

I Least time

II Chemicals!

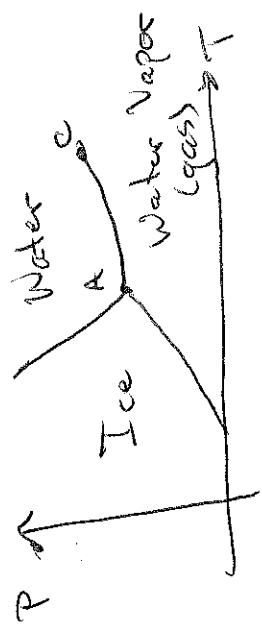
III Equilibrium between phases (again) and general chemical equilibrium.

IV But what is μ ? (and how do we calculate it?)

Meeting

I. Finished derivation of Clausius-Clapeyron eqⁿ.

"Phase diagrams are pure Temptation"



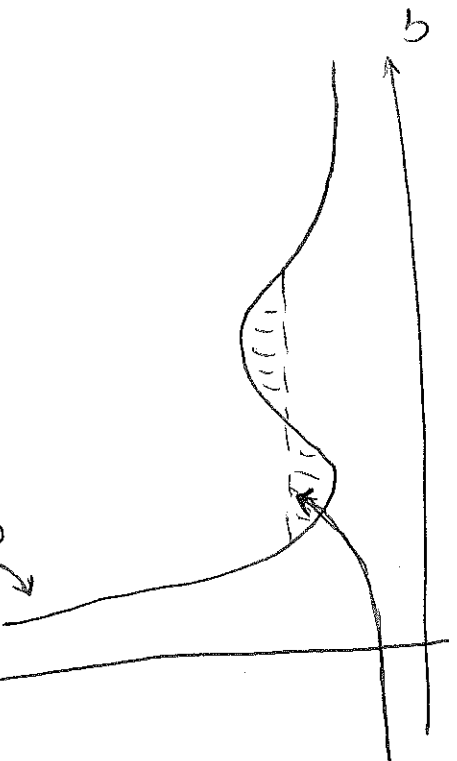
$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T \Delta V}$$

• Vanquished the most difficult derivation in the course

Used the "equation of state" to do the "Maxwell construction" or "equal area rule" to find the actual isotherm curve in the coexistence region

Equation of State

P ↑ const. T isotherm



results $\frac{dQ}{T} = \frac{dE + PdV}{T}$ Pz/c

and $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$ $\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$

Let's define

$\mu_j \equiv - \left(\frac{\partial S}{\partial N_j}\right)_{E,V,N}$

or

$\mu_j \equiv -T \left(\frac{\partial S}{\partial N_j}\right)_{E,V,N}$

$\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N}$

or

$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,P,N}$

μ_j is called the "chemical potential" of species j .

III Cool application of the extensive idea:

II. Consider a homogeneous mixture of m chemicals with E, V and N_i ($i=1, \dots, m$).

Then $S = S(E, V, N_1, N_2, \dots, N_m)$

and $dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_{i=1}^m \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N} dN_i$

If the N_i are fixed we get previous

Then

$dS = \frac{1}{T} dE + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i$

or $dE = T dS - P dV + \sum_i \mu_i dN_i$

Gives another way to write μ_j .

$\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{S,V,N}$

Usual Legendre transforms give additionally

Asise on μ and G
~~Prove~~ Suppose that G only depends
 on one species, say the j th one,

$$G = G(T, p, N_j)$$

and require G be extensive
 $N_j \rightarrow \alpha N_j$ and $G \rightarrow \alpha G$

but then

$$G(T, p, N_j) = N_j g'(T, p)$$

\leftarrow Gibbs free energy per particle.

$$\left. \begin{aligned} E_1 + E_2 = \text{const.} = E & \Rightarrow dE_1 + dE_2 = 0 \\ V_1 + V_2 = \text{const.} = V & \Rightarrow dV_1 + dV_2 = 0 \\ N_1 + N_2 = \text{const.} = N & \Rightarrow dN_1 + dN_2 = 0 \end{aligned} \right\}$$

Equilibrium implies $S = \text{max}$,

$$dS = 0$$

But $S = S_1 + S_2$ and so,

$$dS = \left(\frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \right) + \left(\frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 \right) = 0$$

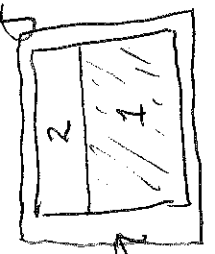
and so

$$\left(\frac{\partial G}{\partial N_j} \right)_{T, p} = \mu_j = g'(T, p)$$

Note that this is no longer true for $G(T, p, N_1, \dots, N_n)$.

End aside

Consider two phases forming an isolated system



or $\mu_1 = \mu_2$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 = 0$$

so

$T_1 = T_2$	Equilibrium
$P_1 = P_2$	$\mu_1 = \mu_2$

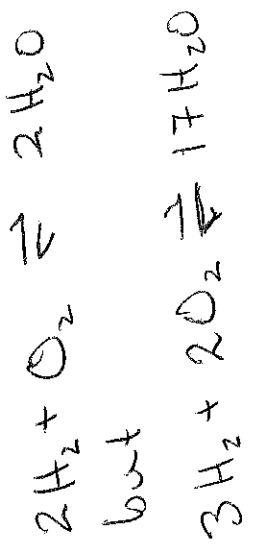
Notice what the last one says

$$g'_1 = g'_2$$

same condition as before

We can arrive at the general condition for chemical equilibrium in a similar way.

First a simple observation - atoms are conserved, so



is fine, but is not! Let B_1, \dots, B_m stand for

to the N_i s. I can multiply the valid equation (*) by any integer and it remains valid, so,

$$dN_i = \lambda b_i \text{ for all } i$$

IF $dN_i > 0$ that molecule was formed and $dN_i < 0$ means that molecule was lost. We're ready to run the argument again

$$S = \max = S(E, N_1, \dots, N_m)$$

the chemical symbols and P_i b_i the coefficient of B_i , then we can always write

$$\sum_{i=1}^m b_i B_i = 0$$

for a reaction. For example



is + for product - for reactant.

$$2\text{H}_2\text{O} - 2\text{H}_2 - \text{O}_2 = 0 (*)$$

Let's relate these observations

$$dS = 0$$

IF $V = \text{const}$, $E = \text{const}$ we

$$\text{have } \sum_i \mu_i dN_i = 0$$

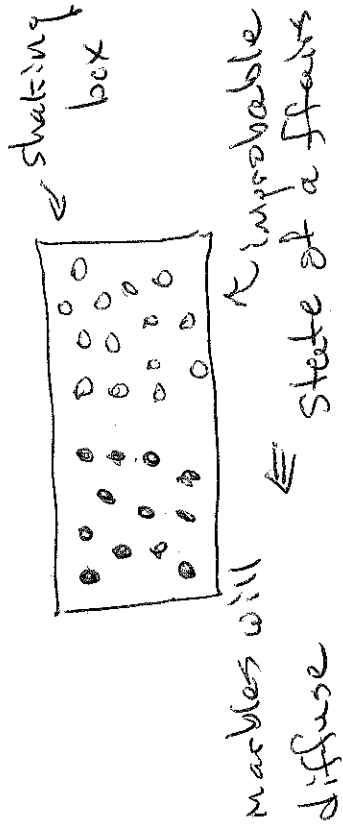
or

$$\sum_i b_i \mu_i = 0$$

You may not be surprised to learn that the same condition follows from $F = \text{min}$ and $G = \text{min}$, the only adjustment being

What μ is a function of.

IV The basic idea of μ is to characterize when a species will diffuse (like T determines when heat will flow)



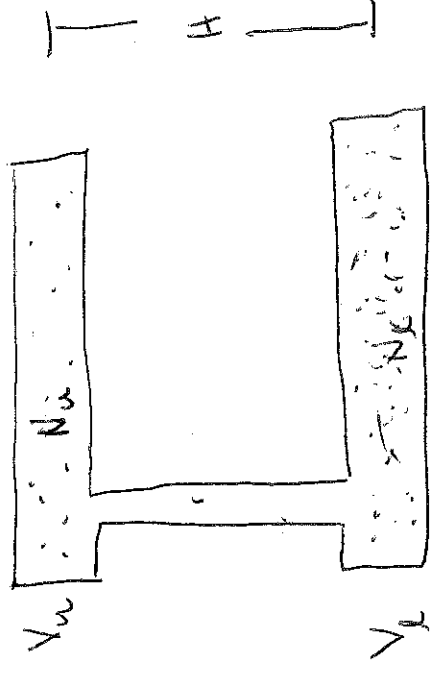
But $Z(N_e, N_u) = Z_e(N_e) \cdot Z_u(N_u)$

At equilibrium the probability is a maximum and so,

$$\frac{\partial \ln Z_e}{\partial N_e} - \frac{\partial \ln Z_u}{\partial N_u} = 0$$

or $\frac{\partial \ln Z_e}{\partial N_e} = \frac{\partial \ln Z_u}{\partial N_u}$

Example with calculation: P5/6



$$P(N_e, N_u) = \sum_{\text{states}} \frac{e^{-E_s/kT}}{Z} = \frac{Z(N_e, N_u)}{Z}$$

with N_e in V_e and N_u in V_u

We know

$$F = -kT \ln Z$$

and so at fixed T and V we have

$$\left(\frac{\partial F_e}{\partial N_e} \right)_{T, V} = \left(\frac{\partial F_u}{\partial N_u} \right)_{T, V}$$

or $\mu_e(T, V_e, N_e) = \mu_u(T, V_u, N_u)$

More explicitly, we know

$$Z_i = \frac{z_i^{N_i}}{N_i!}$$

shift coming from e_0 shift of energy.

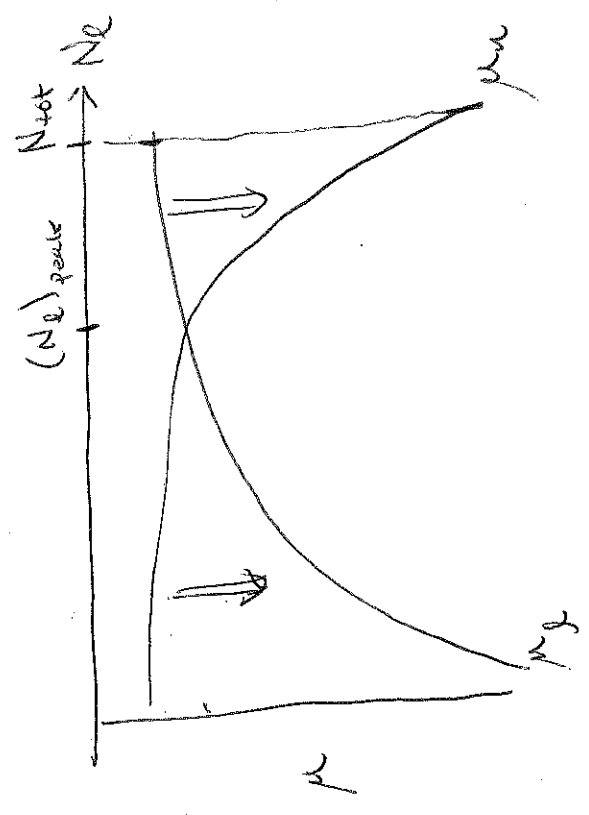
and

$$\Sigma u = \frac{(2\pi m k T)^{3/2} V_u}{h^3} e^{-mgH/kT}$$

let $\lambda_{th} = \frac{h}{\sqrt{2\pi m k T}}$

$$\mu_u = mgH + kT \ln \left(\frac{N_u}{V_u \lambda_{th}^3} \right)$$

$$\mu_l = kT \ln \left(\frac{N_l}{V_l \lambda_{th}^3} \right)$$



Our general conclusion is that

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T, V, N} = -kT \ln \left(\frac{\Sigma_j}{N_j} \right)$$