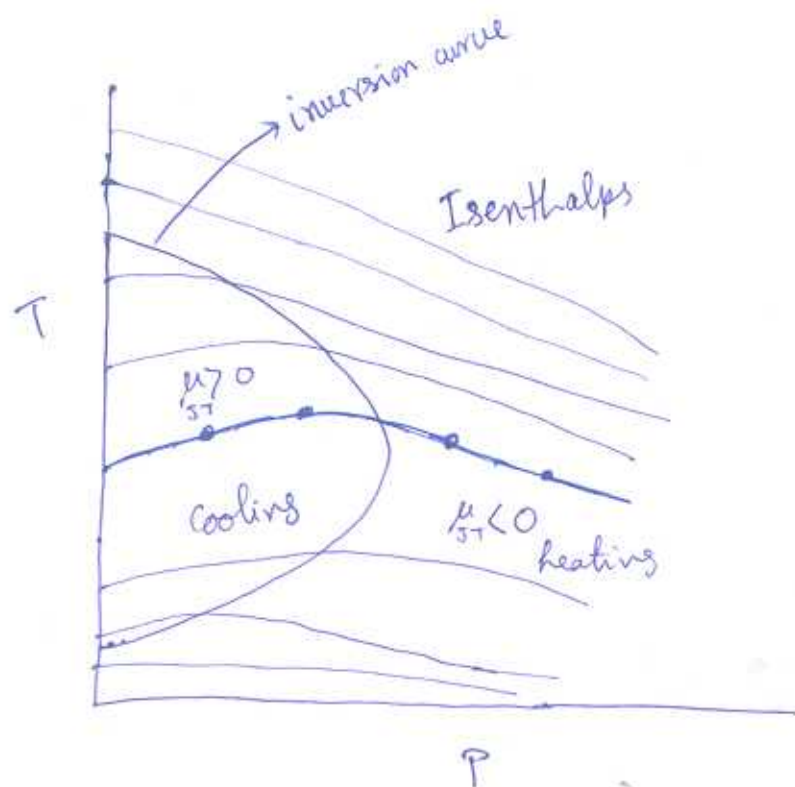
Real gas (V.W): $\mu_{JT} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$

$$\mu_{JT} \neq 0$$

Sign of μ_{JT} (cooling or heating) depends on: identity of the gas, intermolecular interactions, T , P etc.



The temperature at the boundary of the inversion curve is the inversion temperature of a gas at a particular pressure



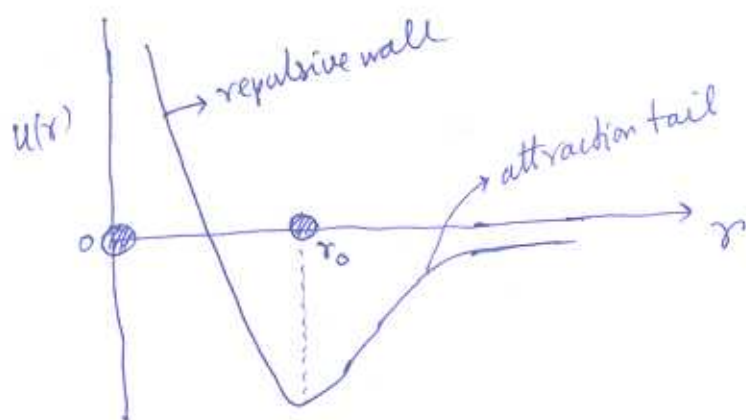
$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H \rightarrow \text{slope}$$

At inversion temperature,
 $\mu_{JT} = 0$
 (ideal behavior)

Cooling or heating ($\mu_{JT} \oplus$ or \ominus) depends on

- 1) Identity of the gas
- 2) Intermolecular interactions (attraction + repulsion)
- 3) T, P etc.

If attractive interactions dominate \rightarrow cooling effect
 repulsive interaction dominate \rightarrow heating effect



Open Systems

- Exchange of matter is allowed; compositions of the components can vary
- Consider homogeneous open systems (components in one phase)

$$G = f(P, T, n_1, n_2, \dots, n_i, \dots, n_N)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum_{i=1}^N \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j} dn_i$$

$$= VdP - SdT + \sum_{i=1}^N \mu_i dn_i$$

$$dG_{P,T} = dW_{e,max} = \sum_{i=1}^N \mu_i dn_i$$

Non-expansion work due to change of composition.

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

Chemical potential of i -th species

- The chemical potential of a component in a homogeneous mixture is equal to the rate of change of Gibbs energy w.r.t. the amount of that species in the mixture at constant T and P .
- For n moles of a pure substance; $G = n G_m$

$$\mu = \left[\frac{\partial (n G_m)}{\partial n} \right]_{T, P} = G_m \text{ (molar Gibbs energy)}$$

Gibbs-Duhem relations

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

at constant T and P :

$$dG_{T,P} = \sum_{i=1}^N \mu_i dn_i \quad \text{--- (1)}$$

The constituents are increased by same proportion (Δn)

i.e. $dn_i = n_i \Delta n$

$$dG_{T,P} = G \cdot \Delta n \quad (\text{as } G \text{ is extensive})$$

$$\therefore G \cdot \Delta n = \left(\sum_{i=1}^N \mu_i n_i \right) \cdot \Delta n \Rightarrow G = \sum_{i=1}^N \mu_i n_i$$

$$dG_{P,T} = \sum_{i=1}^N (\mu_i dn_i + n_i d\mu_i) \quad \text{--- (2)}$$

Comparing eqn 1 and 2: $\sum_{i=1}^N n_i d\mu_i = 0$

$$G = \sum_{i=1}^N \mu_i n_i$$
$$dG_{T,P} = \sum_{i=1}^N \mu_i dn_i$$
$$\sum_{i=1}^N n_i d\mu_i = 0$$

① Chemical potential of one component of a mixture cannot change independently.

Gibbs-Duhem relations

For a binary mixture,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\Rightarrow d\mu_2 = - \frac{n_1}{n_2} d\mu_1$$

if μ_1 increases then

μ_2 must decrease $\rightarrow d\mu_2 \rightarrow \ominus$

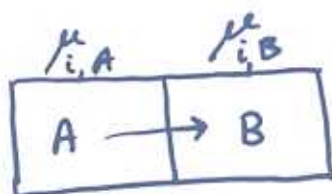
$d\mu_1 \rightarrow \oplus$

Properties of chemical potential

1. For n moles: $G = G^\circ + nRT \ln \frac{P}{P^\circ}$
(Ideal gas)

$$\Rightarrow \mu = \mu^\circ + RT \ln \frac{P}{P^\circ} \quad (\text{per mole})$$

2. Transfer of matter



2-phase system

transfer of a small fraction of component i (dn_i) from A to B

Gibbs energy change: (from Gibbs-Duhem)

$$dG^A = \mu_{i,A} (-dn_i) \text{ \& \; } dG^B = \mu_{i,B} dn_i$$

net change in Gibbs energy:

$$dG = dG^A + dG^B = (\mu_{i,B} - \mu_{i,A}) dn_i$$

Three cases:

Case-I: $\mu_{i,A} > \mu_{i,B} \Rightarrow dG < 0$: Spontaneous transfer (A to B)

Case-II: $\mu_{i,A} < \mu_{i,B} \Rightarrow dG > 0$: no transfer

Case-III: $\mu_{i,A} = \mu_{i,B} \Rightarrow dG = 0$: A and B at equilibrium

Spontaneous transfer of matter occurs from region of high μ to region of low μ ; at equilibrium μ of a component is same in every phase.

Thermodynamics of a mixture of ideal gases.

$$G = G^\circ + nRT \ln \frac{P}{P^\circ} \quad ; \quad \mu = \mu^\circ + RT \ln \frac{P}{P^\circ}$$

i -th component in an ideal gas mixture: $\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$

$$P_i = x_i P \quad (x_i \text{ is mol fraction})$$

$$\mu_i = \mu_i^\circ + RT \ln \frac{x_i P}{P^\circ} = \mu_i^\circ + RT \ln \frac{P}{P^\circ} + RT \ln x_i$$

$$\Rightarrow \boxed{\mu_i = \mu_i^* + RT \ln x_i} \quad \mu_i^* = \mu_i^\circ + RT \ln \frac{P}{P^\circ}$$

ch. potential of pure gas i under same pressure P .

$$\text{as } x_i < 1 \quad ; \quad \mu_i < \mu_i^*$$

ch. pot of gas i in the mixture $<$ ch. pot. of pure gas i at a given T and P .

Gibbs energy for the mixture:

$$G = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N n_i \mu_i^* + RT \sum_{i=1}^N n_i \ln x_i = G^* + RT \sum_{i=1}^N n_i \ln x_i$$

$G^* \rightarrow$ pure state Gibbs energy

$$\Delta G_{\text{mix}} = G - G^* = RT \sum_{i=1}^N n_i \ln x_i = nRT \sum_{i=1}^N x_i \ln x_i$$

$$\Delta S_{\text{mix}} = - \left[\frac{\partial (\Delta G_{\text{mix}})}{\partial T} \right]_{P, N} = -nR \sum_{i=1}^N x_i \ln x_i$$

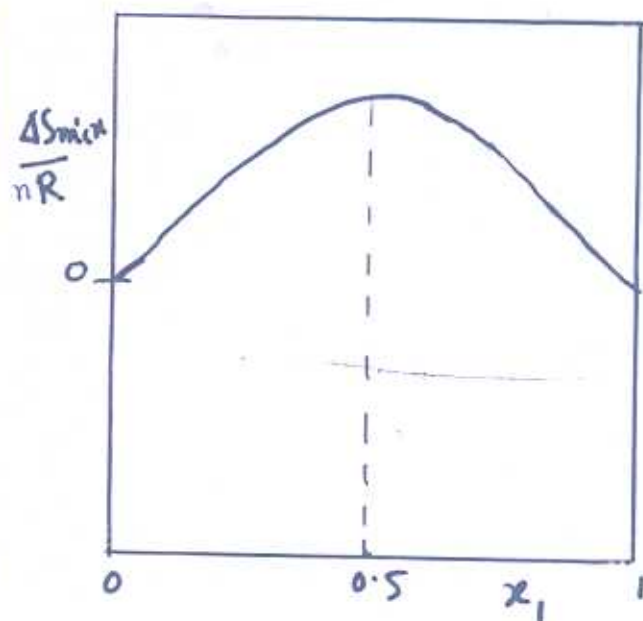
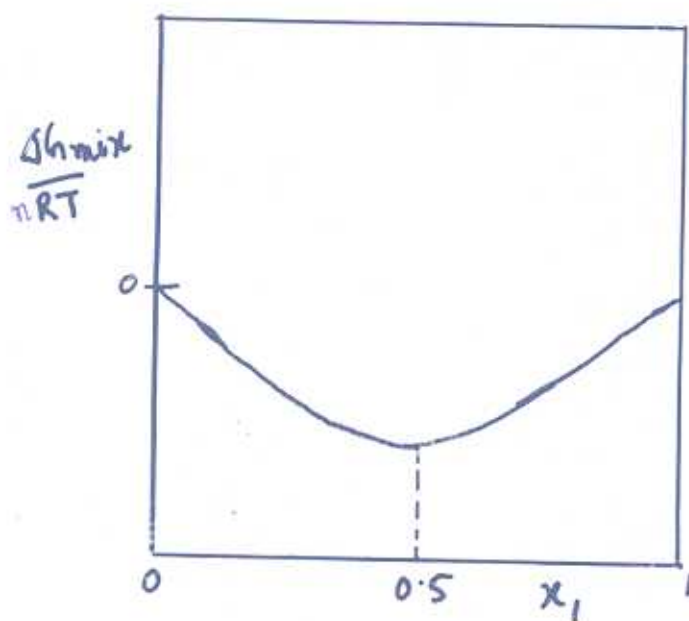
$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = 0$$

As, $x_i < 1$; $\ln x_i < 0$

$\Rightarrow \underline{\Delta G_{mix} < 0}$; similarly, $\underline{\Delta S_{mix} > 0}$

Mixing of gases at constant T and P is a spontaneous process.

Mixing of two ideal gases



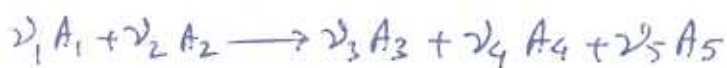
Greatest Gibbs energy change on mixing:

$$\frac{d(\Delta G_{mix})}{dx_1} = 0 \Rightarrow \text{at } \boxed{x_1 = x_2 = 0.5}$$

~~ΔG_{mix}~~

Chemical Equilibrium

A chemical reaction is an example of a mixture of different components (reactants & products), whose quantities vary.



In general, $\sum_{i=1}^N \nu_i A_i = 0$; $\nu_i < 0$ (reactants) $\nu_i > 0$ (products)

assumptions: 1) single reaction in a single phase
2) At constant T and P

As reaction advances, change in Gibbs energy:

$$dG_{P,T} = \sum_{i=1}^N \mu_i dn_i; \quad dn_i = \text{change in the amount (moles) of } i\text{-th species}$$

If the reaction advances by ξ moles (advancement of the reaction)
then, no. of moles of i -th species at any time:

$$n_i = n_i^0 + \nu_i \xi \quad (n_i^0 = \text{no. of moles of } i\text{-th species at start})$$

$$\Rightarrow dn_i = \nu_i d\xi$$

$$dG_{P,T} = \sum_{i=1}^N \mu_i dn_i = \left(\sum_{i=1}^N \mu_i \nu_i \right) d\xi \Rightarrow \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta G_r = \sum_{i=1}^N \nu_i \mu_i$$

$\Delta G_r \rightarrow$ reaction Gibbs energy \rightarrow change in G when ξ changes by 1 mole

Three cases:

- I. $\Delta G_r < 0$: forward reaction is spontaneous
- II. $\Delta G_r > 0$: backward " " "
- III. $\Delta G_r = 0$: chemical equilibrium

Condition of equilibrium: $\Delta G_{r,eq} = \left(\sum_{i=1}^N \nu_i \mu_i \right)_{eq} = 0$ Applies to all chemical equilibria

Consider a general reaction:



Reaction Gibbs energy: $\Delta G_r = \sum_{i=1}^N \nu_i \mu_i$

where, $\mu_i = \mu_i^\circ + RT \ln a_i$

$$\Delta G_r = \gamma \mu_C + \delta \mu_D - \alpha \mu_A - \beta \mu_B$$

$$= \underbrace{(\gamma \mu_C^\circ + \delta \mu_D^\circ - \alpha \mu_A^\circ - \beta \mu_B^\circ)}_{\Delta G_r^\circ} + RT \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta}$$

At equilibrium: $\Delta G_r = 0$

$$\Rightarrow \Delta G_r^\circ = -RT \ln \left(\frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta} \right)_{eq} = -RT \ln K_a$$

$$\boxed{\Delta G_r^\circ = -RT \ln K_a}$$

The standard reaction Gibbs energy is related to K_a . Valid for any system.

For ideal gases; $a_i = P_i$

$$K_p = \frac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta} \quad \text{and} \quad \boxed{\Delta G_r^\circ = -RT \ln K_p}$$

For ideal solution; $a_i = C_i$

$$K_c = \frac{C_C^\gamma C_D^\delta}{C_A^\alpha C_B^\beta} \quad \text{and} \quad \boxed{\Delta G_r^\circ = -RT \ln K_c}$$

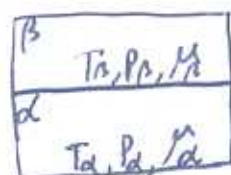
Phase Equilibrium

Phase: Part of a system with uniform composition and physical properties, separated from other parts of the system by boundary surface

e.g. water/ice \rightarrow Two phases of one component

When two phases are in equilibrium:

(i) $\underline{T_\alpha = T_\beta}$; (ii) $\underline{P_\alpha = P_\beta}$; (iii) $\underline{\mu_\alpha = \mu_\beta}$



Phase stability of a pure substance

• dependence on T:

When a solid is heated at constant P:

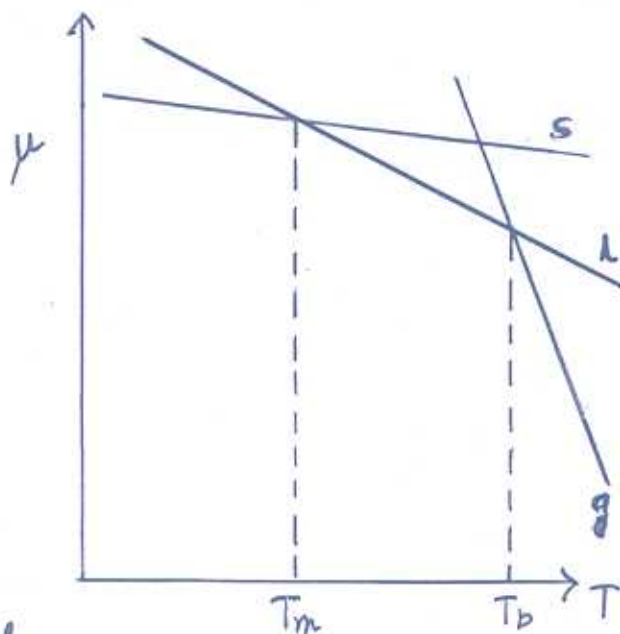
solid \rightarrow liquid \rightarrow gas

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S} \quad (\text{molar entropy})$$

$(\because d\mu = \bar{V}dP - \bar{S}dT)$

\bar{S} is positive ; slope is negative

As $\bar{S}_g \gg \bar{S}_l > \bar{S}_s \rightarrow$ slope is most negative for gas



\rightarrow The phase with lowest μ value is the most stable phase at a particular T and P.

\rightarrow If two phases of a single component have same μ value at a given T and P ; then those phases coexist at equilibrium at that T and P.

when, $T = T_m \Rightarrow \mu_s = \mu_l$: coexistence of solid and liquid phases

$T = T_b \Rightarrow \mu_l = \mu_g$: coexistence of liquid and gas phases

when, $T < T_m$; μ_s is lowest : stable solid phase

$T_m < T < T_b$; μ_l is lowest : stable liquid phase

$T > T_b$; μ_g is lowest : stable gas phase

• dependence on P

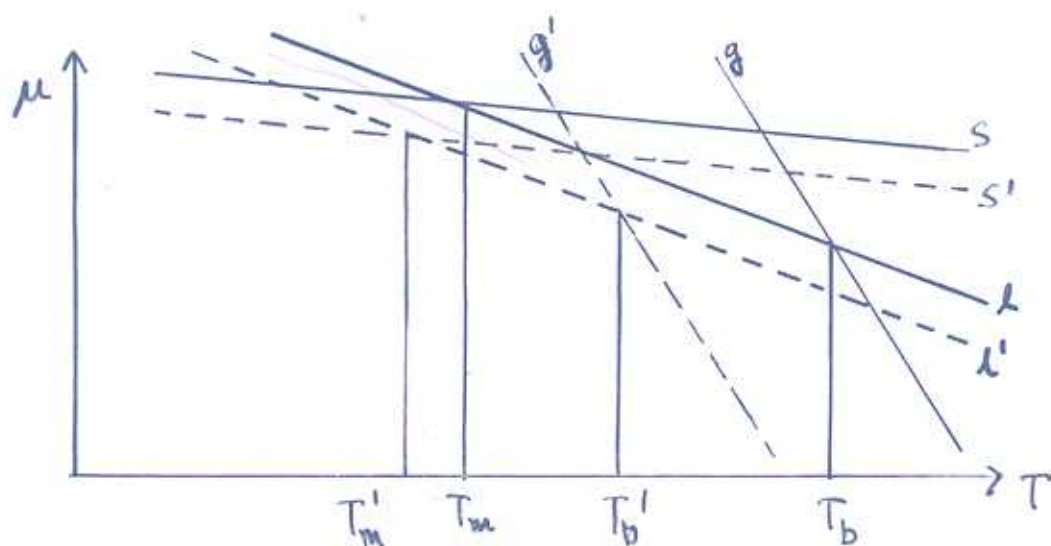
$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} \text{ (molar volume)} \quad (\because d\mu = \bar{V}dP - \bar{S}dT)$$

\bar{V} is positive $\Rightarrow \mu$ decreases as P is decreased at constant T

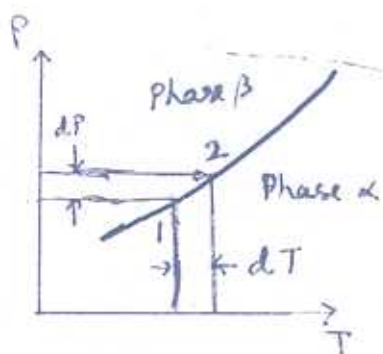
Effect of decreasing P:

Melting : $s \leftrightarrow l$ $\begin{cases} \bar{V}_l > \bar{V}_s : \text{decrease in } T_m \\ \bar{V}_l < \bar{V}_s : \text{increase in } T_m \end{cases}$

Vaporization : $l \leftrightarrow g$; $\bar{V}_g \gg \bar{V}_l$: large decrease in T_b



Clapeyron Equation



Coexistence curve

1 component system with 2 phases in eqm.

$$\alpha \rightleftharpoons \beta \quad ; \quad \mu_{\alpha} = \mu_{\beta}$$

If T changed by dT the P has to be changed by dP ; so that chemical potentials remain equal \Rightarrow Two phases will coexist, but the equilibrium is shifted to new P, T values.

At point 1: $\mu_{\alpha} = \mu_{\beta}$

At point 2: $\mu_{\alpha} + d\mu_{\alpha} = \mu_{\beta} + d\mu_{\beta} \Rightarrow \boxed{d\mu_{\alpha} = d\mu_{\beta}}$

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

So, $\bar{V}_{\alpha}dP - \bar{S}_{\alpha}dT = \bar{V}_{\beta}dP - \bar{S}_{\beta}dT$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\bar{S}_{\beta} - \bar{S}_{\alpha}}{\bar{V}_{\beta} - \bar{V}_{\alpha}} = \frac{\Delta \bar{S}}{\Delta \bar{V}}}$$

$$\Delta \bar{S} = \frac{\Delta \bar{H}}{T} \quad \Delta \bar{H} = \text{molar enthalpy change at } T$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T \Delta \bar{V}}}$$

Clapeyron equation

[can be applied for any phase equilibrium of a pure substance]

Sign of $\frac{dP}{dT}$ depends on signs of $\Delta \bar{H}$ and $\Delta \bar{V}$

(i) vaporization: $\Delta \bar{H}$ is +ve and $\Delta \bar{V}$ is +ve \rightarrow with increase in P , boiling temp. increases

(ii) melting: a) $\Delta \bar{H}$ is +ve and $\Delta \bar{V}$ is +ve \rightarrow with increase in P , melting temp increases (most cases)

b) $\Delta \bar{H}$ is +ve and $\Delta \bar{V}$ is -ve \rightarrow melting temp decreases at high pressure (e.g. ice)

For vaporization (liquid \rightleftharpoons vapor) and sublimation (solid \rightleftharpoons vapor)
Clausius-simplified Clapeyron equation.

assumption: (1) the vapor behaves ideally

(2) molar volume of the gas is much larger

$$\Rightarrow \Delta \bar{V} = (\bar{V}_g - \bar{V}_l) \approx \bar{V}_g \quad (\bar{V}_g \gg \bar{V}_l)$$

$$= \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T \bar{V}_g} = \frac{P \Delta H_{\text{vap}}}{RT^2}$$

$$\boxed{\frac{d \ln P}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}}$$

Clausius-Clapeyron equation

$$\int_{P_1}^{P_2} d \ln P = \frac{\Delta H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \left[\text{assume that } \Delta H_{\text{vap}} \text{ remains constant between } T_1 \text{ and } T_2 \right]$$

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

(valid for vaporization and sublimation)