

2nd law - Isolated systems strive for an equilibrium state that is characterised by maximisation in entropy.

Equilibrium $\Rightarrow dS = 0, S = S_{\max}$

$S \rightarrow$ Extensive quantity

$$dU = dQ_{\text{rev}} + dW_{\text{rev}} = TdS - pdV$$

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

Journey to minimum energy (non-isolated system)

Journey to maximum entropy (Isolated system)

U_1, S_1	U_2, S_2
Q_1, W_1	Q_2, W_2
①	②

Isolated

① Remove a certain work
 $dW_1 < 0$ from ①

→ Create a difference in P.E..

① does not exchange heat with surroundings

$$\Rightarrow dQ_1 = TdS_1 = 0 \Leftrightarrow S_1 = \text{const.}$$

② Hand over ϵdW_1 as heat
 $(1-\epsilon)dW_1$ as work } to ①

$$dW_2 = -dU_1$$

$$dU_2 = dQ_2 + dW_2 = -dW_1 > 0$$

$$dQ_2 = -\epsilon dW_1 > 0 \quad dW_2 = -(1-\epsilon) dW_1$$

If process happens at constant T ,

$$dQ_2 = TdS_2 > 0 \Rightarrow dS_2 > 0$$

$$\rightarrow d(S_1 + S_2) > 0$$

$$dU_1 = dW_1 < 0$$

Conclusion \Rightarrow A non-isolated system with constant entropy ($dS = 0$) heads for a state of minimum energy.

If $E = 0$, $dW_1 = -dW_2$
then $S_1, S_2 = \text{const.}$

\Rightarrow process is reversible

$V, S \Rightarrow$ central thermodynamic state quantity

If we know $U(S, V, \dots)$,

$$dU = TdS - PdV + \dots$$

\Rightarrow Thermodynamic Potential

$$T = \left. \frac{\partial U}{\partial S} \right|_{V, \dots}, \quad -P = \left. \frac{\partial U}{\partial V} \right|_{S, \dots}$$

If we know, $S = S(U, V, \dots)$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV + \dots$$

$$\frac{1}{T} = \left. \frac{\partial S}{\partial U} \right|_{V, \dots}, \quad \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{U, \dots}$$

Mechanics

P.E. \rightarrow Info about most stable state

Difference in P.E. \rightarrow drives a process

Thermodynamics

S \rightarrow Info about most stable state

Difference in P.E. \rightarrow drives a process

$U(S, V, \dots)$

Transformation $\Rightarrow T = \left. \frac{\partial U}{\partial S} \right|_{V, \dots}$

↓
Legendre transformation

$$\Rightarrow L(q_v, \dot{q}_v)$$

$$p_v = \frac{\partial L}{\partial \dot{q}_v} \rightarrow \text{Generalised momentum}$$

$$H(p_v, q_v) = \sum_v \dot{q}_v p_v - L(q_v, \dot{q}_v)$$

$$dH = \sum_v \left\{ p_v d\dot{q}_v + q_v dp_v - \frac{\partial L}{\partial q_v} d\dot{q}_v - \frac{\partial L}{\partial \dot{q}_v} dq_v \right\}$$

$$dH = \sum_v \left\{ q_v dp_v - \frac{\partial L}{\partial q_v} dq_v \right\}$$

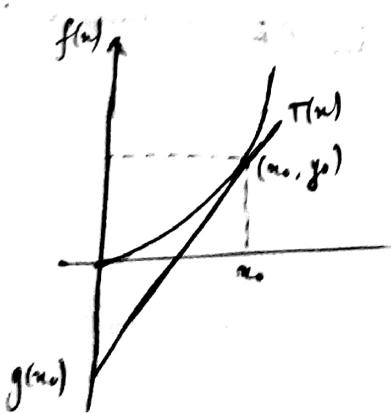
$$H = H(p_v, q_v)$$

$$L(q_v, \dot{q}_v) \rightarrow H(q_v, p_v)$$

General Legendre Transformation

$$df = \frac{\partial f}{\partial x} dx \quad f = f(x) \\ = p(x) \cdot dx \quad p(x) = f'(x)$$

Legendre Transformation \Rightarrow Find a function $g(p)$ of the new variables $p(x) = f'(x)$ which is equivalent to $f(x) \Rightarrow$ one should be able to calculate $g(p)$ from $f(x)$ — unambiguously & vice-versa



$$T(x) = f(x_0) + f'(x_0)(x - x_0)$$

Intersection with \equiv y-axis

$$g = T(0)$$

$$g(x_0) = f(x_0) - x_0 f'(x_0)$$

For an arbitrary point x ,

$$g(x) = f - xp \quad p = f'(x)$$

Legendre Transformation $g = f - xp$

of x

$$dg = df - xdp - pdx \quad (pdx = df)$$

$$dg = -x dp$$

$$\Rightarrow g = g(p)$$

Calculation of $g(p) \Rightarrow g = f(x) - xf'(x)$

eliminate x with $p = f'(x)$

if there exists the "inverse" $(f')^{-1}$

$$\cancel{x} = (f')^{-1} p$$

$$\cancel{g(p)} = f[(f')^{-1} p] - (f')^{-1}(p) \cdot p$$

$$f(x) = x^2 \quad f'(x) = p = 2x = \cancel{2x}$$

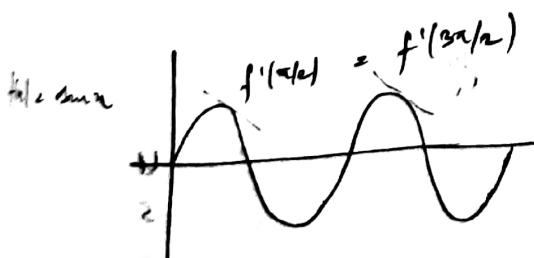
Example $L.T. \Rightarrow g = x^2 - px \quad (f')^{-1}(p) = x = p/2$

$$g(p) = f(\frac{1}{2}p) - (\frac{1}{2}p) \cdot p$$

$$= \frac{p^2}{4} - \frac{p^2}{2} = \frac{-p^2}{4}$$

Example $f(x) = x^n \quad f'(x) = p = 1$

$$L.T. \Rightarrow g(x) = x - p^x = 0$$



slope $f'(x)$ has to be monotonic

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

$$df = p(x, y) dx + q(x, y) dy$$

$$p(x, y) = \frac{\partial f}{\partial x} \Big|_y \quad \text{and} \quad q(x, y) = \frac{\partial f}{\partial y} \Big|_x$$

$$x \rightarrow p$$

$$g(x, y) = f(x, y) - xp$$

$$\begin{aligned} dy &= df - p dx - x dp \\ &= -x dp + q dy \end{aligned}$$

$$g = g(p, y)$$

$p(x, y) = \frac{\partial f}{\partial x} \Big|_y$ has to be invertible

for each value of y .

$$g = f - xp$$

$$g = g(p, y).$$

~~$$h(p, q) = f(x, y) - px - qy$$~~

$$u(p, q) = f(x, y) - px - qy$$

Helmholtz Free Energy

$$U(s, v, \dots)$$

$$\rightarrow T = \frac{\partial U}{\partial S} \Big|_{v, \dots}$$

$$\begin{aligned} f &\rightarrow U \\ x &\rightarrow s \\ p &\rightarrow T \end{aligned}$$

$$L.T. \rightarrow F = U - TS$$

$F \Rightarrow$ Helmholtz Free Energy

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= (TdS - PdV) - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

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

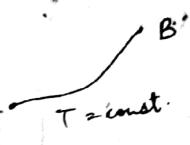
Equations of State \Rightarrow

$$\begin{aligned} -S &= \frac{\partial F}{\partial T} \Big|_V \\ -P &= \frac{\partial F}{\partial V} \Big|_T \end{aligned}$$

Importance of Free Energy

In an isothermal transformation
Change in $F =$ Max possible work done by
the system

Proof \Rightarrow



$$\text{2nd Law} \Rightarrow \int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

$$\Delta Q \leq T \Delta S$$

$$\Delta Q = \int_A^B dQ$$

W.D. by system, $\Delta W = \Delta U - \Delta Q$

$$\Delta W - \Delta U = -\Delta Q \geq -T \Delta S$$

~~$\Delta W - \Delta U \geq -T \Delta S$~~

$$\Delta W \geq \Delta U - T \Delta S = \Delta F$$
$$\Delta F \leq \Delta W'$$

Reversible $\Rightarrow \Delta F = \Delta W$

Mechanically isolated system $\Rightarrow \Delta W = 0$
 $\therefore \Delta F \leq 0$

\Rightarrow Journey towards equilibrium for mechanically isolated system
at constant temperature is accompanied by
minimizing free \Leftrightarrow energy

For spontaneous process,

$$\Delta F = \Delta U - T\Delta S < 0$$

For ΔF to minimize, ~~ΔU has to minimize~~,

ΔU has to minimize + ΔS has to maximize.

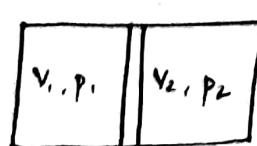
$F(T, V) \rightarrow$ contains full info about the system
while $U(T, V)$ does not but $U(S, V)$ does.

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

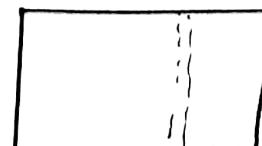
$$dF(T, V) = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$\hookrightarrow S$ $\hookrightarrow P$

Principle of minimization of
energy



\rightarrow



Gas in a cylinder
at const. T ,
Release the piston &
let it slide

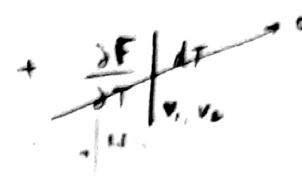
What is eqm position?

Eqm position is when F is minimum.

When F is minimum i.e. equilibrium, $dF = 0$

$$F = F(V_1, V_2, T)$$

$$dF = \frac{\partial F}{\partial V_1} \Big|_{V_2, T} dV_1 + \frac{\partial F}{\partial V_2} \Big|_{V_1, T} dV_2$$



$$dF = 0 \Rightarrow \left[\left(\frac{\partial F}{\partial V_1} \right)_T - \left(\frac{\partial F}{\partial V_2} \right)_T \right] dV_1 = 0$$

$$V_1 + V_2 = \text{const}$$

$$dV_1 = -dV_2$$

$$\left(\frac{\partial F}{\partial V_1} \right)_T = \left(\frac{\partial F}{\partial V_2} \right)_T$$

↓
 P_1 P_2

Enthalpy

Understand chemical reactions

¶

happen under influence of atmospheric pressure

⇒ Look for a potential that depends on P , and not V .

$$U = U(s, v) \quad P = -\frac{\partial U}{\partial V} \Big|_S$$

$$L.T. \rightarrow H = U + PV \quad H \Rightarrow \text{enthalpy}$$

$$dH = dU + PdV + VdP$$
$$= TdS + VdP$$

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

$$T = \frac{\partial H}{\partial S} \Big|_P \quad V = \frac{\partial H}{\partial P} \Big|_S$$

Interpretation \rightarrow For isobaric change of state, change in H
 \rightarrow Amount of heat exchanged with surroundings
+ utilizable work other than volume work
against constant P .

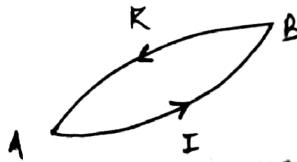
$$dH|_P = dU|_P + P dV|_P + dW_{\text{other}}|_P$$

$$= dQ|_P + dW_{\text{other}}|_P$$

if $dW_{\text{other}}|_P = 0 \Rightarrow dH|_P = dQ|_P$

if it is isobaric & adiabatic $dH|_P = dW_{\text{other}}|_P$

Note - $dW_{\text{rel. work}} = -P dV \Rightarrow$ Reversible process



$$\int \frac{dQ}{T} \leq 0$$

$$\int_{I-A}^B \frac{dQ_{\text{in}}}{T} + \int_{R-B}^A \frac{dQ_{\text{rev}}}{T} < 0$$

$$\Rightarrow \int_{I-A}^{dQ_{\text{in}}} \frac{dQ_{\text{in}}}{T} - \int_{R-A}^{dQ_{\text{rev}}} \frac{dQ_{\text{rev}}}{T} < 0$$

$$\Rightarrow dQ_{\text{in}} < dQ_{\text{rev.}} = T dS$$

$$\therefore dW_{\text{in.}} > dW_{\text{rev.}} = -P dV$$

For adiabatic isobaric process

$$\Delta H \leq \Delta W_{\text{in.}}$$

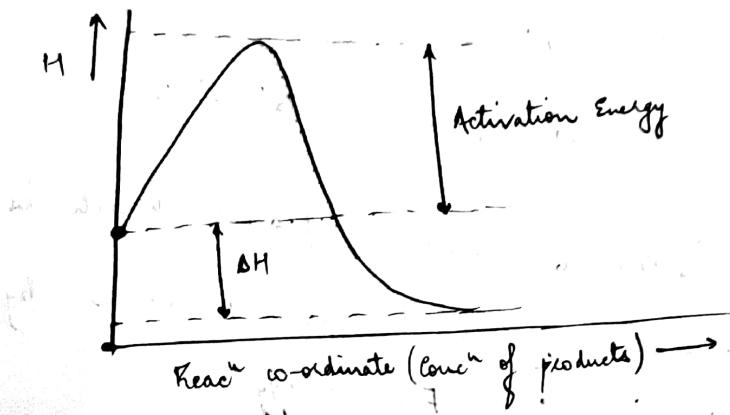
other

if $\Delta W_{\text{in.}} = 0 \Rightarrow \Delta H \leq 0$

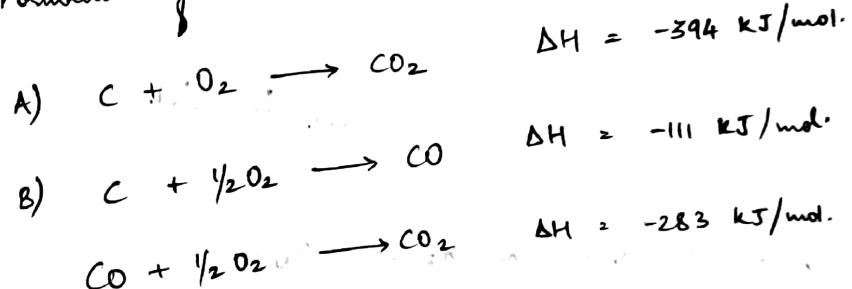
In an adiabatic, isobaric process, if the system spontaneously changes its thermodynamic state, it does so by minimizing its enthalpy.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If $\Delta H < 0 \rightarrow \text{React}^n \text{ happens spontaneously}$



Example \rightarrow Formation of CO_2



Gibbs Free Energy / Free Enthalpy

$$U(s, v) \quad U \quad G_f = U - TS + PV$$

$$\downarrow T \quad P \quad dG_f = dU - Tds - SdT + pdv + Vdp$$

$$= -SdT + Vdp$$

$$G_f = G_f(T, P)$$

$$S = \left. \frac{\partial G_f}{\partial T} \right|_P, \quad V = \left. \frac{\partial G_f}{\partial P} \right|_T$$

$$G_f = F + PV$$

$$\Delta G_f = \Delta F + P\Delta V + V\Delta P$$

$$\text{constant } T, P \text{ process} \rightarrow \Delta G = \Delta F + P\Delta V$$

$$\Delta F \leq \Delta W$$

$$\Delta F = \Delta W_{\text{volume}} - \Delta W_{\text{other}} \leq 0$$

$$(\Delta F + P\Delta V) - \Delta W_{\text{other}} \leq 0$$

$$\Delta G \leq \Delta W_{\text{other}}$$

$$\text{Reversible} \Rightarrow \Delta G = \Delta W_{\text{other}}$$

$$\text{General process where } \Delta W_{\text{other}} = 0, \Delta G \leq 0$$

\Rightarrow In an isothermal, isobaric process, which is spontaneous, system reaches equilibrium by minimizing Gibbs Free Energy

Chemical Potential

$$V = V(V, S, n_1, n_2, \dots, n_N)$$

$\{n_i\}$ \rightarrow set of moles for N different systems

~~$\partial V / \partial n_i$~~ $\equiv v_i + \dots$

$$dV(V, S, n) = \frac{\partial V}{\partial V} \Bigg|_{S, n} dv + \frac{\partial V}{\partial S} \Bigg|_{V, n} ds + \frac{\partial V}{\partial n_1} \Bigg|_{V, S, n'} dn_1 + \dots + \frac{\partial V}{\partial n_N} \Bigg|_{V, S, n'} dn_N$$

$$n \rightarrow \{n_1, n_2, \dots, n_N\}$$

n' \rightarrow All n 's except the one in partial derivative

$$\left. \frac{\partial U}{\partial V} \right|_{S, n} = -P$$

$$\left. \frac{\partial U}{\partial S} \right|_{V, n} = T$$

$$\boxed{\left. \frac{\partial U}{\partial n_j} \right|_{V, S, n'} = \mu_j} \quad \Rightarrow \text{chemical potential of the } j\text{-th substance}$$

$$dU(V, S, n) = -P dV + T dS + \sum_{j=1}^N \mu_j dn_j$$

~~$dW_c = \sum_j \mu_j dn_j$~~ → Reversible chemical work

 Work done to change the mole no.
 of j^{th} system from $n_j \rightarrow n_j + dn_j$

$\mu_j \rightarrow$ Energy required to add a mole of
 j^{th} system into the big system

$\mu \rightarrow$ Intensive $n \rightarrow$ Extensive

$$\mu_j = \mu_j(V, S, n')$$

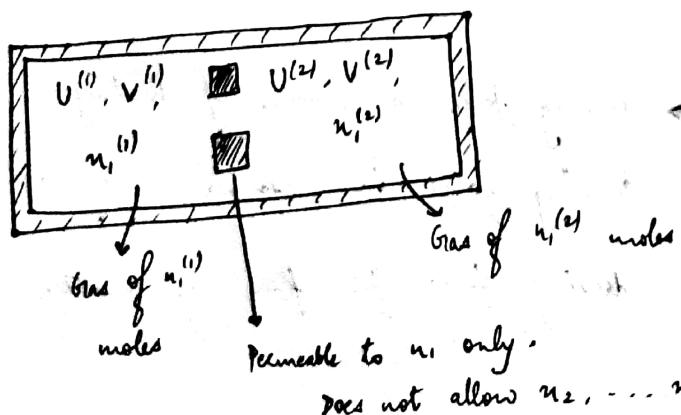
~~$dF(V, T, n) = -P dV - S dT + \sum_j \mu_j dn_j$~~

$$dH(P, S, n) = V dP + T dS + \sum_j \mu_j dn_j$$

$$dG(P, T, n) = V dP - S dT + \sum_j \mu_j dn_j$$

Situations where P, T are held constant

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{P, T, n'}$$



~~Ex~~

Change in internal energy of entire system = dU
 $= TdS + \sum_{j=1}^N ll_i du_i$

$$du_j = 0 \\ j = 2, \dots, N$$

$$\Rightarrow dS = \frac{dU}{T} - \frac{ll_1}{T} du_1$$

$$dS = ds^{(1)} + ds^{(2)} \\ = \frac{dU^{(1)}}{T^{(1)}} + \frac{dU^{(2)}}{T^{(2)}} - \frac{ll_1^{(1)} du_1^{(1)}}{T^{(1)}} - \frac{ll_1^{(2)} du_1^{(2)}}{T^{(2)}}$$

$$du_1 = du_1^{(1)} + du_1^{(2)} = 0$$

$$du_1^{(1)} = -du_1^{(2)}$$

$$dU^{(1)} = -dU^{(2)}$$

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} - \left(\frac{ll_1^{(1)}}{T^{(1)}} - \frac{ll_1^{(2)}}{T^{(2)}} \right) du_1^{(1)}$$

~~Ex~~ Two chambers are in equilibrium

$$\Rightarrow dS = 0$$

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}$$

$$\frac{Tll_1^{(1)}}{T^{(1)}} = \frac{ll_1^{(2)}}{T^{(2)}}$$

$$\therefore T^{(1)} = T^{(2)} \quad \& \quad ll_1^{(1)} = ll_1^{(2)}$$

$T \rightarrow$ driving force for process of heating

$P \rightarrow$ driving force for performance of mechanical work

$ll \rightarrow$ driving force for flow of matter

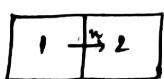
What if the system not in equilibrium & comes to equilibrium through an irreversible process?

$$\rightarrow dS > 0$$

$$\text{Consider } T^{(1)} = T^{(2)} = T$$

$$\frac{u_i^{(2)} - u_i^{(1)}}{T} d n_i^{(1)} > 0$$

if $u_i^{(1)} > u_i^{(2)} \Rightarrow d n_i < 0$ & vice-versa



$u \rightarrow \text{Thermodynamic variable}$

Grand Potential \Rightarrow

$$V = V(S, V, u)$$

$$\Omega = V - TS - \mu n$$

$$d\Omega = dV - TdS - SdT - \mu dn - \nu d\mu$$

$$d\Omega = -SdT - \mu dn - \nu d\mu$$

$$\Omega = \Omega(T, V, u)$$

$$-S = \left. \frac{\partial \Omega}{\partial T} \right|_{V, \mu}, \quad -\mu = \left. \frac{\partial \Omega}{\partial V} \right|_{T, \mu}, \quad -\nu = \left. \frac{\partial \Omega}{\partial u} \right|_{T, V}$$

Interpretation of Ω

Consider an isothermal process with u fixed

Spontaneous reversible process:

$$TdS > dQ$$

$$dW + \mu dN = dV - dQ$$

$$dQ = dV - \mu dN - dW$$

$$TdS \geq dV - \mu dN - dW$$

$$dW \geq dV - \mu dN - TdS$$

$$\delta w \geq dR|_{T, u}$$

For mechanically isolated system,

$$dR \leq 0$$

Spontaneous process

Only isothermal $\rightarrow dF \leq 0$

Isothermal, isobaric $\rightarrow dG \leq 0$

Isothermal, fixed chemical potential $\rightarrow dR \leq 0$

Isobaric, adiabatic $\rightarrow dH \leq 0$

We want $V(S, V, n)$ to transform to $\psi(T, P, u)$

$$\psi = V - TdS + Pv - un$$

$$dV = TdS - pdV + undn$$

$$\cancel{V}(\alpha S, \alpha V, \alpha n) = \alpha V(S, V, n)$$

$$\text{Let } \alpha = 1 + \varepsilon, \varepsilon \ll 1$$

$$V[(1+\varepsilon)S, (1+\varepsilon)V, (1+\varepsilon)n] = V + \frac{\partial V}{\partial S}(\varepsilon S) + \frac{\partial V}{\partial V}(\varepsilon V) + \frac{\partial V}{\partial n}(\varepsilon n)$$

$$V + \varepsilon V = \cancel{V} + T(\varepsilon S) + -p(\varepsilon V) + u(\varepsilon n)$$

$$\cancel{V} = TS - PV + un$$

$$dV = TdS + SdT - pdV - Vdp + undn + nndl$$

$$\text{Now, } dV = TdS - pdV + undn$$

$$\therefore \boxed{SdT - pdV + undn = 0}$$

\Rightarrow Gibbs-Duhem relation

$$\Psi = U - TS + PV - UW$$

$$\Rightarrow \Psi = 0$$

Exact Differentials

Theorem 1 \Rightarrow Given a differential of the form

$df = g(A, B) dA + h(A, B) dB$
then condition ~~to be exact~~ that df be exact is

$$\Leftrightarrow \frac{\partial g}{\partial B} = \frac{\partial h}{\partial A}$$

Theorem 2 \Rightarrow If $f(A, B)$ is a totally differentiable function
then

$$\frac{\partial^2 f}{\partial A \partial B} = \frac{\partial^2 f}{\partial B \partial A}$$

Maxwell Relations

$$dU = TdS - PdV + \mu dW$$

$$= \left. \frac{\partial U}{\partial S} \right|_{V, W} dS + \left. \frac{\partial U}{\partial V} \right|_{S, W} dV + \left. \frac{\partial U}{\partial W} \right|_{S, V} dW$$

$$\frac{\partial}{\partial V} \left(\left. \frac{\partial U}{\partial S} \right|_{V, W} \right)_{S, W} = \frac{\partial}{\partial S} \left(\left. \frac{\partial U}{\partial V} \right|_{S, W} \right)_{V, W}$$

$$U \rightarrow \boxed{\begin{aligned} \left. \frac{-\partial P}{\partial S} \right|_{V, W} &= \left. \frac{\partial T}{\partial V} \right|_{S, W} \\ \left. \frac{\partial T}{\partial W} \right|_{S, V} &\quad \left. \frac{\partial \mu}{\partial S} \right|_{V, W} \\ \left. \frac{-\partial \mu}{\partial W} \right|_{S, V} &= \left. \frac{\partial \mu}{\partial V} \right|_{S, W} \end{aligned}}$$

$$dF = -SdT - pdV + Udw$$

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

$$U = -\left(\frac{\partial F}{\partial w}\right)_{T,V}$$

$$\frac{\partial}{\partial V} \left[-\left(\frac{\partial F}{\partial T}\right)_{V,w} \right]_{T,w} = \frac{\partial}{\partial T} \left[-\left(\frac{\partial F}{\partial V}\right)_{T,w} \right]_{V,w}$$

$F \rightarrow$

$\frac{\partial S}{\partial V} \Big _{T,w} = \frac{\partial p}{\partial T} \Big _{V,w}$
$-\frac{\partial S}{\partial w} \Big _{T,V} = \frac{\partial U}{\partial T} \Big _{V,w}$
$-\frac{\partial p}{\partial w} \Big _{T,V} = \frac{\partial U}{\partial V} \Big _{T,w}$

$$dH = Tds + vdp + Udw$$

$$T = \frac{\partial H}{\partial S} \Big|_{P,w}, \quad V = \frac{\partial H}{\partial P} \Big|_{S,w}$$

$$\frac{\partial}{\partial P} \left[\frac{\partial H}{\partial S} \Big|_{P,w} \right]_{S,w} = \frac{\partial}{\partial S} \left[\frac{\partial H}{\partial P} \Big|_{S,w} \right]_{P,w}$$

~~H~~ $H \rightarrow$

$\frac{\partial T}{\partial P} \Big _{S,w} = \frac{\partial V}{\partial S} \Big _{P,w}$
$\frac{\partial T}{\partial w} \Big _{S,P} = \frac{\partial U}{\partial S} \Big _{P,w}$
$\frac{\partial V}{\partial w} \Big _{S,P} = \frac{\partial U}{\partial P} \Big _{S,w}$

$\Delta H \rightarrow$

$$\frac{\partial S}{\partial P} \Big|_{T,u} = \frac{\partial U}{\partial T} \Big|_{P,u}$$

$$-\frac{\partial S}{\partial u} \Big|_{T,P} = \frac{\partial U}{\partial T} \Big|_{P,u}$$

$$\frac{\partial V}{\partial u} \Big|_{T,P} = \frac{\partial U}{\partial P} \Big|_{T,u}$$

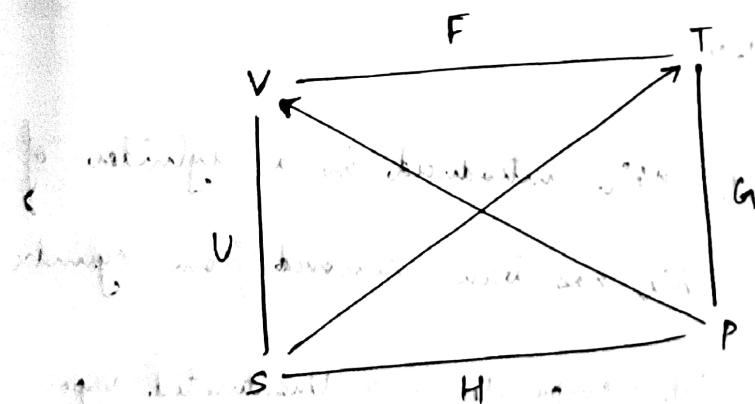
$\Delta L \rightarrow$

$$\frac{\partial S}{\partial V} \Big|_{T,u} = \frac{\partial P}{\partial T} \Big|_{V,u}$$

$$\frac{\partial S}{\partial u} \Big|_{T,V} = \frac{\partial u}{\partial T} \Big|_{V,u}$$

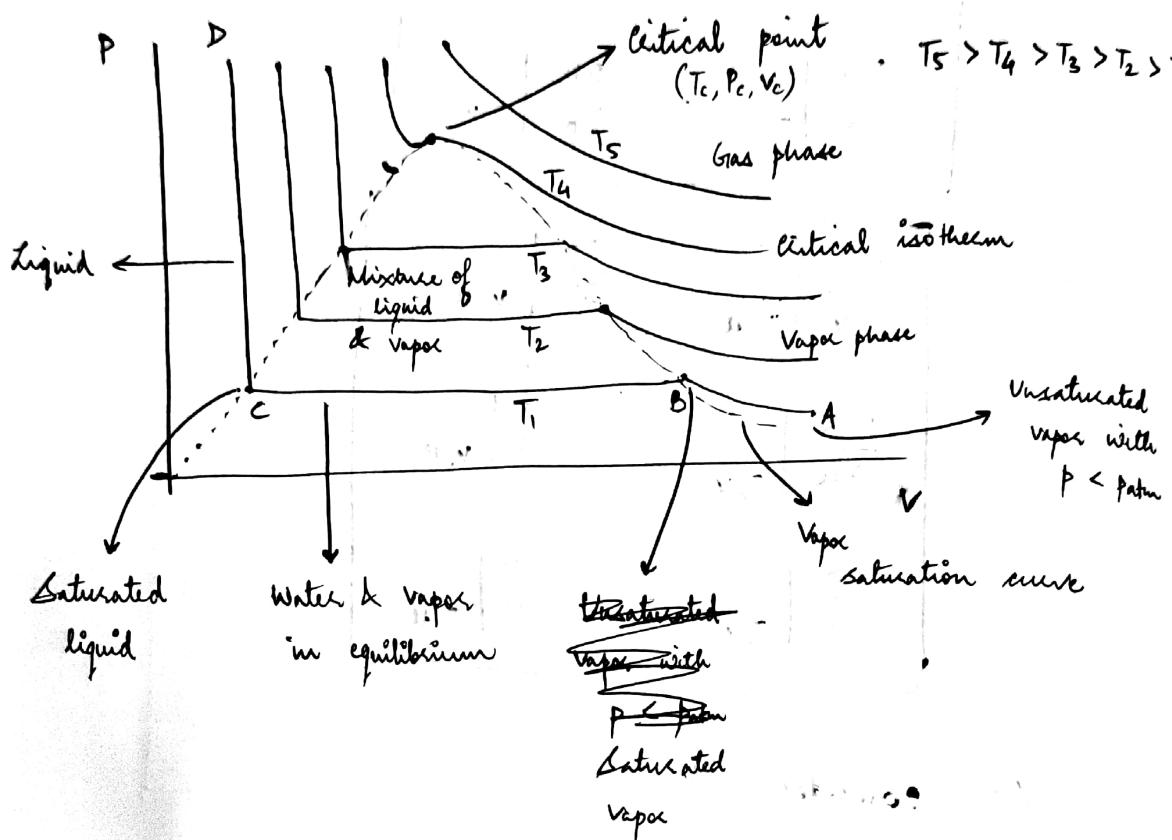
$$\frac{\partial P}{\partial u} \Big|_{T,V} = \frac{\partial u}{\partial V} \Big|_{T,u}$$

Let's consider $du = 0$



Thermodynamic rectangle

Different phase transition



Pure system H_2O

- 1 gm water at $94^\circ C$ introduced in a cylinder of 2L volume. Air has been removed from cylinder.
Water will evaporate \rightarrow Unsaturated vapor
- Compress the vapor slowly & isothermally \rightarrow P increases till it reaches a state of saturated vapor (B)
- Continue the compression \rightarrow condensation occurs
 P remains constant

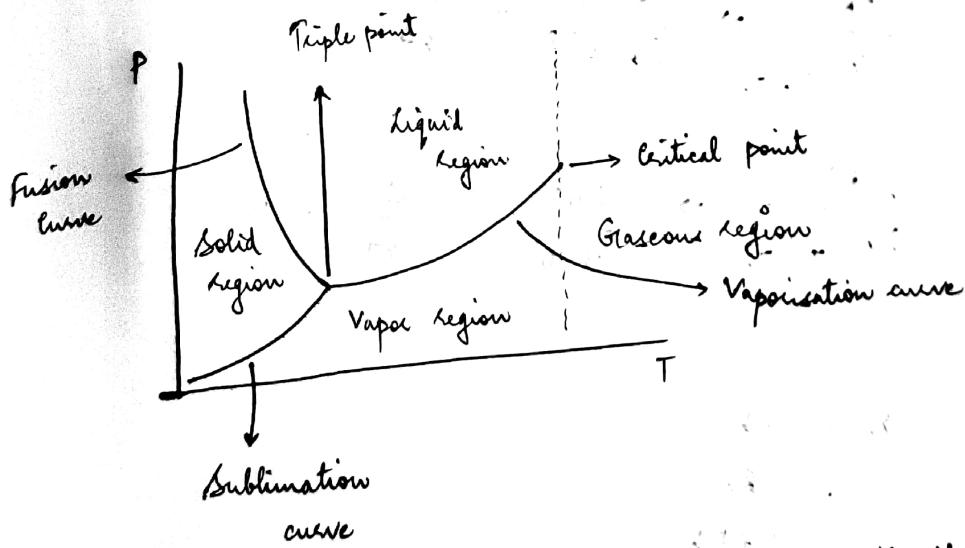
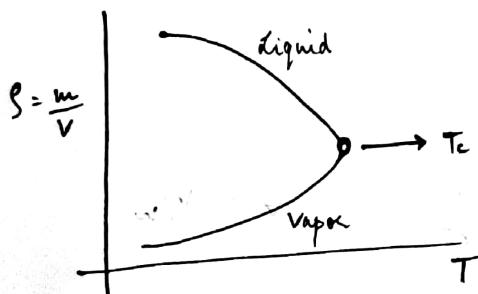
$BC \rightarrow$ Isothermal, isobaric condensation of vapor

$P \rightarrow$ vapor pressure

ABCD \rightarrow Typical isothermal of a pure substance

Critical ~~ext~~ point \rightarrow Meeting point of liquid & vapor saturation curves

Specific volume of liquid = Specific volume of vapor
of equal mass



- Compress the substance at triple point until there is no vapor left & P of the resulting mixture of liquid & solid is increased

Solid-vapor coexistence : $0 < T < T_{\text{triple}}$

Solid-liquid coexistence : ~~$T_{\text{triple}} < T < T_c$~~ $T_{\text{triple}} < T < \infty$

Liquid-vapor coexistence : $T_{\text{triple}} < T < T_c$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0$$

$T_c \Rightarrow$ point of inflection on ~~critical~~ isotherm

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

Example \Rightarrow Van der Waals gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad V = v/n$$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \Rightarrow \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0.$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0 \Rightarrow \frac{2RT}{(V-b)^3} - \frac{ab}{V^4} = 0$$

$$V_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{a}{27b^2}$$

$$\text{Van-der-Waals eqn of state} \Rightarrow \frac{RT_c}{P_c V_c} = 2.67$$

$$\text{Ideal gas} \Rightarrow \frac{RT_c}{P_c V_c} = 1$$

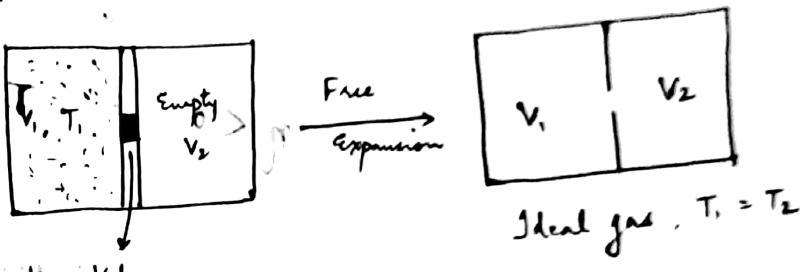
Joule - Thompson Experiment

phase transition by looking at melting of ice & vaporization of water

N_2, H_2, He

Joule - Thompson expansion
Throttling process

Free Expansion of gas



$$\Delta U = 0 \Rightarrow \Delta U_1 = -\Delta U_2$$

$$U = U(T) \rightarrow \text{Ideal gas}$$

$$\text{for non-ideal gas} \Rightarrow T_2 = T_1 + \int_{V_1}^{V_2} \eta dV$$

$$v = V/n \quad \eta = \left(\frac{\partial T}{\partial V} \right)_n \rightarrow \text{Joule Coefficient}$$

$$dU = TdS - pdV$$

$$\text{For } dU = 0 \Rightarrow T \left[\left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \right] - pdV = 0$$

$$\text{Maxwell} \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

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

$$C_V dT + \left[\left(\frac{\partial p}{\partial T} \right)_V - p \right] dV = 0$$

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

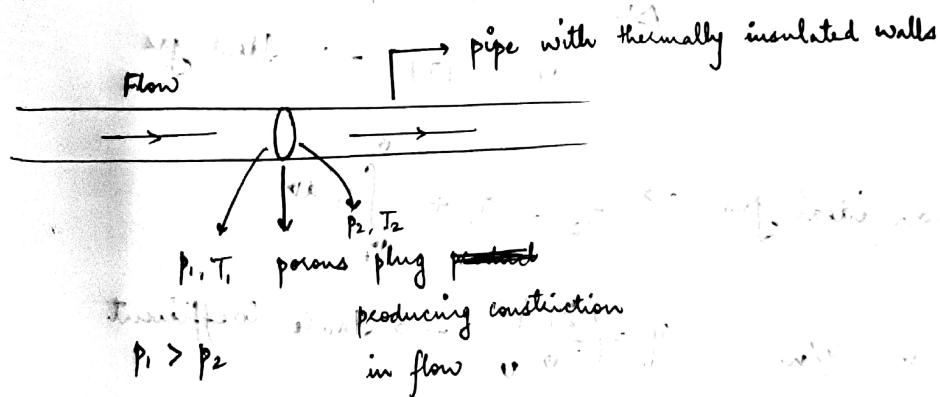
$$\eta = \frac{-\left(T \frac{\partial P}{\partial T} - P\right)}{C_V}$$

$$\text{Van-der Waal gas} \Rightarrow T \left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} = P + \frac{a}{V^2}$$

$$\eta = \frac{-a}{V^2 C_V}$$

$$\eta < 0 \Rightarrow T_2 < T_1$$

Joule - Thompson Throttling



consider a gas of mass m

In the process, $\Delta U = U_2(T_2, P_2) - U_1(T_1, P_1)$

Work done by gas $\Delta W = P_2 V_2 - P_1 V_1$

$$\Delta Q = Q$$

$$(U_2 + P_2 V_2) - (U_1 + P_1 V_1) = 0$$

$$H_2 = H_1$$

$$\text{Ideal gas} \Rightarrow H = U + PV$$

$$= U(T) + nRT$$

$$H = H(T) \Rightarrow T_2 = T_1$$

$$\text{Real gas} \Rightarrow H \neq H(T) \Rightarrow T_2 \neq T_1$$

$$T_2 - T_1 = \int_{P_1}^{P_2} u dp \quad u = \left(\frac{\partial T}{\partial p} \right)_H$$

$u \Rightarrow$ Joule-Thompson coefficient

Since, $\Delta p < 0, \Delta T < 0$ if $u > 0$

$$dH = Tds + Vdp$$

Throttling $\Rightarrow dH = 0$

$$T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dp \right] + Vdp = 0$$

$$\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \quad C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dp = 0$$

$$\Rightarrow u = \left(\frac{\partial T}{\partial P} \right)_H = \left(\frac{\partial T}{\partial P} \right)_H$$

$$u = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - V}{C_P}$$

$$v = V/n$$

Molar Volume

$$u = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - v}{C_P}$$

Van-der-Waal gas

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27kb}$$

$$\frac{P}{P_c} = \frac{P' + \frac{RT \times 27b^2}{a(v-b)} - \frac{27b^2}{v^2}}{1}$$

$$P' = \frac{(8/3)T'}{v' - 1/3} - \frac{3}{v'^2} \quad v' = v/v_c$$

$$T' = T/T_c$$

$$P' = P/P_c$$

$$\alpha = \frac{v_c}{c_p} \alpha'$$

$$\alpha' = T' \left(\frac{\partial v'}{\partial T'} \right)_{P'} - v'$$

$$\alpha = \frac{v_c}{3c_p} \left[\frac{\frac{27}{4} \left(1 - \frac{1}{3v'} \right)^2 - T'}{T' - \frac{27}{4} \left(1 - \frac{1}{3v'} \right)^2 \cdot \frac{1}{3v'}} \right]$$

Introduce $T_{inv} = \frac{27T_c}{4} \left(1 - \frac{1}{3v'} \right)^2$

$$= \frac{2a}{Rb} \left(1 - \frac{b}{v} \right)^2$$

$T < T_{inv}, \alpha > 0 \Rightarrow$ cooling

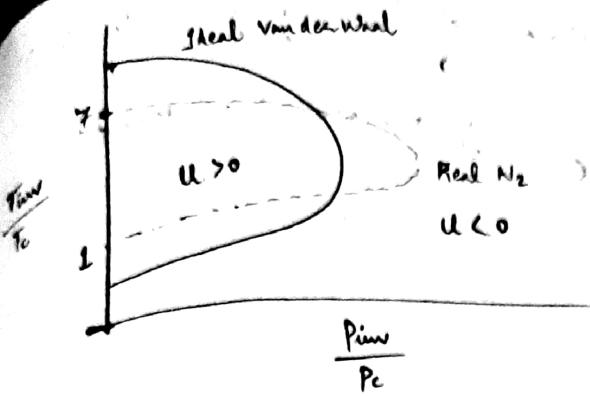
$T > T_{inv}, \alpha < 0 \Rightarrow$ heating

$T_{inv} \Rightarrow$ Inversion temperature

Let $P = P_{inv}$, when $T = T_{inv}$,

$$\text{then } \frac{T_{inv}}{T_c} = \frac{27}{4} \left(1 - \frac{1}{3v'} \right)^2$$

$$\frac{P_{inv}}{P_c} = \frac{18}{v'} - \frac{9}{v'^2}$$



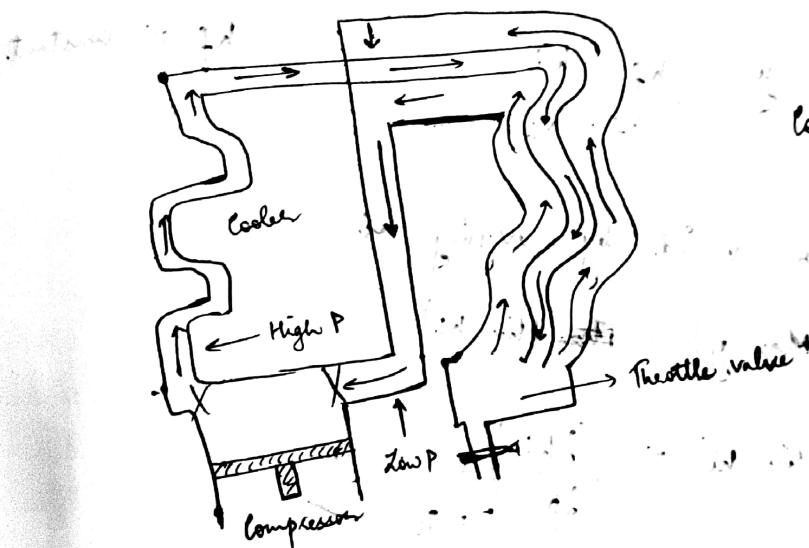
$$(T_{in})_{\max} \approx \frac{27}{4} T_c$$

$$(T_{in})_{\max}^{He} = 35 K (34 K)$$

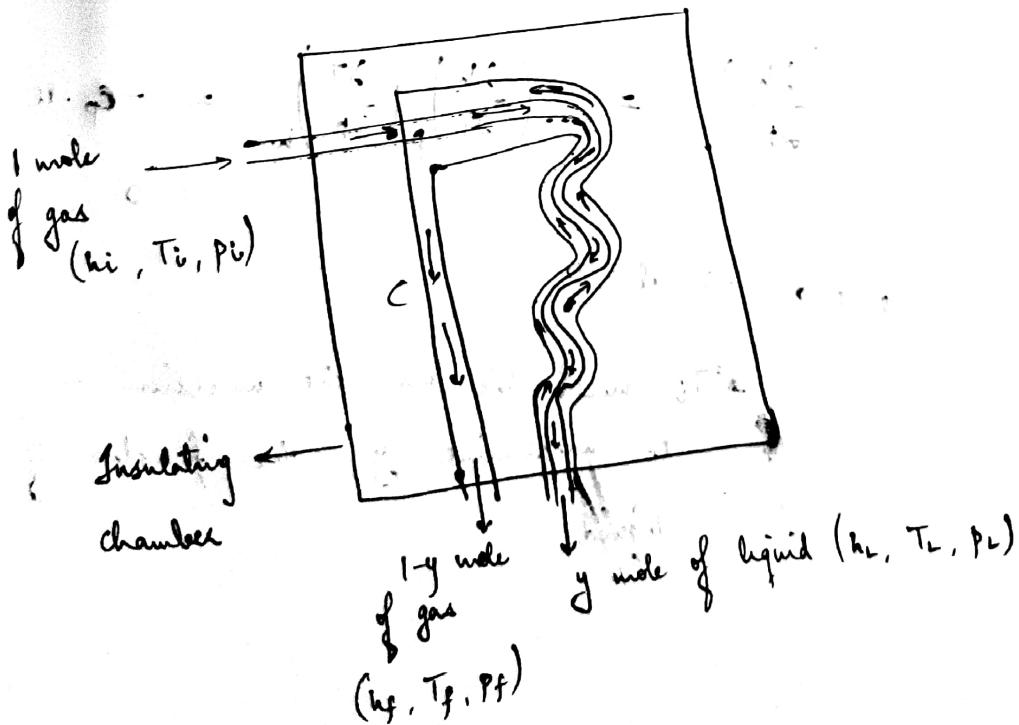
$$(T_{in})_{\max}^{N_2} = 852 K (625 K)$$

$$(T_{in})_{\max}^{O_2} = 1044 K (760 K)$$

Theoretical Experimental



counter current heat exchanger



$h_i \rightarrow$ molar enthalpy of incoming gas at T_i, p_i

For 1 mole of gas, y (a fraction) is liquified

& $(1-y)$ returns to pump.

$$h_i = y h_L + (1-y) h_f$$

$h_L \rightarrow$ Molar enthalpy of outgoing liquid at T_L, p_L

$h_f \rightarrow$ Molar enthalpy of outgoing gas at T_f, p_f

$$y = \frac{h_f - h_i}{h_f - h_L} \quad h_f \Rightarrow \text{constant}$$

y can be varied by varying h_i

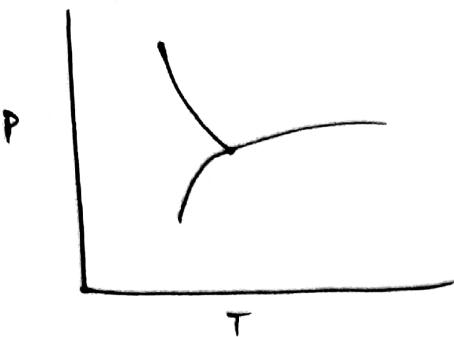
$$\text{Max}(y) = \cancel{\text{Min}(h_i)}$$

$$\text{Min}(h_i) \Rightarrow \left(\frac{\partial h_i}{\partial p} \right)_{T=T_i} = 0$$

$$\left(\frac{\partial h}{\partial p} \right)_T = - \left(\frac{\partial h}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_{h=0} = -C_p \cdot u = 0$$

$$C_p \neq 0 \Rightarrow u = 0$$

T_i must lie on the inversion curve to maximise y , the fraction of liquid.



$P, T \Rightarrow$ intensive quantities

These 2 are independent variables

Q How many independent variables are required to determine the state of the system?
What about mixed system?

A - Gibbs Phase Rule

start from an isolated system

chemical components
(K)

Phases (solid, liquid, etc)
(P)

Each K can be in P phases

Reversible change of state :-

$$dU^{(i)} = T^{(i)} dS^{(i)} - P^{(i)} dV^{(i)} + \sum_{l=1}^K \mu_l^{(i)} dN_l^{(i)}$$

$$l = 1, 2, \dots, P$$

$$V^{(i)} = V^{(i)}(S^{(i)}, V^{(i)}, N_1^{(i)}, \dots, N_K^{(i)})$$

$V^{(i)}$ depends on $(k+2)$ variables

Total no. of extensive variables
 $= P(k+2)$

Equilibrium conditions :-

$T^{(1)} = T^{(2)} = \dots = T^{(P)} \Rightarrow$ Thermal

$p^{(1)} = p^{(2)} = \dots = p^{(P)} \Rightarrow$ Mechanical - (1)

$u_e^{(1)} = u_e^{(2)} = \dots = u_e^{(P)} \Rightarrow$ Chemical

Each of these correspond to $(P-1)$ equations

(1) is a system of $(P-1)(k-2)$ equations

$T^{(i)}, p^{(i)}, u^{(i)}$ are functions of $s^{(i)}, v^{(i)}, n_e^{(i)}$

\Rightarrow To describe the system, we need

$$P(k+2) = (k+2)(P-1)$$

= $(k+2)$ extensive variables

\Rightarrow Independent of no. of phases

Independent intensive variables $\Rightarrow F = k+2-P$

Gibbs Phase Rule

Example :-

i) Pure substance
($k=1$)

a) $P=1$ (single phase)

$$V \Rightarrow F = 2$$

Ex. liquid water

one of the F is P

Fix P at 1 atm

$$0^\circ\text{C} < T < 100^\circ\text{C}$$

independent of P

\Rightarrow Both T & P are independent

b) $P = 2$ (2 coexisting phases)

$$\Rightarrow F = 1$$

Ex. A glass of boiling water in equilibrium with saturated steam

Let F be P

Let $P = 1 \text{ atm}$

$T = 100^\circ\text{C} \Rightarrow T$ is not independent of P

Only F is P .

c) $P = 3$

$$F = 0$$

~~At $T = T_{\text{Triple}}$, 3 phases coexist~~

Ex. At $T = T_{\text{Triple}}$, 3 phases coexist
Triple point occurs only at a specific combination of T & P .

First Order Phase Transition

T, P remains constant while S & V change

Consider ~~n~~ no. moles of a material in phase i .

Molar entropy $S^{(i)} = S^{(i)}(T, P)$

Molar volume $v^{(i)} = v^{(i)}(T, P)$

$\Rightarrow S^{(i)}, v^{(i)} \Rightarrow$ constant during phase transition

$$i \rightarrow f \Rightarrow S^{(f)} \\ v^{(f)}$$



Let x = fraction of i that is transformed to f

$$\text{for mixture} \left\{ \begin{array}{l} s = n_0(1-x)s^{(i)} + n_0x s^{(f)} \\ v = n_0(1-x)v^{(i)} + n_0x v^{(f)} \end{array} \right.$$

If this phase transition occurs reversibly at constant P , the change of entropy per mole

$$\Delta h = T(s^{(f)} - s^{(i)})$$

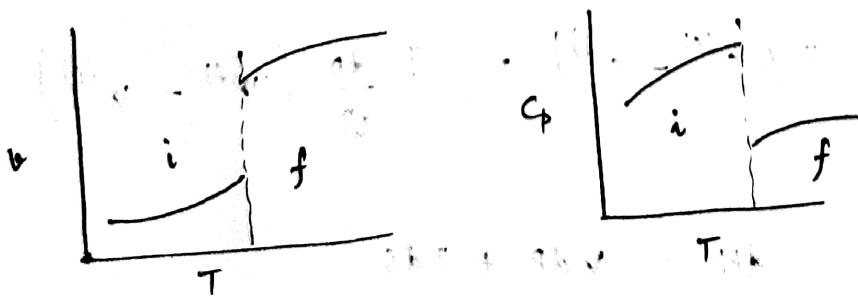
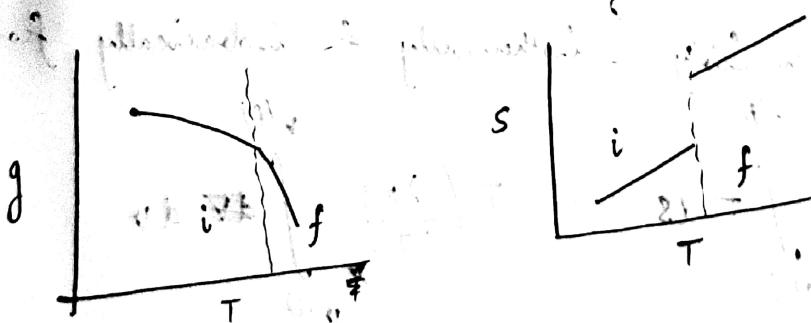
$$\text{Now, } dg = -s dT + v dp$$

$$s = -\left(\frac{\partial g}{\partial T}\right)_P, \quad v = \left(\frac{\partial g}{\partial p}\right)_T$$

Phase transition can be characterised by

- 1) changes in s & v
- 2) g changes discontinuously

Illustrations in support of 1st order phase transition



$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \rightarrow \infty$$

~~$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)$$~~

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow \infty$$

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

$$S = S(T, V)$$

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

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

$$= C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

- When 1 mole of substance undergoes a phase transition reversibly & isothermally & isobarically from $i \rightarrow f$

$$\int_{S(i)}^{S(f)} T dS = T \left(\frac{\partial P}{\partial T} \right) \int_{V(i)}^{V(f)} dV$$

$$\Rightarrow T(S(f) - S(i)) = T \frac{dp}{dT} (V(f) - V(i))$$

$$dH = V dp + T ds$$

$$\text{For } dp = 0 \Rightarrow dH = T ds$$

$$\frac{dp}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}$$

Clausius - Clapeyron Equation

Applicable only at a 1st order phase transition

(one that happens at constant T, P)

$$h^{(f)} - h^{(i)} \Big|_P = \text{molar latent heat}$$

$\Delta G_f = 0 \Rightarrow$ At phase transition,

$$g^{(i)} = g^{(f)}$$

For a phase transition at $T + dT$, $P + dp$

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(f)}$$

$$\Rightarrow dg^{(i)} = dg^{(f)}$$

$$\Rightarrow -s^{(i)}dT + v^{(i)}dp$$

$$= -s^{(f)}dT + v^{(f)}dp$$

$$\frac{dp}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}$$

Liquid - Vapor Transformation



$$s^{(f)} - s^{(i)} = s^{(v)} - s^{(l)}$$

$$\frac{\Delta Q_{L \rightarrow V}}{T}$$

$$\frac{dp}{dT} = \frac{\Delta Q'_{L \rightarrow V}}{T(v^{(v)} - v^{(l)})}$$

Ideal gas, $v^{(v)} \approx 22400 \text{ cm}^3$

at atm $v^{(l)} \approx 18 \text{ cm}^3$

& Room T

$$v^{(v)} \ggg v^{(l)}$$

$$\frac{dp}{dT} = \frac{\Delta Q'_{L \rightarrow V}}{T v^{(v)}}$$

We can find out the vapor pressure of a liquid in equilibrium with its vapor.

Assumptions \Rightarrow ~~Vapor pressure~~

1) Vapor behaves like ideal gas

2) Evaporation heat per mole is independent of T, P

$$v^{(v)} = \frac{kT}{P}$$

$$\frac{dp}{dT} = \frac{P}{kT^2} \Delta Q'$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{-\Delta Q'}{K} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

$$P(T) = P_0(T_0) \exp \left[-\frac{\Delta Q'}{K} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

$\Delta Q' > 0 \Rightarrow p(T)$ strongly increases with T

~~solid \rightarrow vapor transformation~~

Solid-Vapor Transformation

$$v(v) \gg v(s)$$

$$\text{But } \Delta Q'_{s \rightarrow v} \gg \Delta Q_{l \rightarrow v}$$

$$p(T) = p_0(T_0) \exp \left[\frac{-\Delta Q'}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

Solid-Liquid Transformation

$$v(s) \approx v(l)$$

$$\frac{dp}{dT} = \frac{\Delta Q'}{T(v(l) - v(s))}$$

$$\frac{dp}{dT} \rightarrow \infty$$

$$\text{Water} \Rightarrow v(s) > v(l)$$

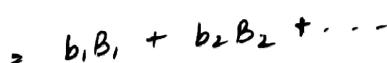
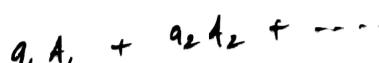
$$\Delta Q'_{s \rightarrow l} > 0$$

water is less

$$\frac{dp}{dT} < 0$$

Law of Mass Action

A vessel containing a mixture of ideal gases that mutually interact according to

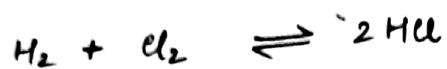


{ai} \rightarrow no. of particles of reactant species

{Ai} \rightarrow set " "

{bi} \rightarrow no. of particles of product species

{Bi} \rightarrow set " "



$$\Delta U = -92.3 \text{ kJ/mol}$$

$$\text{Heat released} = 92.3 \text{ kJ/mol}$$

$$U_{\text{ideal gas}} = \frac{3NkT}{2}$$

$$U_i(N_i, T, P_i) = N_i E_i + \frac{3}{2} N_i kT$$

$$P_i V = N_i kT$$

zero points of energy scales of
respective particles

$$2E_{HCl} - E_{H_2} - E_{Cl_2} \Rightarrow \text{Binding Energy difference b/w}$$

2 molecules of HCl
& 1 molecule each of
H₂ & Cl₂

$$\text{Ideal gas} \Rightarrow u_i(p_i, T) = \epsilon_i + k_B T \left[\frac{u_i(p_0, T_0)}{k_B T_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p_i} \right)^2 \right\} \right]$$

Define

$$\frac{p_i}{p} = \frac{N_i}{N} = x_i \rightarrow \text{Molar fraction of component } i$$

$$\text{Then } \frac{p_0}{p_i} = \left(\frac{p_0}{p} \right) \left(\frac{p}{p_i} \right) = \frac{p_0}{p x_i}$$

$$\Rightarrow u_i(p_i, T) = \epsilon_i + k_B T \left[\frac{u_i(p_0, T_0)}{k_B T_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right)^2 \right\} \right] + k_B T \ln x_i$$

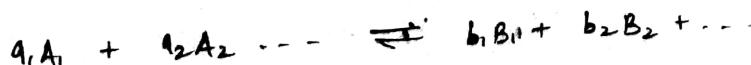
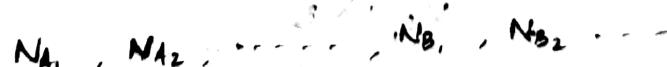
$$u_i(p_i, T) = u_i(p, T) + k_B T \ln x_i$$

\downarrow u of a pure gas of particle
of component i species i with total pressure
(in a mixture) P
with partial pressure p_i

$$u_i(p_i, T) = u_i(p, T) + k_B T \ln x_i$$

valid also for dilute soln of different components
in a solvent

Ideal soln



Let dR be an arbitrary no. of moles

$$dN_{A_1} = -a_1 dR$$

$$dN_{A_2} = -a_2 dR$$

{

$$dN_{B_1} = +b_1 dR$$

$$dN_{B_2} = +b_2 dR$$

$$ds = \frac{dU}{T} + \frac{P}{T} dv - \frac{1}{T} \sum_i u_i dN_i = 0$$

If U, V are constant then $\sum_i u_i dN_i = 0$

$$\Rightarrow \sum_i a_i u_i = \sum_j b_j u_j$$

$$\sum_i a_i u_i (p_i, T) = \sum_j b_j u_j (p_j, T)$$

$$\Rightarrow \sum_i a_i u_i (p_i, T) - \sum_j b_j u_j (p_j, T)$$

$$= k_B T \left(\sum_j b_j \ln x_j - \sum_i a_i \ln x_i \right)$$

$$\Rightarrow \exp \left\{ \frac{1}{k_B T} \left(\sum_i a_i u_i (p_i, T) - \sum_j b_j u_j (p_j, T) \right) \right\}$$
$$= \frac{x_{B_1}^{b_1} \cdot x_{B_2}^{b_2} \cdots}{x_{A_1}^{a_1} \cdot x_{A_2}^{a_2} \cdots}$$

Determines x_{B_1}, x_{B_2}, \dots

x_{A_1}, x_{A_2}, \dots

$k(p, T) \Rightarrow$ Eqbm. constant of the exch. rate

$$k(p, T) = k(p_0, T_0) \cdot \exp \left\{ -\Delta E \left(\frac{1}{k_B T} - \frac{1}{k_B T_0} \right) \right\} \left[\left(\frac{T}{T_0} \right)^{\alpha/2} \left(\frac{p}{p_0} \right)^{\beta-\alpha/2} \right]$$

$$\Delta E = \sum_{\text{bif}} \epsilon_{\text{bif}} - \sum_{\text{uni}} \epsilon_{\text{uni}}$$

Raoult's law

Calculate the dependence of vapor pressure of a solvent on the conc' of a dissolved substance & the resulting increase of the boiling point.

$$\cancel{u_i(p_i, T) = u_i(p, T) + k_B \ln x_i}$$

$$x_i = \frac{p_i}{p} = \frac{N_i}{N}$$

(molar fraction of component i)

Assumption - Consider the vapor & the soln to be ideal.

Solution - Chemical eqbm. demands

$$u^{(v)}(p, T) = u^{(l)}(p, T, x_{(l)})$$

$$u_i(p_i, T) = u_i(p_i, T, x_i) = u_i(p, T, x_i=1) + k_B T \ln x_i$$

$$x_{(l)} = \frac{N_{(l)}}{N_{(l)} + N_{\text{sol}}} \quad !$$

$$u^{(l)}(p, T, x_{(l)}) = u^{(l)}(p, T, 1) + k_B T \ln x_{(l)}$$

$$\left. \frac{\partial u^{(v)}}{\partial p} \right|_T = \left. \frac{\partial u^{(l)}(p, T, 1)}{\partial p} \right|_T \quad dP$$

$$+ k_B T \frac{d x_{(l)}}{x_{(l)}}$$

Duhem
Gibbs-Duhem Relation \Rightarrow

$$SdT + NdU = VdP \geq 0$$

$$dU = \frac{-S}{N} dT + \frac{V}{N} dP$$

$$\left. \frac{\partial U}{\partial P} \right|_T = \frac{V}{N} \neq v$$

$$v^{(v)} dp = v^{(l)} dp + k_B T \frac{dx_{(l)}}{x_{(l)}}$$

$$[v^{(v)} - v^{(l)}] dp = k_B T \frac{dx_{(l)}}{x_{(l)}}$$

$$\frac{dp}{dx_{(l)}} = \frac{k_B T}{[v^{(v)} - v^{(l)}] x_{(l)}}$$

Consider $v^{(v)} \gg v^{(l)}$

$$\frac{dp}{dx_{(l)}} \approx \frac{k_B T}{v^{(v)} \cdot x_{(l)}}$$

$$\frac{dp}{dx_{(l)}} = \frac{P}{x_{(l)}}$$

$$\frac{dp}{P} = \frac{dx_{(l)}}{x_{(l)}} \Rightarrow \frac{P}{P_0} = \frac{x_{(l)}}{1}$$

$$v^{(v)} = \frac{V}{N(v)} \approx \frac{k_B T}{P}$$

If we have vapor pressure, $P(T, x=1)$ for a pure solvent at temp. T , vapor pressure $P(T, x)$ at same temp. but for conc. $x_{(l)}$:

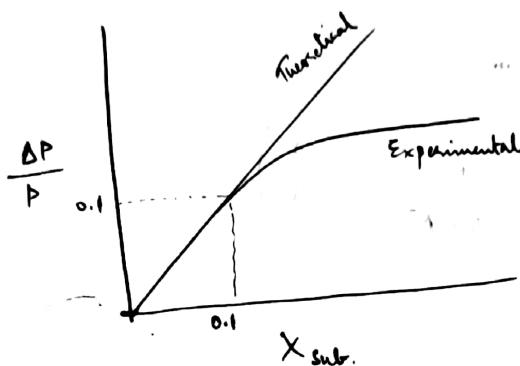
$$P(T, x) = P(T) \cdot x_{(l)}$$

$P(T)$ → vapor pressure of pure liquid
 $x_{\text{sub.}}$ → mole fraction of dissolved substance

Relative decrease in vapor pressure of the liquid:

$$\Delta P' = P(T) - P(T, x)$$

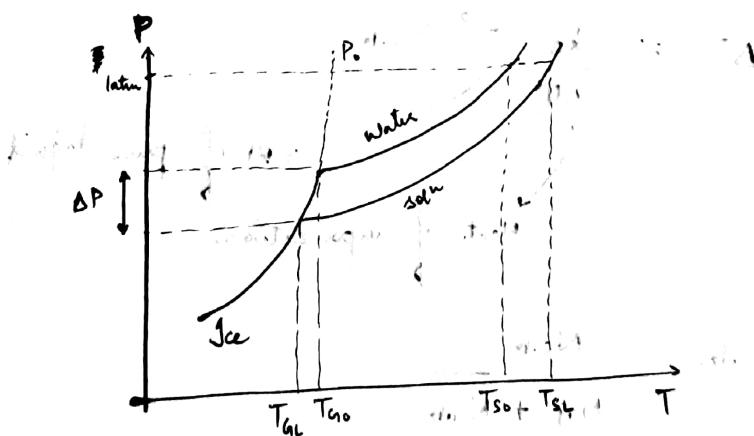
$$= P(T) \cdot x_{\text{sub.}}$$



Discrepancy b/w theory & experiment is fixed by introducing

$a_{\text{sub.}}$

Activity of dissolved substance.



Vapor pressure of a liquid in eqbm. with its vapor

$$P(T) = P_0(T_0) \cdot \exp \left\{ \frac{-\Delta Q'}{k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}$$

Assumption - 1) Evaporation heat $\Delta Q'$ is independent of P, T
 2) vapor is an ideal gas

$$P(T + \Delta T, x_{(l)}) = P(T, 1)$$

$$P(T, l) = P_0$$

$$\Delta P_0 = P_0 - P(T + \Delta T)$$

$$\Rightarrow (P_0 - \Delta P) \exp \left\{ \frac{-\Delta Q'}{k_B} \left(\frac{1}{T+\Delta T} - \frac{1}{T_0} \right) \right\} = P_0 \exp \left\{ \frac{-\Delta Q'}{k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}$$

$$1 - \frac{\Delta P}{P_0} = 1 - x_{\text{sub.}}$$

$$\ln(1 - x_{\text{sub.}}) \approx \frac{\Delta Q'}{k_B} \left(\frac{1}{T+\Delta T} - \frac{1}{T} \right)$$

For $x_{\text{sub.}} \ll 1$

~~$\ln(1 - x_{\text{sub.}}) \approx x_{\text{sub.}}$~~

$$\frac{1}{T+\Delta T} \approx \frac{1}{T} \left(1 - \frac{\Delta T}{T} \right) \quad (\text{Appears})$$

$$\Delta T \approx \frac{k_B}{\Delta Q'} T^2 x_{\text{sub.}}$$

\downarrow
Heat of vaporization

$$x_{\text{sub.}} = \frac{N_{\text{sub.}}}{N_{\text{L}} + N_{\text{sub.}}}$$

Example - What happens to v.p. of a liquid if a non-soluble gas is mixed with the liquid vapor?

Total pressure P of gaseous phase

Partial pressure
of vapor $P_{(v)}$

Partial pressure
of gas P_g

$$u_{(v)}^{\text{gas}}(P, T) = u_{(v)}(P, T) + k_B T \ln \frac{P_{(v)}}{P}$$

$$X = \frac{P_{(v)}}{P}$$

Equilibrium condition, $u_{(v)}^{\text{gas}}(P, T) = u_{(v)}(P, T)$

$$P = P_{(v)} + P_g$$

$$\left. \frac{\partial u_{(v)}}{\partial P} \right|_T = v'_{(v)}, \quad \Rightarrow \left. \frac{\partial u_{(v)}}{\partial P} \right|_T = v'_{(v)} = \frac{k_B T}{P}$$

$$v'_{(v)} dP = \frac{k_B T}{P} dP + k_B T d\left(\ln \frac{P_{(v)}}{P}\right)$$

$$= \cancel{\frac{k_B T}{P} dP} + k_B T d\left(\ln \frac{P_{(v)}}{P}\right) - \cancel{\frac{k_B T dP}{P}}$$

\Rightarrow

$$\frac{d \ln P_{(v)}}{dP} = \frac{v'_{(v)}}{k_B T}$$

Change in saturation vapor pressure
 $P_{(v)}$ with change in total
pressure when a gas is
mixed with it.

$$P = P_{(v)} + P_g$$

$$\cancel{P_{(v)} + P_g = P}$$

$$\ln \frac{P_{(v)}}{P_{(v)}^0} = \int_{P_{(v)}^0}^P \frac{dP}{k_B T} \frac{v'_{(v)}}{k_B T}$$

$$\approx \frac{v'_{(v)}}{k_B T} (P - P_{(v)}^0)$$

$P_{(v)}^0 \Rightarrow$ ~~Saturation vapor~~

Vapor pressure of pure liquid vapor

1) Physics of single objects

↓ ↓
deterministic failed for
description based microscopic objects
on Newton's laws be treated with QM

2) Physics of systems

↓ ↓
~~stochastic~~ Quantities are
description in introduced without
terms of energy, ~~reference to~~
heat, T, S, V, P, etc. microscopic compositions

Kinetic Theory of Gases

Concerned not only with systems in equilibrium but also how
equilibrium is reached.

How collective properties of system evolve with time

Need

Workable Model

Constituents
(particles)

Interaction
(collisions)

Equilibrium properties



Model of a perfect gas

- Gas consists of particles called molecules which are stable & alike for a given gas.
- Molecules are in motion in the space occupied by the gas, colliding with each other & with the wall of the container.
- Motion is governed by Newton's laws.
- They behave like elastic spheres of diameter d .
- In perfect gases average distance b/w molecules $\gg d$.
 \Rightarrow volume occupied by molecules is negligible.
- No appreciable force of attraction/repulsion b/w molecules & b/w molecules & container.

Why can't we use Newton's laws to solve for motion of all the particles?

1) Too much information - 10^{23} particles
For a given time, \vec{x} & \vec{v} for all of them require 10^{12} TB storage.

2) Sensitivity to initial conditions & perturbations

Particle motion is random \Rightarrow undeterministic/chaotic

Particle by particle description is useless

Look at average behaviour & relate bulk properties to that

$\Rightarrow \{\vec{u}\}, \{\vec{v}\} \rightarrow$ Random variables

Average energy of a N particle system (gas particles)

$$\langle E \rangle = N \langle mv^2/2 \rangle$$

Mean velocity of particles $\Leftrightarrow \langle v \rangle = \bar{u}$

$$\text{Let } \vec{v} = \bar{u} + \vec{w}$$

where \vec{w} = peculiar velocity

such that $\langle \vec{w} \rangle = 0$

$$\langle E \rangle = N \frac{m}{2} \langle |\bar{u} + \vec{w}|^2 \rangle$$

$$M = Nm$$

$$\frac{Mu^2}{2} + N \underbrace{\langle mv^2/2 \rangle}_{\substack{\text{avg. energy of} \\ \text{random motion of} \\ \text{particles}}} \downarrow$$

$$\text{K.E.} = K \quad \text{Internal Energy } U$$

~~How~~ How U is related to E , the exact energy of the system?

We find that $N \rightarrow \infty$

$$\langle E \rangle - E \ll 1$$

True for other bulk quantities

$$\text{Exact energy } E = \sum_{i=1}^N \frac{mv_i^2}{2}$$

$$\langle (E - U)^2 \rangle = \langle E^2 \rangle - U^2 \quad (\text{let } \bar{u} = 0)$$

$$= \sum_{i,j} \left(\frac{mv_i^2}{2} \times \frac{mv_j^2}{2} \right) - \left(\sum_i \langle \frac{mv_i^2}{2} \rangle \right)^2$$

$$\begin{aligned}
 &= \sum_i \left\langle \frac{m^2 v_i^4}{4} \right\rangle + \sum_{i \neq j} \left\langle \frac{mv_i^2}{2} \right\rangle \left\langle \frac{mv_j^2}{2} \right\rangle - \left(\sum_i \left\langle \frac{mv_i^2}{2} \right\rangle \right)^2 \\
 &= N \left\langle \frac{m^2 v^4}{4} \right\rangle + N(N-1) \left\langle \frac{mv^2}{2} \right\rangle^2 - \left(N \left\langle \frac{mv^2}{2} \right\rangle \right)^2 \\
 &= N \frac{m^2}{4} \left(\langle v^4 \rangle - \langle v^2 \rangle^2 \right)
 \end{aligned}$$

KMS fluctuation of energy

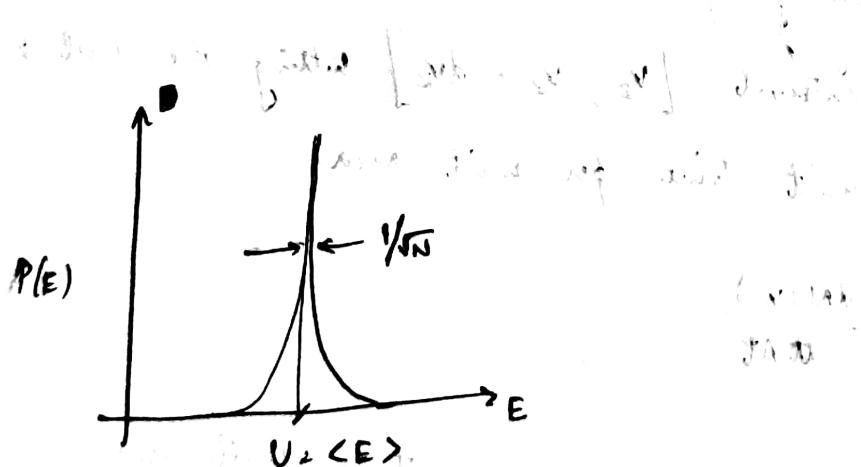
$$\Delta E_{\text{rms}} = \sqrt{\langle (E - \bar{v})^2 \rangle}$$

$$= \sqrt{N \left(\frac{m^2}{4} \right) \left(\langle v^4 \rangle - \langle v^2 \rangle^2 \right)}$$

$$= \sqrt{N \left(\frac{m^2}{2} \right)}$$

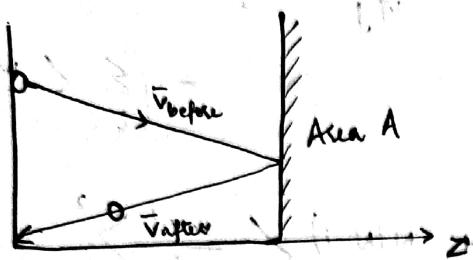
$$\approx \sqrt{\left[\frac{\langle v^4 \rangle}{\langle v^2 \rangle^2} - 1 \right]} + \frac{1}{\sqrt{N}} \ll 1$$

for $N \rightarrow \infty$



$$\frac{\langle v^4 \rangle}{\langle v^2 \rangle^2} - 1$$

Calculation of Pressure



How pressure P felt by walls of a container is related to average properties of velocity distribution of moving particles.

$$v_z \text{ (after)} = -v_z \text{ before}$$

\Rightarrow Momentum delivered to wall by the particle $\Delta p = 2mv_z$

Consider the particle velocity's z -component lying b/w

$$v_z \& v_z + dv_z, dv_z \ll v_z$$

Contribution of these particles to pressure

$$\begin{aligned} dP(v_z) &= \Delta p d\phi(v_z) \\ &= 2mv_z d\phi(v_z) \end{aligned}$$

$d\phi(v_z) \Rightarrow$ Differential particle flux

= No. of particles with velocities in the interval $[v_z, v_z + dv_z]$ hitting the wall per unit time per unit area.

$$d\phi(v_z) = \frac{dN(v_z)}{\Delta t A}$$

~~At~~ $dN(v_z) \Rightarrow$ No. of particles hitting wall area A over a time t & having velocity b/w

$$v_z \& v_z + dv_z$$

$$dN(v_z) = Av_z t \times n \times f(v_z) dv_z$$

$Av_z t \Rightarrow$ Volume where a particle with velocity v_z must be to hit the wall during time t .

$$n = \frac{N}{V} \text{ (Density of particles)}$$

$f(v_z) dv_z \Rightarrow$ Fraction of particles whose velocities are in the interval, $[v_z, v_z + dv_z]$

$$\int_{-\infty}^{\infty} f(v_z) dv_z = 1$$

$$d\phi(v_z) = \frac{dN(v_z)}{At} = \frac{Av_z t \times n \times f(v_z) dv_z}{At} = nv_z f(v_z) dv_z$$

$$dp(v_z) = 1/2mv_z d\phi(v_z)$$

$$= \frac{1}{2}mv_z^2 f(v_z) dv_z$$

$$P = \int_0^{\infty} 2mv_z^2 f(v_z) dv_z$$

Consider only the particles moving towards the wall i.e. $v_z \geq 0$



$$f(v_z) = f(-v_z)$$

$$\Rightarrow P = mn \int_{-\infty}^{\infty} v_z^2 f(v_z) dv_z$$

$$= mn \langle v_z^2 \rangle$$

3-D Generalisation $\Rightarrow f(v_z) \rightarrow f(v_x, v_y, v_z) = f(\vec{v})$

$$f(v_z) dv_z \rightarrow f(\vec{v}) dv_x dv_y dv_z$$

$$f(v_z) = \int_{-\infty}^{\infty} dv_z \int_{-\infty}^{\infty} dv_y f(v_x, v_y, v_z)$$

$$P = mn \int d^3v v_z^2 f(v_z) = mn \langle v_z^2 \rangle$$

Isotropic system $\Rightarrow \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$P = \frac{1}{3} m n \langle v^2 \rangle$$

$$P = \frac{2}{3} \frac{U}{V}$$

$$\left(U = E = N \left\langle \frac{mv^2}{2} \right\rangle \right)$$

$$\cancel{\text{v}} \quad \boxed{P = \frac{2}{3} \frac{U}{V}}$$

$U/V \Rightarrow$ Internal Energy density

Insight \Rightarrow What does isotropy imply for probability distribution function?

$$\text{Isotropic system} \Rightarrow f(\vec{v}) = f(|\vec{v}|) \\ = f(v)$$

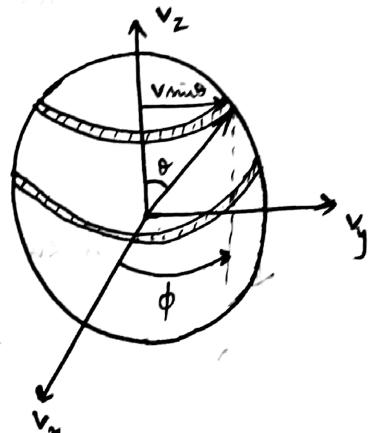
$$(v_x, v_y, v_z) \mapsto (v, \theta, \phi)$$

If we knew $f(v_x, v_y, v_z)$

What is $\bar{f}(v, \theta, \phi)$

$$f(v) dv_x dv_y dv_z \\ = f(v) v^2 \sin \theta d\theta d\phi dv$$

$$\Rightarrow \bar{f}(v, \theta, \phi) = f(v) v^2 \sin \theta$$



Cartesian $\Rightarrow f(v_x, v_y, v_z) dv_x dv_y dv_z$

Spherical $\Rightarrow \bar{f}(v, \theta, \phi) dv d\theta d\phi$

$$\bar{f}(v) = \int_0^\pi \int_0^{\frac{\pi}{2}} \int_0^{2\pi} f(v, \theta, \phi) \cdot 4\pi v^2 f(v)$$

$$v_z = v \cos \theta$$

$$\underline{P} = mn \langle v_z^2 \rangle$$

$$= mn \int d^3v^+ v_z^2 f(\vec{v})$$

$$= mn \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^\infty dv \cdot v^4 f(v)$$

$$\frac{4\pi}{3} mn \int_0^\infty dv v^4 f(v)$$

$$= \frac{1}{3} mn \int_0^\infty dv v^2 \bar{f}(v)$$

$$= \frac{1}{3} mn \langle v^2 \rangle$$

Equilibrium velocity distribution of gas molecules in random motion
in a container of volume V

1) If there is no special direction $f(\vec{v}) = f(v) = g(v^2)$

2) Conjecture from Maxwell

3 components of velocity are independent random variables

$$f(v) = h(v_x^2) h(v_y^2) h(v_z^2)$$

$$h(v_x^2) = h(v_y^2) = h(v_z^2) \rightarrow \text{Isotropy}$$

$$h(v_x^2) = h((v_x)^2) \rightarrow \text{Mirror symmetry}$$

$$h(v_x^2) h(v_y^2) h(v_z^2) = g(v^2) v_x^2 g(v_x^2 + v_y^2 + v_z^2)$$

$$\text{Denote } g(v_x^2) = \ln h(v_x^2)$$

$$\Psi(v^2) = \ln g(v^2)$$

$$Q(v_x^2) + Q(v_y^2) + Q(v_z^2) \stackrel{?}{=} \Psi(v_x^2 + v_y^2 + v_z^2) \quad \text{--- ①}$$

This is satisfied only if Q & Ψ are linear functions of their arguments.

$$\left. \begin{aligned} Q(v_x^2) &= -\alpha v_x^2 + \beta \\ Q(v_y^2) &= -\alpha v_y^2 + 3\beta \end{aligned} \right\} \quad \text{--- ②}$$

Proof \Rightarrow Differentiate ① w.r.t. v_x^2 , keep $v_y^2, v_z^2 = \text{const.}$

$$\Psi'(v_x^2 + v_y^2 + v_z^2) = Q'(v_x^2)$$

Differentiate again w.r.t. v_y^2 , keep others const.

$$\Psi''(v_x^2 + v_y^2 + v_z^2) = 0$$

$$\Psi''(v^2) = 0$$

$\therefore \Psi(v^2) = -\alpha v^2 + 3\beta$: (Substitute in ① & let $v_y^2 = 0$, $v_z^2 = 0$)

$$Q(v_x^2) + 2Q(0) = \Psi(v_x^2)$$

$$= -\alpha v_x^2 + 3\beta$$

$$\text{Let } v_x^2 = 0$$

$$\therefore Q(0) = -\beta$$

$$\therefore Q(v_x^2) = -\alpha v_x^2 + \beta$$

$$\text{Eqn ②} \Rightarrow f(v) = g(v^2) = e^{\Psi(v^2)}$$

$$f(v) = ce^{-\alpha v^2} \quad \text{--- ③}$$

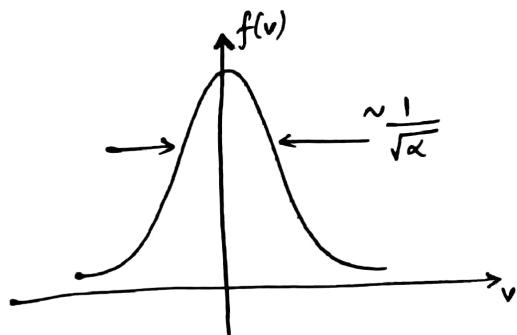
$$\text{where } c = e^{3\beta}$$

Gaussian distribution $\rightarrow e^{-\alpha v^2} \rightarrow \int d^3v (f(\vec{v})) = 1$

$$c = \left(\frac{\alpha}{\pi}\right)^{3/2}$$

$$f(\vec{v}) = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha v^2}$$

depends only on 1 scalar parameter α



$$\frac{1}{\sqrt{\alpha}} = v_{th} \rightarrow \text{Thermal Speed}$$

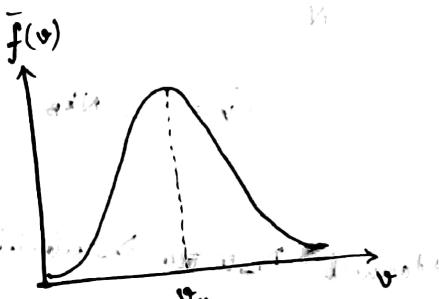
$v \gg v_{th} \rightarrow \text{Impulsive}$

$$T \propto \frac{1}{(\sqrt{\pi} v_{th})^3} e^{-v^2/v_{th}^2}$$

Maxwell distribution

$$\bar{f}(v) = \frac{4\pi v^2}{(\sqrt{\pi} v_{th})^3} e^{-v^2/v_{th}^2}$$

$$P = \frac{1}{3} mn \int d^3v \frac{v^2}{(\sqrt{\pi} v_{th})^3} e^{-v^2/v_{th}^2}$$



$v_{th} \rightarrow \text{Most probable speed}$

$$P = \frac{mn v_{th}^2}{2}$$

$$v_{th} = \sqrt{\frac{2P}{mn}}$$

mode of ideal gas

$$\kappa = N/V$$

$$\frac{mv_{th}^2}{2} = k_B T$$

$$N = N_A = 6 \times 10^{23}$$

$$PV = RT$$

$$R = 8.3 \text{ J/K}$$

$$P = \kappa k_B T$$

$$k_B = R/N_A$$

$$v_{th} = \sqrt{\frac{2k_B T}{m}}$$

$$\frac{1}{2} k_B T = \frac{m \langle v_n^2 \rangle}{2} \quad (\text{Equipartition Theorem})$$

Mean energy per particle per degree of freedom

$$U = N \left\langle \frac{mv^2}{2} \right\rangle$$

$$\frac{U}{N} = \frac{m \langle v^2 \rangle}{2}$$

$$\langle v^2 \rangle = 3 \langle v_n^2 \rangle$$

$$\frac{U}{N} = \frac{3}{2} m \langle v_n^2 \rangle = \frac{3}{2} k_B T$$

$$C_V = \frac{3}{2} N k_B$$

Maxwell Distribution

$$f(\vec{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

Full thermodynamics of classical

monoatomic ideal gas

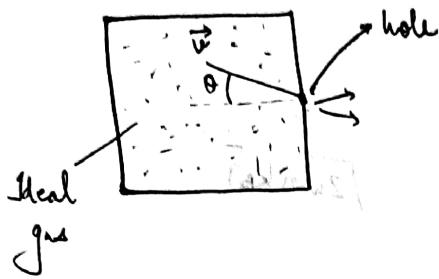
Formula
for U

Formula
for C_V

Eq'n of
state

Full Velocity distribution
which is to be
used to calculate
other interesting
properties

Effusion



Diameter of hole

$$d \ll L$$

$L \rightarrow$ mean free path

Questions \rightarrow a) Given some distribution in the container, $f(\vec{v})$ what will be distribution of particle emerging through the hole?

b) What is the particle flux through the hole?
Given an area A , how many particles escape through it per unit time?

No. of particles having velocity $[\vec{v}, \vec{v} + d\vec{v}]$ reaching the hole per unit time per unit area

$$\begin{aligned} d\phi(\vec{v}) &= n v_z f(\vec{v}) d^3 v \\ &= n v^3 f(v) dv \underbrace{\cos \theta \sin \theta d\theta d\phi}_{\text{Angular distribution}} \end{aligned}$$

$d\phi$ is called speed distribution

Let's consider event at boundaries

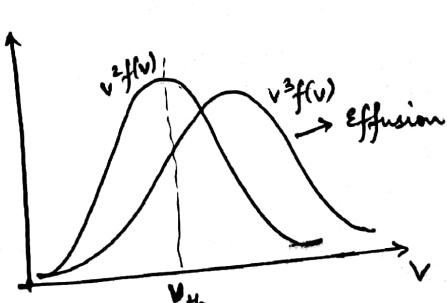
$$f(\vec{v})_{in} = f(v)$$

$$v_z = v \cos \theta$$

$$d^3 v = v^2 \sin \theta d\theta d\phi d\omega$$

$$\begin{aligned} d\tilde{\phi}(v) &\propto n v^3 f(v) dv \int_0^{\pi/2} \cos \theta \sin \theta d\theta \times \int_0^{2\pi} d\phi \end{aligned}$$

$$\begin{aligned} &= \pi n v^3 f(v) dv \\ &= \frac{1}{4} n v \tilde{f}(v) dv \end{aligned}$$



$$\tilde{f}(v) = 4\pi v^2 f(v)$$

$\tilde{f}(v)$ \rightarrow Distribution of speed inside container

$$\tilde{\phi}(v) = \frac{1}{4} \int dv \ n \ \tilde{f}(v)$$

Total flux

$$= \frac{1}{4} n \langle v \rangle$$

of emerging
particles

$$= \frac{1}{4} n \sqrt{\frac{8k_B T}{\pi m}} = \frac{n}{\sqrt{2m k_B T}}$$

$$\text{For given P,T} \Rightarrow \tilde{\phi} \propto m^{-1/2}$$

Collision

Equilibrium distribution means

$$1) t \gg \tau_c$$

→ collision time

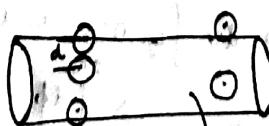
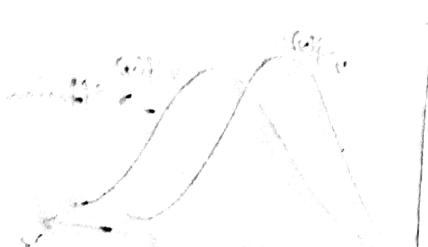
$$2) L \gg \lambda_{mfp}$$

→ Mean free path

Calculation of τ_c , λ_{mfp}

Particles are hard spheres of diameter d .

They can be considered to have collided if their centres approach each other within a distance d .



$$\delta = \pi d^2$$

$\delta \Rightarrow$ collision cross-section

density n

Volume swept by a particle over time t moving

through cylinder of \propto cross-section $\Rightarrow \delta v t$

$\frac{1}{\delta v t n} \Rightarrow$ Average no. of other particles in this volume

If $\delta v t n > 1$ then there is at least one collision
in time t .

$$6v T_c n = P$$

$$T_c = \frac{1}{\pi d^2 n v_{th}} = \frac{1}{\pi d^2 n} \sqrt{\frac{m}{2k_B T}}$$

$$\lambda_{diff} = \cancel{v_{th}} T_c$$

Assumptions \Rightarrow n, P, T are constant in space

\downarrow
No flow

Particle distribution function in ~~position~~ & velocity space

$F(t, \vec{r}, \vec{v}) d^3 r d^3 v$ = Average no. of particles

with velocities in 3-D

volume $[v_x, v_x + dv_x] \times$

$[v_y, v_y + dv_y] \times$

$[v_z, v_z + dv_z]$

finding themselves in
spatial cube at
time t .

Normalization

$$\int d^3 r \int d^3 v F(t, \vec{r}, \vec{v}) = N \rightarrow \text{Total no. of particles}$$

$$\int d^3 v F(t, \vec{r}, \vec{v}) = n(t, \vec{r}) \rightarrow \text{Particle density}$$

$$\int n(t, \vec{r}) d^3 r = N$$

Homogeneous system

$$n(\vec{v}) = n = \text{constant}$$

$$\begin{aligned} F(\vec{r}, \vec{v}) &= F(v) \\ &= n f(v) \end{aligned}$$

$$\int f(v) d^3 v = 1$$

$$\int d^3 v \ n \ f(v) = n$$

Mean particle flux

$$\int d^3 v \ n \ \vec{F}(t, \vec{r}, \vec{v}) = n \bar{n}(t, \vec{r}) \bar{u}(t, \vec{r})$$

Mean particle density

Mean velocity of gas flow

Mean momentum

density

Mean Energy Density

$$\vec{v} = \vec{u} + \vec{w}$$

$$\langle \vec{w} \rangle = 0$$

$$\int d^3 v \frac{mv^2}{2} F(t, \vec{r}, \vec{v})$$

$$= \cancel{\int d^3 w} \frac{m|\vec{u} + \vec{w}|^2}{2} F(t, \vec{r}, \vec{v})$$

$$= \frac{mu^2}{2} \int d^3 w F + m\vec{u} \int d^3 w \vec{w} F + \int d^3 w \frac{mw^2}{2} F$$

$$= \frac{mu^2}{2} + \left\langle \frac{mw^2}{2} \right\rangle u$$

Energy density
of average motion

Internal
energy density



$$\text{Total ordered energy} \quad K = \int d^3x \frac{mn\omega^2}{2}$$

$$\text{Total disordered (internal) energy} \quad U_i = \int d^3x \epsilon(t, \vec{x})$$

$$\epsilon(t, \vec{x}) = \left\langle \frac{m\omega^2}{2} \right\rangle u(t, \vec{x})$$

How to calculate F ?

length & time scales of inhomogeneities
are such that

$$l_{\text{inhom}} \gg \lambda_{\text{mfp}}$$

$$t_{\text{inhom}} \gg T_c$$

\Rightarrow Break up the gas into fluid elements of
size Δl & consider them for time Δt
such that

$$l_{\text{inhom}} \gg \Delta l \gg \lambda_{\text{mfp}}$$

$$t_{\text{inhom}} \gg \Delta t \gg T_c$$

In these scales, fluid elements behave like
homogeneous systems with locally \approx constant
density n , moving at some locally constant
mean velocity \bar{u} .



$$F_m(t, \vec{x}, \vec{v}) = n(t, \vec{x}) \left[\frac{m}{2\pi k_B T(t, \vec{x})} \right]^{3/2} \exp \left[-\frac{m|\vec{v} - \bar{u}(t, \vec{x})|^2}{2k_B T(t, \vec{x})} \right]$$

$$= \frac{n(t, \vec{x})}{(\sqrt{\pi} v_{th})^3} e^{-\frac{m\omega^2}{v_{th}^2}}$$

$$v_m = \sqrt{\frac{2k_B T(t, \vec{r})}{m}}$$

$\vec{v} = \vec{u} + \vec{\omega}$

↓

velocity of fluid element
w.r.t. global gas

velocity of
particle w.r.t.
local volume

Local pressure

$$P(t, \vec{r}) = n(t, \vec{r}) k_B T(t, \vec{r})$$

$$= \frac{2}{3} E(t, \vec{r})$$

Local temperature

$$T(t, \vec{r}) = \frac{2}{3} \times \text{Mean energy per particle}$$

$$= \frac{2}{3} \frac{E(t, \vec{r})}{n(t, \vec{r})}$$

$$= \frac{2}{3} \left\langle \frac{m \omega^2}{2} \right\rangle$$

$$= \left\langle m \omega_n^2 \right\rangle \xrightarrow{\text{Isotropy}}$$

$$\left\langle \omega_n^2 \right\rangle = \left\langle \omega_y^2 \right\rangle = \left\langle \omega_z^2 \right\rangle = \frac{1}{3} \left\langle \omega^2 \right\rangle$$

Conservation Laws

Isolated & closed

1) Particles are conserved

$$\int d^3 \vec{r} n = N = \text{const.}$$

2) Momentum is conserved

$$\int d^3 \vec{r} m \vec{n} \cdot \vec{u} = 0$$

Fix the frame moving with centre of
mass of system



3) Energy conservation

$$\int d^3\vec{r} \left(\frac{m u u^2}{2} + E \right) = K + U = \text{const.}$$

Temperature

Simple situation

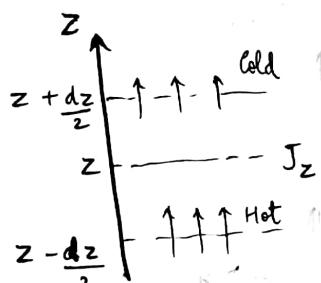
$$\vec{u} = 0, \quad u = \text{const. (globally)}$$

\therefore Energy density

$$E = n c_1 T(t, \vec{r})$$

Heat capacity
per particle

1-D problem



$$T = T(t, z)$$

J_z = Internal energy flowing along z -axis per unit time through unit area perpendicular to z -axis

Rate of change of internal energy in a small volume: $A \times \left[z - \frac{dz}{2}, z + \frac{dz}{2} \right]$

$$= \frac{\partial}{\partial t} (n c_1 T \cdot A \cdot dz)$$

$$= \underbrace{J_z(z - \frac{dz}{2}) \times A}_{\text{Energy flowing in}} - \underbrace{J_z(z + \frac{dz}{2}) \times A}_{\text{Energy flowing out}}$$

$$\Rightarrow n c_1 \frac{\partial T}{\partial t} = - \frac{[J_z(z + \frac{dz}{2}) - J_z(z - \frac{dz}{2})]}{dz}$$

$$= \frac{-\partial J_z}{\partial z} \quad \text{as } dz \rightarrow 0$$

generalize to 3D

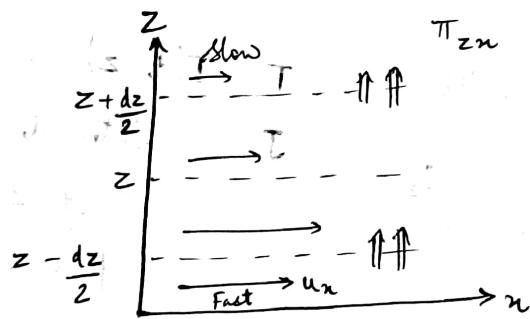
$$\frac{\partial}{\partial t} \int_V d^3x n C_1 T = - \int_V \vec{dA} \cdot \vec{J}$$
$$= - \int_V d^3x \vec{\nabla} \cdot \vec{J}$$

$$\Rightarrow n C_1 \frac{\partial T}{\partial t} = - \vec{\nabla} \cdot \vec{J}$$

Local statement of energy conservation

Derived keeping density n constant

Transport in Ideal Gas



z -dependent flow velocity along $x \Rightarrow \vec{u} = u_x(t, z) \hat{x}$
(shear flow)

Momentum flux :
 $\Pi_{zn}(z)$: Momentum in x -direction flowing along z per unit time through unit area perpendicular to z -axis

$$\frac{\partial}{\partial t} \left\{ mn u_x \cdot A dz \right\} = \underbrace{\Pi_{zn} \left(z - \frac{dz}{2} \right) A}_{\text{momentum flowing in}} - \underbrace{\Pi_{zn} \left(z + \frac{dz}{2} \right) A}_{\text{momentum flowing out}}$$

$$mn \frac{\partial u_n}{\partial t} = - \frac{\partial \Pi_{zn}}{\partial z}$$

Considering \rightarrow arbitrary volume, in gas

$$\frac{\partial}{\partial t} \int d^3x mn u = - \int dS \cdot \vec{\Pi}$$

$$\text{Tensor notations} \Rightarrow \frac{\partial}{\partial t} \int d^3x mn u_j = - \int dS_i \Pi_{ij}$$

Π \rightarrow Stress tensor

$\Pi_{ij} \Rightarrow$ Flux of j^{th} component of momentum
in i^{th} direction

$$\frac{\partial}{\partial t} \int d^3x mn u_j = - \delta_{ij} \Pi_{ij}$$

Expectation from thermodynamics \Rightarrow

$$1) J_z \neq 0 \text{ only if } \frac{\partial T}{\partial z} \neq 0$$

$$2) \text{sgn}(J_z) = -\text{sgn}\left(\frac{\partial T}{\partial z}\right)$$

$$3) \Pi_{zn} \neq 0 \text{ only if } \frac{\partial u_n}{\partial z} \neq 0$$

$$4) \text{sgn}(\Pi_{zn}) = -\text{sgn}\left(\frac{\partial u_n}{\partial z}\right)$$

Flux \propto - (gradient)
(conjecture)

$$J_z \left(\frac{\partial T}{\partial z} \right) = J_z(0) + J_z'(0) \frac{\partial T}{\partial z} + \dots$$

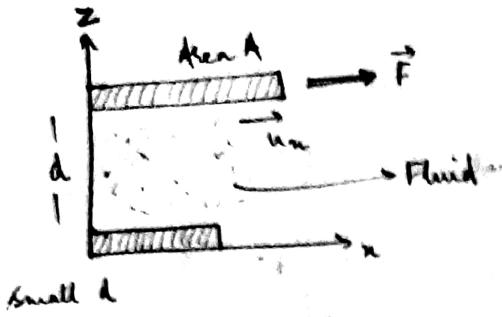
$$= -K \frac{\partial T}{\partial z}$$

Thermal conductivity

$$\Pi_{zn} \left(\frac{\partial u_n}{\partial z} \right) = \Pi_{zn}(0) + \Pi_{zn}'(0) \frac{\partial u_n}{\partial z} + \dots$$

$$= -\eta \frac{\partial u_n}{\partial z}$$

Dynamical viscosity



$$\frac{F}{A} \propto \eta \frac{u_x}{d} = \eta \frac{\partial u_x}{\partial z}$$

Independent of u_x, d, A

Force/Area = Momentum/time-area
= Momentum flux
downward

$$\frac{F}{A} = -\Pi_{xz}$$

$$n C_i \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial z^2}$$

$$m u \frac{\partial u_x}{\partial t} = \eta \frac{\partial^2 u_x}{\partial z^2}$$

} Transport Equations
or Diffusion

$$K, \eta \Rightarrow \text{constants}$$

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial z^2}$$

$$\frac{\partial u_x}{\partial t} = \nu \frac{\partial^2 u_x}{\partial z^2}$$

D_T : Thermal diffusivity

$$D_T = \frac{K}{\rho c_p}$$

ν : Kinematic diffusivity

$$= \frac{\eta}{m u}$$

$$\frac{\partial^2}{\partial z^2} = \nabla^2$$

$$\int u \nabla^2 u \, dv = \int u \frac{\partial u}{\partial n} \, ds - \int |\nabla u|^2 \, dv$$

Green's identity

If boundary conditions are such that either u or $\frac{\partial u}{\partial n}$ vanishes at the boundary

$$\int_S u \frac{\partial u}{\partial n} dS = 0$$

$$\int_V (u \nabla^2 u + \underbrace{|\nabla u|^2}_{>0}) dV = 0$$

$$\Rightarrow \int_V u \nabla^2 u dV < 0$$

$$\therefore \langle \nabla^2 u, u \rangle \Leftrightarrow < 0$$

$\therefore \langle \frac{\partial T}{\partial t} \rangle$ & $\langle \frac{\partial u}{\partial x} \rangle$ will be negative
so the system will reach equilibrium

If initial distribution of temperature

$$T(t=0, z) = \sum_k \hat{T}_0(k) e^{ikz}$$

$$T(t, z) = \sum_k \hat{T}(t, k) e^{ikz}$$

$$\frac{\partial \hat{T}}{\partial t} = -D_T k^2 \hat{T} \Rightarrow \hat{T}(t, k) = \hat{T}_0(k) e^{-D_T k^2 t}$$

$$\hat{T}(t, k) \approx e^{-t/\tau_{\text{diff.}}}$$

$$\tau_{\text{diff.}} = \frac{lk}{D_T k^2}, \quad l \approx k^{-1}$$

$$\approx \frac{l^2}{D_T}$$

Q : For the assumption that locally Maxwellian distribution prevails,

$$l \gg \lambda_{\text{mfp}}, \quad \tau_{\text{diff.}} \gg \tau_c$$

Are they true?

Consider a sub-population of particles with density n^*
 (carry some identifiable property)
 (mean energy/momentum)

The evolution equation for n^* must have same form as
 the evolution equation for energy/momentum of gas.

Let at time t , mean density of labelled particles at
 z is $n^*(t, z)$

Q : What will it be at some location after a
 short time Δt ?

$$n^*(t + \Delta t, z) = \langle n^*(t, z - \Delta z) \rangle$$

↓
positions

where particles arriving at z
 at $(t + \Delta t)$ were at time t .

Consider Δt small enough

$$\Rightarrow \Delta z \ll \left(\frac{1}{n^*} \frac{\partial n^*}{\partial z} \right)^{-1}$$

$$n^*(t + \Delta t, z) \approx \langle n^*(t, z) - \Delta z \frac{\partial n^*}{\partial z} + \frac{\Delta z^2}{2} \frac{\partial^2 n^*}{\partial z^2} \rangle$$

$$\approx n^*(t, z) + \frac{\langle \Delta z^2 \rangle}{2} \frac{\partial^2 n^*}{\partial z^2}$$

$$\frac{n^*(t + \Delta t, z) - n^*(t, z)}{\Delta t} = \frac{\langle \Delta z^2 \rangle}{2 \Delta t} \frac{\partial^2 n^*}{\partial z^2}$$

$$\Delta t \rightarrow 0$$

$\frac{\partial^2 n^*(t, z)}{\partial t}$	$= D \frac{\partial^2 n^*}{\partial z^2}$
-------------------------------------------	-------------------------------------------

$$D = \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta z^2 \rangle}{2 \Delta t}$$

as $\Delta t \rightarrow 0 \Rightarrow \Delta t \ll T_{\text{diff}}$

can be $\gg T_c$

Diffusion constant

Is D finite?

$$\Delta z = \sum_{i=1}^N s_{zi} \quad s_{zi} \rightarrow \begin{cases} \text{Independent random} \\ \text{displacements} \end{cases}$$

$$\langle s_{zi} \rangle = 0$$

$$\langle s_{zi}^2 \rangle = \lambda_{\text{mfp}}^2$$

$$N = \frac{\Delta t}{T_c}$$

↓
No. of collisions with walls
at time Δt

Central limit theorem

In the limit, $N \rightarrow \infty$

$$X = \sqrt{N} \left(\frac{1}{N} \sum_{i=1}^N s_{zi} - \langle s_{zi} \rangle \right)$$

will have a Gaussian distribution

$$\text{with mean } = 0, \text{ variance: } \langle s_{zi}^2 \rangle - \langle s_{zi} \rangle^2 = \lambda_{\text{mfp}}^2$$

$$f(x) = \frac{1}{\lambda_{\text{mfp}} \sqrt{2\pi}} e^{-\frac{x^2}{2\lambda_{\text{mfp}}^2}}$$

$$\therefore \Delta z = X \sqrt{N}$$

We conclude that for $N = \frac{\Delta t}{T_c} \gg 1$

$$D = \frac{\langle \Delta z^2 \rangle}{2 \Delta t} = \frac{\langle X^2 \rangle}{2 T_c} = \frac{\lambda_{\text{mfp}}^2}{2 T_c}$$

$$T_{\text{diff}} \sim \frac{l^2}{D}$$

Since \rightarrow

$$D \sim v_{th}^2 T_c \sim v_{th} \lambda_{mfp}$$

$$\lambda_{diff} \sim \left(\frac{l}{\lambda_{mfp}} \right)^2 T_c$$

$$\lambda_{diff} \gg T_c \text{ if } l \gg \lambda_{mfp}$$

• Central limit theorem \Rightarrow When independent random variables are summed up, their property normalized sum tends towards a Gaussian distribution even if the original variables themselves do "not" follow that distribution.

If x_1, x_2, \dots, x_n are random samples

drawn from a population with mean μ

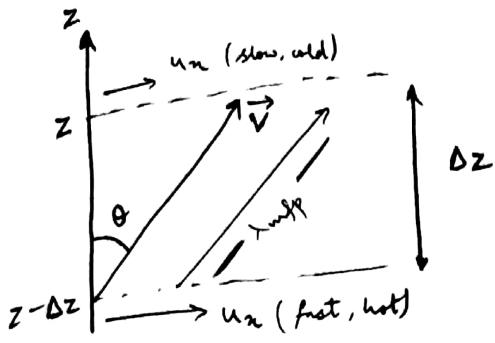
and standard deviation s : variance s^2 & if \bar{x}_n is the mean of first N sample of the distribution.

Normal distribution

$$\bar{x}_n = \frac{1}{N} \sum_{i=1}^N x_i$$

$$f(x) = \frac{1}{s\sqrt{2\pi}} e^{-\frac{1}{2} \frac{(x-\mu)^2}{s^2}}$$

Viscosity



No. of particles with velocity
 \vec{v} that cross the
 plane/time/area

$$d\phi(\vec{v}) = n v_z f(\vec{v}) d^3 v \\ = n v^3 f(v) dv \cos \theta \sin \theta d\theta d\phi$$

$$\Delta z = \lambda_{\text{mfp}} \cos \theta$$

$$u_z = u_z(z)$$

$$(\Delta z \ll l)$$

$$\Delta p = m u_z(z - \Delta z) - m u_z(z)$$

$$\approx -m \frac{du_z}{dz} \Delta z$$

$$= -m \frac{du_z}{dz} \lambda_{\text{mfp}} \cos \theta$$

$$\Pi_{zn} = \int d\phi(\vec{v}) \Delta p \\ = -m n \frac{du_z}{dz} \lambda_{\text{mfp}} \int_0^\infty dv v^3 f(v) \int_0^{\pi} d\theta \cos^2 \theta \sin \theta \int_0^{2\pi} d\phi$$

$$\Pi_{zn} = -\frac{1}{3} m n \lambda_{\text{mfp}} \langle v \rangle \frac{du_z}{dz}$$

$$\eta = \frac{1}{3} m n \lambda_{\text{mfp}} \langle v \rangle$$

$$= \frac{2}{3\sqrt{\pi}} m n \lambda_{\text{mfp}} v_{th}$$

$$\eta = \frac{2}{3\pi d^2} \sqrt{\frac{2m k_B T}{\pi}}$$

Diffusivity

$$\Delta E = C_1 T(z - \Delta z) - C_1 T(z) \approx -C_1 \frac{\partial T}{\partial z} \Delta z = -C_1 \frac{\partial T}{\partial z} \lambda_{\text{mfp}} \cos \theta$$

$$J_z = \int d\phi(\vec{v}) \Delta E = -\frac{1}{3} n C_1 \lambda_{\text{mfp}} \langle v \rangle \frac{\partial T}{\partial z}$$

$$K = \frac{1}{3} n C_1 \lambda_{\text{mfp}} \langle v \rangle = \frac{2 C_1}{3\pi d^2} \sqrt{\frac{2k_B T}{\pi m}}$$