

$$(12) \quad L \leq -\Delta F$$

$$p \cdot dV = - \left. \frac{\partial F}{\partial V} \right|_T dV = -p = \left. \frac{\partial F}{\partial V} \right|_T$$

$$F = U - TS \quad \text{ideal gas}$$

$$= C_v T + W - (C_v T + R \log V + a) T \quad \text{eq 119}$$

$$= C_v T + W - T (C_p \log T - R \log p + a + R \log R) \quad \text{eq 120}$$

$$\text{eq (12)} \quad L \leq -\Delta F$$

$$\rightarrow pV(B) - pV(A) \leq F(A) - F(B) *$$

$$\text{define } \Phi = F + pV = U - TS + pV$$

* becomes

$$pV(B) + F(B) \leq pV(A) + F(A)$$

$$\Phi(B) \leq \Phi(A)$$

From both, ~~if Φ is fixed~~ to find an equilibrium state

for a system that has pressure & temperature fixed

we look for the minimum of the Gibbs free energy Φ .

For a general system find what remains constant as it transforms

be it volume, pressure, temperature etc & then minimize the correct

thermodynamic potential be it $F = U - TS$
 $\Phi = U - TS + pV$ etc.

(121) $\Phi = U - TS + pV$

$$\frac{\partial \Phi}{\partial p|_T} = \frac{\partial U}{\partial p|_T} - T \frac{\partial S}{\partial p|_T} + V + p \frac{\partial V}{\partial p|_T}$$

$$dQ = T dS = dU + p dV$$

$$T \frac{\partial S}{\partial p|_T} = \frac{\partial U}{\partial p|_T} + p \frac{\partial V}{\partial p|_T} \quad \text{putting this in the above}$$

$$\frac{\partial \Phi}{\partial p|_T} = \frac{\partial U}{\partial p|_T} - \frac{\partial U}{\partial p|_T} - p \frac{\partial V}{\partial p|_T} + V + p \frac{\partial V}{\partial p|_T} = V \quad \text{eq (123)}$$

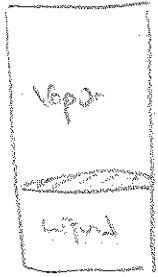
$$\frac{\partial \Phi}{\partial T|_p} = \frac{\partial U}{\partial T|_p} - S - T \frac{\partial S}{\partial T|_p} + p \frac{\partial V}{\partial T|_p}$$

$$T dS = dU + p dV$$

$$\therefore T \frac{\partial S}{\partial T|_p} = \frac{\partial U}{\partial T|_p} + p \frac{\partial V}{\partial T|_p} \quad \text{put in above}$$

$$\frac{\partial \Phi}{\partial T|_p} = \frac{\partial U}{\partial T|_p} - S - \frac{\partial U}{\partial T|_p} + p \frac{\partial V}{\partial T|_p} + p \frac{\partial V}{\partial T|_p}$$

$$\frac{\partial \Phi}{\partial T|_p} = -S$$



$$\Phi = U - TS + pV$$

$$\Rightarrow \Phi = \Phi_1 + \Phi_2$$

T same for both vapor & liquid
 + P same for both vapor & liquid at least at the surface or in zero gravity? Ah

i.e. on the space shuttle or w/ very little liquid

$$pV = RT \quad pV$$

$$\Phi = m_1 \phi_1(T) + m_2 \phi_2(T)$$

$$m_1 \rightarrow m_1 + \Delta m_1$$

$$\Phi' = (m_1 + \Delta m_1) \phi_1(T) + (m_2 - \Delta m_1) \phi_2(T)$$

↑
isothermal
trans

$$= \Phi + \Delta m_1 (\phi_1 - \phi_2)$$

As Φ was at a minimum

In order that the value of Φ' not be different from Φ

we must have $\phi_1 = \phi_2$

$$U_1 - TS_1 + pV_1 = U_2 - TS_2 + pV_2$$

$$U_2 - U_1 - T(S_2 - S_1) + p(V_2 - V_1) = 0$$

$\frac{\partial}{\partial T}$

$$\frac{1}{T} (U_2 - U_1) - (S_2 - S_1) - T \frac{1}{T} (S_2 - S_1) + \frac{dp}{dT} (V_2 - V_1) + p \frac{1}{T} (V_2 - V_1) = 0$$

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$$T \frac{ds}{dT} = \frac{du}{dT} + p \frac{dv}{dT} \quad \text{for both phases separately.}$$

$$\frac{du}{dT} - T \frac{ds}{dT} + p \frac{dv}{dT} = 0$$

$$\therefore -\underbrace{(s_2 - s_1)} + \frac{1}{T} (v_2 - v_1) = 0$$

$$\frac{1}{T}$$

$$\frac{dv}{dT} = \frac{1}{T(v_2 - v_1)}$$

$$\Phi = U - TS + pV$$

$$= C_v T + w - T(C_p \log T - R \log p + a + R \log R) + pV$$

$$= C_v T + w + pV - T(C_p \log T - R \log p + a + R \log R)$$

$$\parallel$$
$$RT$$

$$C_v + R = C_p$$

$$= C_p T + w - T(C_p \log T - R \log p + a + R \log R)$$

$$\Phi_i = \Phi_i(T, P, \mu_{i1}, \mu_{i2}, \dots, \mu_{in})$$

$$\Phi_i(T, P, \mu_{i1}, \mu_{i2}, \dots, \mu_{in}) = \left(\Phi_i(T, P, \mu_{i1}, \mu_{i2}, \dots, \mu_{in}) \right)^{\text{power} = 1}$$

\Rightarrow homogeneous of degree 1

$$\mu_{i1} = \mu_{i1} - \delta m \quad \mu_{i2} = \mu_{i2} + \delta m$$

$$\delta \Phi = \delta \Phi_i + \delta \Phi_j$$

$$= \frac{\partial \Phi_i}{\partial \mu_{i1}} (-\delta m) + \frac{\partial \Phi_j}{\partial \mu_{j2}} (\delta m)$$

$$= \frac{\partial \Phi_j}{\partial \mu_{j2}} \delta m - \frac{\partial \Phi_i}{\partial \mu_{i1}} \delta m = 0$$

$$\frac{\partial \Phi_j}{\partial \mu_{j2}} = \frac{\partial \Phi_i}{\partial \mu_{i1}}$$

How many equations like this do we have?

f phases
+ n components

Since each component, n of them, in a given phase i can go to any of the other $f-1$ phases (nothing happens if it goes to itself)

We have $n(f-1)$ equations for equilibrium.

each $\frac{\partial \xi_i}{\partial \Pi}$ depends only on ratios of the w_{ki} 's

The # of ratios there are like this are $n-1$

Then for all $\frac{\partial \xi_i}{\partial \Pi}$ derivatives the # of unknown ratios is

$$f(n-1)$$

w/ T, p we have $f(n-1) + 2$ variables

let $V = \# \text{ unknowns} - \# \text{ equations}$

$$= (n-1)f + 2 - n(f-1)$$

$$= n(f-1) - f + 2 - n(f-1) + n = 2 + n - f \quad \text{eq (131)}$$

Ex 1:

$$V = 2 + 1 - 1 = 2$$

Ex 2:

$$V = 2 + 2 - 1 = 3$$

Ex 3:

2 phases solid & liquid $f = 2$

1 comp $n = 1$

$$V = 2 + n - f = 2 + 1 - 2 = 1$$

Ex 4: $n = 1, f = 3$

$$V = 2 + n - f = 2 + 1 - 3 = 0$$

$$L = eV$$

Power exerted by DC current is given

$$\text{By } P = VI$$

$V = \text{voltage}$

$I = \text{current} = \text{charge/time}$

Thus work = voltage times charge

$$e = \text{charge}$$

$$U(T, e) = U(T) - eV(T)$$

$$\Delta U = -eV(T)$$

1 factor of Boltzmann

$$L - T \frac{dL}{dT} = -\Delta U$$

$$eV = T \frac{d(eV)}{dT} = +eV$$

$$V - T \frac{dV}{dT} = +V$$

eq 134

$$e = C_V(T)$$

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

energy of an isolated capacitor is

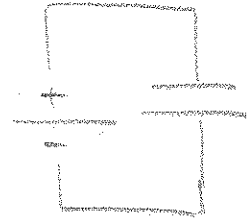
$$\frac{1}{2} \frac{e^2}{C}$$

$$dL = -d\left(\frac{1}{2} \frac{e^2}{C}\right) = \frac{1}{2} \frac{e^2}{C^2} dC$$

$$\text{But } e = C_V \quad dL = \frac{1}{2} \frac{C_V^2 v^2}{C^2} dC = \frac{1}{2} v^2 dC$$

$$\underbrace{U(T, e)}_{\text{new energy}} = U(T) - eU(T) = U(T) - C_V(T)U(T)$$

+ energy now present in condenser
heat released/absorbed when



$$dQ = dU + dL = d\left[U(T) - C_V(T)U(T) + \frac{1}{2}C_V v^2(T)\right] + \frac{1}{2}dC v^2$$

$$= dT \left[\frac{dU}{dT} - C_V \frac{dU}{dT} - C_V \frac{dU}{dT} + C_V \frac{dv}{dT} \right]$$

$$+ dC \left[-vU + \frac{1}{2}v^2 + \frac{1}{2}v^2 \right]$$

$$dS = \frac{dQ}{T} = \frac{dT}{T} \left[\frac{dU}{dT} - C_V \frac{dU}{dT} - C_V \frac{dU}{dT} + C_V \frac{dv}{dT} \right]$$

$$+ \frac{dC}{T} [v^2 - vU]$$

$$\frac{\partial}{\partial C} \left[\frac{\frac{dU}{dT} - C_V \frac{dU}{dT} - C_V \frac{dU}{dT} + C_V \frac{dv}{dT}}{T} \right] = \frac{\partial}{\partial T} \left[\frac{v^2 - vU}{T} \right]$$

$$+ \frac{1}{T} \left[-v \frac{dU}{dT} - U \frac{dv}{dT} + v \frac{dv}{dT} \right] = -\frac{(v^2 - vU)}{T^2} + \frac{2v v' - v'U - vU'}{T}$$

$$\Rightarrow -\frac{v}{T} \frac{dU}{dT} - \frac{U}{T} \frac{dv}{dT} + \frac{v}{T} \frac{dv}{dT} = \frac{2v}{T} \frac{dv}{dT} - \frac{U}{T} \frac{dv}{dT} - \frac{v}{T} \frac{dU}{dT} - \frac{v^2}{T^2} + \frac{vU}{T^2}$$

$$\frac{v^2}{T^2} - \frac{vU}{T^2} = \frac{v}{T} \frac{dv}{dT}$$

$$\frac{V}{T} - \frac{U}{T} = \frac{1}{T}$$

with the method

$$\Rightarrow V - \frac{U}{T} = 0 \quad \text{eq (31)}$$

Answer: 31

... ..

... ..

① Phase rule $V = 2 + n - f$

Saturated solution of a solid dissolved in the solvent

have 2 phases = liquid solution + solid (know this is correct pg 86 gives example of salt in H_2O)
 + 2 components $n = 2$ solid component
 + liquid component

$$V = 2 + 2 - 2 = 2$$

∴ we can specify 2 variables T + p arbitrary.

I would think the correct answer would be T only

(I know that increasing the temperature increases the solubility)

but I am not sure about the pressure)

② I am told the amounts of H_2O + Air

Assume Air contains N_2, O_2, H_2 only + H_2O vapor

Then $f = \#$ of phases = 2

$n = \#$ of components = 4

$$V = 2 + 4 - 2 = 4$$

But we are told the amount of H_2O + Air so we are told

$$M_{H_2O} =$$

$$\textcircled{3} \quad V(t) = V_0 + v_1 t + v_2 t^2 \quad \begin{array}{l} V_0 = .924 \\ v_1 = .0015 \\ v_2 = .0000061 \end{array}$$

$$[t] = \text{sec}$$

$$[V] = \text{volts}$$

$$e = 1 \text{ coulomb}$$

$$\text{From pg 96} \quad \Delta Q = \Delta V + \Delta L$$

$$\parallel -eV(t) + eV(t)$$

But from eq of Helmholtz $U(t) = V - T \frac{dV}{dt}$. Thus eq of Helmholtz gives a functional form for the energy lost per unit charge

$$U(t) = V_0 + v_1 t + v_2 t^2 - T [v_1 + 2v_2 t] \quad [T] = \text{of}$$

$$= (V_0 + T v_1) + (v_1 - 2v_2 T) t + v_2 t^2$$

$$\text{Then} \quad \Delta Q = -e \left(V - T \frac{dV}{dt} \right) + eV$$

$$= eT \frac{dV}{dt} \quad \therefore \text{but need } U(t) \text{ actual}$$

$$\Delta Q = eT \frac{dV}{dt} \quad ? = eT (v_1 + 2v_2 t)$$

$$e = 1 \text{ coulomb}$$

$$T = (273.15 + 13)^\circ \text{K}$$

$$t = 18^\circ \text{C}$$

In eq (136) if $K(T) \ll 1$

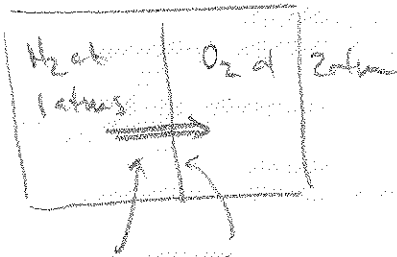
$$[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r} = K(T) [B_1]^{m_1} [B_2]^{m_2} \dots [B_s]^{m_s}$$

$$\rightarrow \text{generally } [A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r} \ll 1$$

So reaction is shifted to Right

$$[A] = \frac{\text{moles of A}}{\text{Volume}}$$

$$[A]M = \frac{\text{mass of A}}{\text{Volume}}$$



flux of
H₂ molecules

Semipermeable to H₂

$$-P V_i$$

$$= -n_i RT$$

$$L_I = -RT \sum_{i=1}^n n_i$$

$$P V_i = n_i RT$$

$$P \propto \frac{n}{V} RT$$

$$\Rightarrow P \propto [A] RT$$

pressure is proportional to the
mole concentration,

To insure that we get n_1 moles in the 1st cylinder which we can extend to ∞ we

must require $V_1[B_1] = n_1 = V_1 = \frac{n_1}{[B_1]}$

$[B_1]$ concentration of element B_1

$$L = L_I + L_{II}$$

$$= RT \left(\sum_{j=1}^s n_j - \sum_{i=1}^s n_i \right) = -\Delta F \quad \text{as this process is isothermal + reversible}$$

$$F_I = n_1 \left\{ C_{v,1} T + w_1 - T(C_{v,1} \log T + R \log \left(\frac{1}{\lambda_{1,0}} \right) + a_1 \right\}$$

$$= n_1 \left\{ C_{v,1} T + w_1 - T(C_{v,1} \log T - R \log \lambda_1 + a_1 \right\}$$

Free energy initially

$$F_I = \sum_{i=1}^s n_i \left\{ C_{v,i} T + w_i - T(C_{v,i} \log T - R \log \lambda_i + a_i \right\}$$

$$F_F = \sum_{j=1}^s n_j \left\{ C_{v,j} T + w'_j - T(C_{v,j} \log T - R \log [B_j] + a'_j \right\}$$

$$F_I - F_F = L$$

$$RT \left(\sum_{j=1}^s n_j - \sum_{i=1}^s n_i \right) = \sum_{i=1}^s n_i \left\{ C_{v,i} T + w_i - T(C_{v,i} \log T - R \log \lambda_i + a_i \right\}$$

$$- \sum_{j=1}^s n_j \left\{ C_{v,j} T + w'_j - \dots \right\}$$

$$RT \left(\sum_{j=1}^s w_j - \sum_{i=1}^r n_i \right) =$$

$$\sum_{i=1}^r \frac{n_i C_{v,i} T + n_i w_i - n_i T C_{v,i} \log T + n_i R \log(A_i) + n_i a_i T}{RT}$$

$$- \sum_{j=1}^s \frac{w_j C_{v,j} T + w_j w_j - w_j T C_{v,j} \log T + w_j R \log(B_j) + w_j a_j T}{RT}$$

$\div RT$

$$\Rightarrow \sum_{j=1}^s w_j - \sum_{i=1}^r n_i =$$

$$\sum_{i=1}^r \frac{n_i C_{v,i}}{R} + \frac{n_i w_i}{RT} - \frac{n_i C_{v,i} \log T}{R} + n_i \log(A_i) + \frac{n_i a_i}{R}$$

$$- \sum_{j=1}^s \frac{w_j C_{v,j}}{R} + \frac{w_j w_j}{RT} - \frac{w_j C_{v,j} \log T}{R} + w_j \log(B_j) + \frac{w_j a_j}{R}$$

$$\Rightarrow \sum_{i=1}^r n_i \log(A_i) - \sum_{j=1}^s w_j \log(B_j)$$

$$= - \sum_{i=1}^r \frac{n_i C_{v,i}}{R} + \frac{n_i w_i}{RT} - \frac{n_i C_{v,i} \log T}{R} + \frac{n_i a_i}{R} + n_i$$

$$+ \sum_{j=1}^s \frac{w_j C_{v,j}}{R} + \frac{w_j w_j}{RT} - \frac{w_j C_{v,j} \log T}{R} + \frac{w_j a_j}{R} + w_j$$

$$\Rightarrow \log \frac{[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r}}{[B_1]^{m_1} [B_2]^{m_2} \dots [B_s]^{m_s}} =$$

$$\left. \sum_{i=1}^r \frac{n_i C_{v,i} \log T}{R} - \sum_{j=1}^s \frac{m_j C_{v,j} \log T}{R} \right\} \text{ on temperature dependence}$$

$$- \left. \sum_{i=1}^r \frac{n_i \omega_i}{RT} + \sum_{j=1}^s \frac{m_j \omega_j}{RT} \right\} \text{ second temp depend}$$

$$- \left. \sum_{i=1}^r \left(\frac{n_i C_{v,i}}{R} + \frac{n_i a_i}{R} + n_i \right) \right\} \text{ 3rd temp depend (Now)}$$

$$+ \sum_{j=1}^s \left(\frac{m_j C_{v,j}}{R} + \frac{m_j a_j}{R} + m_j \right)$$

$$\Rightarrow \log (\quad) =$$

$$\log \frac{T^{\frac{n_1 C_{v,1}}{R}} T^{\frac{n_2 C_{v,2}}{R}} T^{\frac{n_3 C_{v,3}}{R}} \dots T^{\frac{n_r C_{v,r}}{R}}}{T^{\frac{m_1 C_{v,1}}{R}} T^{\frac{m_2 C_{v,2}}{R}} \dots T^{\frac{m_s C_{v,s}}{R}}}$$

$$- \sum_{i=1}^r \log \exp \left(\frac{n_i \omega_i}{RT} \right) + \sum_{j=1}^s \log \left(\exp \left(\frac{m_j \omega_j}{RT} \right) \right)$$

$$- \sum_{i=1}^r \log \left(\exp \left(\frac{n_i c_i}{R} + \frac{n_i a_i}{R} + n_i \right) \right) \\ + \sum_{j=1}^s \log \left(\exp \left(\frac{m_j c_j}{R} + \frac{m_j a_j}{R} + m_j \right) \right)$$

$$\Rightarrow \log \left(\right) = \log T^{\frac{1}{R} \sum_{i=1}^r n_i c_i - \frac{1}{R} \sum_{j=1}^s m_j c_j}$$

$$+ \log \left[\frac{\exp \left(\sum_{j=1}^s \frac{m_j c_j}{R} \right)}{\exp \left(\sum_{i=1}^r \frac{n_i c_i}{R} \right)} \right] + \log \left[\frac{\exp \left(\sum_{j=1}^s \frac{m_j c_j}{R} + \frac{m_j a_j}{R} + m_j \right)}{\exp \left(\sum_{i=1}^r \frac{n_i c_i}{R} + \frac{n_i a_i}{R} + n_i \right)} \right]$$

taking exponentials

$$\frac{[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r}}{[B_1]^{m_1} [B_2]^{m_2} \dots [B_s]^{m_s}} =$$

$$\exp \left[\frac{1}{R} \left\{ \sum_{j=1}^s \sum_{i=1}^s m_j (R + c_j + a_j) - \sum_{i=1}^r n_i (R + c_i + a_i) \right\} \right]$$

$$T \left[\frac{1}{R} \left(\sum_{i=1}^S n_i c_i - \sum_{j=1}^S m_j c_j \right) \right]$$

$$\exp \left[\frac{1}{RT} \left(\sum_{j=1}^S m_j w_j - \sum_{i=1}^S n_i w_i \right) \right]$$

pulling out A minus gives eq (139)

$$p_i V = n_i R T \quad p = \frac{nRT}{V}$$

$$p = \sum p_i = \frac{RT}{V} \sum n_i$$

$$F = U - TS$$

$$\Phi = U - TS + pV$$

Free energy

$$G_i T + W_i - T(G_i \log T - R \log(A_i) + a_i)$$

$$V(A_i) \{ G_i T + W_i - T(G_i \log T - R \log(A_i) + a_i) \}$$

$$F = V \sum_{i=1}^r (A_i) \{ G_i T + W_i - T(G_i \log T - R \log(A_i) + a_i) \}$$

$$+ V \sum_{j=1}^s (B_j) \{ G_j T + W_j - T(G_j \log T - R \log(B_j) + a_j) \} \quad \text{eq (10)}$$

$$\delta F = - \frac{\delta F}{\delta(A_1)} \epsilon_{A_1} - \frac{\delta F}{\delta(A_2)} \epsilon_{A_2} - \frac{\delta F}{\delta(A_3)} \epsilon_{A_3} - \dots - \frac{\delta F}{\delta(A_r)} \epsilon_{A_r}$$

$$+ \frac{\delta F}{\delta(B_1)} \epsilon_{B_1} + \frac{\delta F}{\delta(B_2)} \epsilon_{B_2} + \dots + \frac{\delta F}{\delta(B_s)} \epsilon_{B_s} = 0$$

$$\Rightarrow - (A_1) \frac{\delta F}{\delta(A_1)} - (A_2) \frac{\delta F}{\delta(A_2)} - \dots - (A_r) \frac{\delta F}{\delta(A_r)} + (B_1) \frac{\delta F}{\delta(B_1)} + (B_2) \frac{\delta F}{\delta(B_2)} + \dots + (B_s) \frac{\delta F}{\delta(B_s)} = 0$$

From (14b)

$$\frac{\partial F}{\partial A_i} = V \sum_{i=1}^r \left\{ C_{v_i} + w_i - T(C_{v_i} \log T - R \log [A_i] + a_i) \right\} \\ + V \sum_{i=1}^r \frac{[A_i]}{[A_i]} \left\{ \frac{RT}{[A_i]} \right\} = VRT$$

→ This is incorrect. You are taking the derivative of the concentration $[A_i]$ not the summative variable $[A_i]$.
The above is taking the derivative of the summative index $[A_i]$

$$\frac{\partial F}{\partial A_i} = V \left\{ C_{v_i} T + w_i - T(C_{v_i} \log T - R \log [A_i] + a_i) \right\} \\ + V [A_i] \left(\frac{RT}{[A_i]} \right)$$

$$= V \left\{ C_{v_i} T + w_i - T(C_{v_i} \log T - R \log [A_i] + a_i) \right\} + VRT$$

$$\downarrow \text{sim } \frac{\partial F}{\partial [B_i]} =$$

Then

$$\delta F = - [A_1] V \left[C_{v_1} T + w_1 - T(C_{v_1} \log T - R \log [A_1] + a_1) + RT \right] \\ - [A_2] V \left[C_{v_2} T + w_2 - T(C_{v_2} \log T - R \log [A_2] + a_2) + RT \right] \\ \dots$$

$$- [A_r] v [c_{r,T} T + w_r - T(c_{r,T} \log T - R \log [A_r] + a_r) + RT]$$

$$+ [B_s] v [c'_{s,T} T + w'_s - T(c'_{s,T} \log T - R \log [B_s] + a'_s) + RT]$$

$$+ \dots$$

$$+ [B_s] v [c'_{s,T} T + w'_s - T(c'_{s,T} \log T - R \log [B_s] + a'_s) + RT] = 0$$

$$= - \sum_{i=1}^r n_i \{ c_{i,T} T + w_i - T(c_{i,T} \log T - R \log [A_i] + a_i) + RT \}$$

$$+ \sum_{j=1}^s n_j \{ c'_{j,T} T + w'_j - T(c'_{j,T} \log T - R \log [B_j] + a'_j) + RT \} = 0$$

$$\frac{1}{k(T)} \sum$$

$$k(T) = e$$

$$\Delta U = \sum_{j=1}^s n_j (c'_{j,T} T + w'_j) - \sum_{i=1}^r n_i (c_{i,T} T + w_i)$$

$$H = -\Delta U = \sum_{i=1}^r n_i (c_{i,T} T + w_i) - \sum_{j=1}^s n_j (c'_{j,T} T + w'_j)$$

$$\frac{1}{dT} \log k(T) = \frac{1}{TR} \left(\sum_{i=1}^r c_{i,T} n_i - \sum_{j=1}^s c'_{j,T} n_j \right) + \frac{1}{RT^2}$$

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4

To evaluate the logarithmic derivative of $H(T)$ write

$$H(T) = G_T e^{-\frac{G_2}{RT}}$$

$$\log(H(T)) = \log G + G_2 \log T - \frac{G_2}{RT} \log e$$

$$= \log G + G_2 \log T - \frac{G_2}{RT}$$

$$\frac{1}{T} \log(H(T)) = \frac{G_2}{T} + \frac{G_2}{RT^2}$$

$$= \frac{1}{RT} \left(\sum_{i=1}^r c_{v,i} n_i - \sum_{j=1}^s c_{v,j} m_j \right) + \frac{1}{RT^2} \left(\sum_{i=1}^r n_i w_i - \sum_{j=1}^s m_j w_j \right)$$

$$= \frac{\sum_{i=1}^r T c_{v,i} n_i + n_i w_i - \sum_{j=1}^s T c_{v,j} m_j + m_j w_j}{RT^2}$$

$$RT^2$$

$$= \frac{H}{RT^2}$$

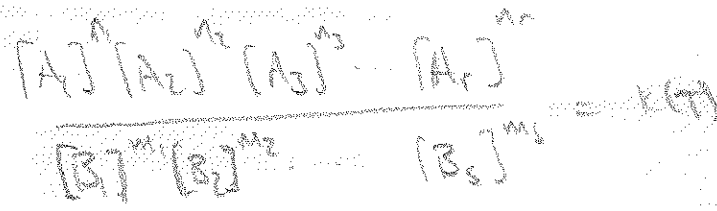
Note $H = H(T)$

Thus there is a temperature dependence there also.

$$\text{If } n_1 + n_2 + \dots + n_r < m_1 + m_2 + \dots + m_s$$

Then shifting eq to the right \Rightarrow increases pressure

Increasing pressure

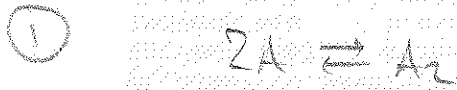


Compress the system, shrinking $V \Rightarrow [A] \downarrow [B] \uparrow$ increase

Since $m_1 + m_2 + \dots + m_s > n_1 + n_2 + \dots + n_r$

L.H.S decreases to prevent this $[A] \uparrow$ while $[B]$ stays

the same \Rightarrow Reaction shifts towards the reactants



$$\frac{[A]^2}{[A_2]} = K(T) \quad \text{law of mass action}$$

$$[A] = \frac{\# \text{ moles}}{\text{Volume}} \quad K(18^\circ\text{C}) = 17 \cdot 10^{-4}$$

Dalton's law of partial pressure says that

$$P = P_{\text{total}} = P_A + P_{A_2}$$

W/ P_A = partial pressure of A

+ P_{A_2} = partial pressure of A_2

Then $P_A = \frac{n_A RT}{V} = [A] RT$ $P_{A_2} = [A_2] RT$

$$P = ([A] + [A_2]) RT$$

$$[A]^2 = K(T) [A_2] \quad \text{put in above}$$

$$P = \left([A] + \frac{[A]^2}{K(T)} \right) RT \Rightarrow \frac{[A]^2}{K(T)} + [A] - \frac{P}{RT} = 0$$

quadratic eq for [A]

$$\frac{P}{RT} = \frac{1.01 \cdot 10^5 \text{ Pa}}{(8.314 \text{ J/mol} \cdot \text{K}) (273.15 + 18)} = \frac{41.72 \text{ mol}^3}{\text{mol}} = 41.72 \frac{\text{mol}}{\text{m}^3}$$

$$[A] = \frac{-1 \pm \sqrt{1 - 4\left(\frac{1}{K_1}\right)\left(-\frac{P}{RT}\right)}}{2\left(\frac{1}{K_1}\right)} = \frac{-1 \pm \sqrt{1 + \frac{4}{K_1}\left(\frac{P}{RT}\right)}}{\frac{2}{K_1}}$$

$$= 8.413 \cdot 10^{-2} \text{ mol/V}$$

$$[A_2] = \frac{RT}{P} - [A] = 41.72 - 8.413 \cdot 10^{-2} = 41.64 \frac{\text{mol}}{\text{m}^3}$$

check $\frac{[A]^2}{[A_2]} \stackrel{?}{=} 1.6997 \cdot 10^{-4} \checkmark$

went percentage of A.

$$n_A = [A]V$$

$$n_{A_2} = [A_2]V$$

$$\% A = \frac{n_A}{n_A + n_{A_2}} = \frac{[A]V}{[A]V + [A_2]V}$$

$$= \frac{[A]}{[A] + [A_2]} = 2.01 \cdot 10^{-3}$$

$$= .201 \cdot \%.$$

② $H = 50,000 \text{ cal/mol}$ why no temperature dependence (independent of T)

degree of dissociation =

$H > 0 \Rightarrow$ exothermic reaction expect raising the temp to shift towards

29 MS \rightarrow

the left & we shall have an increase in the concentration of A

$$\frac{d}{dT} (\log k(T)) = \frac{H}{RT^2}$$

$$\log k(T) = C_1 + \frac{-H}{RT}$$

$$k(T) = C_2 e^{-\frac{H}{RT}}$$

$$\therefore \frac{[A]^2}{[A_2]} = C_2 e^{-\frac{H}{RT}} = k(T)$$

what is C_2 ? know

$$k(T=18^\circ\text{C}=291.15) = 1.7 \cdot 10^{-4}$$

$$RT = (8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(291.15 \text{ K}) = 2.42 \cdot 10^3 \frac{\text{J}}{\text{mol}}$$

$$R = .2388 \text{ cal}$$

$$\therefore RT = 5.78 \cdot 10^3 \frac{\text{cal}}{\text{mol}}$$

$$\frac{H}{RT} = \frac{50,000 \frac{\text{cal}}{\text{mol}}}{5.78 \cdot 10^3 \frac{\text{cal}}{\text{mol}}} = 8.64 \cdot 10^1$$

{ If I write the eq for }

the chemical reaction

in the other order, I would

flip the concentration ratio

$\frac{[A]^2}{[A_2]}$ but would not

change the term $e^{-\frac{H}{RT}}$

which would give a different

equation, where is

the inconsistency, would be

that H should be given

as the heat of reaction from left

to right, which if we switch

the order of the chemical

equation we switch

the sign of H .

$$C_2 \exp(-8.64 \cdot 10^4) = 1.7 \cdot 10^{-4}$$

$$C_2 = \exp(8.64 \cdot 10^4) 1.7 \cdot 10^{-4} = 5.66 \cdot 10^{33}$$

Hyge !! can't!

$$\begin{aligned} \therefore \text{Then } k(T=19^\circ\text{C}) &= 5.66 \cdot 10^{33} \exp\left(\frac{-H}{RT}\right) \\ &= 2.07 \cdot 10^{-4} \leftarrow \text{new } k(T) \end{aligned}$$

Find % of A

$$P = P_A + P_{A_2} = [A]RT + [A_2]RT$$

$$[A] + [A_2] = \frac{P}{RT} + [A]^2 = k(T)[A_2]$$

$$[A] + \frac{[A]^2}{k(T)} = \frac{P}{RT} \Rightarrow \frac{[A]^2}{k(T)} + [A] - \frac{P}{RT} = 0$$

$$[A] = \frac{-1 \pm \sqrt{1 - 4\left(\frac{1}{k(T)}\right)\left(\frac{P}{RT}\right)}}{2\left(\frac{1}{k(T)}\right)} = 9.26 \cdot 10^{-2} > 8.41 \cdot 10^{-2}$$

yes
 ↓
 old value
 ↓
 prob. 1

$$[A_2] = \frac{[A]^2}{k(T)} \Rightarrow [A_2] = 4.14 \cdot 10^1 < 4.16 \cdot 10^1$$

↑
 yes
 correct
 direction

↑
 old value
 prob. 2

$$\% A = 2.22 \cdot 10^{-3} \Rightarrow .22 \% \quad \text{increased As it should have.}$$

$$U = U(p, T, \frac{N_1}{N_0}, \frac{N_2}{N_0}, \dots, \frac{N_g}{N_0})$$

↑ ↑
 Spring constant or amount of compression Amt of Bond energy

$$= U_0(p, T) + \frac{N_1}{N_0} U_1(T, p) + \frac{N_2}{N_0} U_2(T, p) + \dots + \frac{N_g}{N_0} U_g(T, p)$$

Then

$$U = N_0 U_0(T, p) + N_1 U_1(T, p) + N_2 U_2(T, p) + \dots + N_g U_g(T, p)$$

$$= \sum_{i=0}^g N_i U_i(T, p)$$

$V =$

Why don't we have to worry about the other terms, i.e. the "bonded" solvent terms?

$$dS = \frac{dU}{T} = \frac{1}{T} (dU + p dV)$$

micro

$$= \frac{1}{T} \left(\sum_{i=0}^g N_i dU_i + p \sum_{i=0}^g N_i dV_i \right)$$

$$= \sum_{i=0}^g N_i \left(\frac{dU_i + p dV_i}{T} \right) \quad \text{eq (10)}$$

Set of fun S: $dS = \frac{dU + p dV}{T}$

$$S = \sum_{i=0}^g N_i S_i(T, p) + C(N_0, N_1, \dots, N_g)$$

$$S_i = C_{p,i} \log T - R \log p_i + a_i + R \log R$$

$$P_i = \frac{P N_i}{N_1 + N_2 + \dots + N_g}$$

$$S = \sum_{i=0}^g N_i \left(C_{p,i} \log T - R \log \left(\frac{P N_i}{N_1 + N_2 + \dots + N_g} \right) + a_i + R \log R \right)$$

$$= \sum_{i=0}^g N_i (C_{p,i} \log T - R \log P + a_i + R \log R$$

$$- R \sum_{i=0}^g N_i \log \left(\frac{N_i}{N_1 + N_2 + \dots + N_g} \right)$$

$$S_i = C_{p,i} \log T - R \log p_i + a_i + R \log R$$

$$+ C(N_0, N_1, \dots, N_g) = -R \sum_{i=0}^g N_i \log \left(\frac{N_i}{N_0 + N_1 + \dots + N_g} \right)$$

eq (154)

Applies to original solution also

$$S = \sum_{i=0}^g N_i S_i(T, p) - R \sum_{i=0}^g N_i \log \left(\frac{N_i}{N_0 + N_1 + \dots + N_g} \right)$$

eq (155)

Remembering $N_i \ll N_0, \dots, N_g \ll N_0$

$$N_0 \log \left(\frac{N_0}{N_0 + N_1 + \dots + N_g} \right)$$

$$= N_0 \log \left(\frac{1}{1 + \frac{N_1}{N_0} + \frac{N_2}{N_0} + \dots + \frac{N_g}{N_0}} \right)$$

$$\approx N_0 \left(-\frac{N_1}{N_0} - \frac{N_2}{N_0} - \dots - \frac{N_g}{N_0} \right)$$

$$= -N_1 - N_2 - \dots - N_g$$

$$+ N_i \log \left(\frac{N_i}{N_0 + N_1 + \dots + N_g} \right)$$

$$= N_i \log \left(\frac{\frac{N_i}{N_0}}{1 + \frac{N_1}{N_0} + \dots + \frac{N_g}{N_0}} \right)$$

$$\approx N_i \left[\log \left(\frac{N_i}{N_0} \right) \right]$$

$$\log \left(\frac{1}{1+k} \right) = -\log(1+k)$$

$$= 0 - \frac{1}{1+k} k$$

$$= -\frac{1}{(1+k)^2} k^2 + O(k^3)$$

$$= -k + k^2 + O(k^3)$$

$$\log \left(\frac{k}{1+k} \right) = \log k - \log(1+k)$$

$$= \log k - k + k^2 - O(k^3)$$

$$S = \sum_{i=0}^g N_i S_i(\text{TP}) - R(-N_1 - N_2 - \dots - N_g) - R \sum_{i=1}^g N_i \log \left(\frac{N_i}{N_0} \right)$$

$$= N_0 S(\text{TP}) + \sum_{i=1}^g (S_i + R) N_i - R \sum_{i=1}^g N_i \log \left(\frac{N_i}{N_0} \right)$$

Defining the f_i 's

$$G_0(T, P) = G(T, P)$$

$$G_1(T, P) = \Delta_1(T, P) + R$$

$$\vdots$$

$$G_g(T, P) = g(T, P) + R$$

$$S = \sum_{i=0}^g N_i G_i(T, P) - R \sum_{i=1}^g N_i \log \frac{N_i}{N_0} \quad \text{eq (157)}$$

$$F = U - TS$$

$$F = \sum_{i=0}^g N_i u_i(T) - T \sum_{i=0}^g N_i G_i(T) + RT \sum_{i=1}^g N_i \log \frac{N_i}{N_0}$$

$$= \sum_{i=0}^g N_i \underbrace{[u_i(T) - T G_i(T)]}_{f_i(T)} + RT \sum_{i=1}^g N_i \log \frac{N_i}{N_0}$$

$$= \sum_{i=0}^g N_i f_i(T) + RT \sum_{i=1}^g N_i \log \frac{N_i}{N_0} \quad \text{eq 159}$$

$$\bar{F} = F + PV = U - TS + PV$$

$$= \sum_{i=0}^g N_i (u_i(T) - T G_i(T)) + RT \sum_{i=1}^g N_i \log \left(\frac{N_i}{N_0} \right)$$

$$+ P \sum_{i=0}^g N_i v_i(T) = \sum_{i=0}^g N_i (u_i(T) - T G_i(T) + P v_i(T)) + RT \sum_{i=1}^g N_i \log \left(\frac{N_i}{N_0} \right)$$

$$\text{eq (161)}$$

07-08-01 1

pg 119 Fermi

$$[P] = \frac{\rho g L}{L^2} = \frac{\rho L}{L^2} = \frac{\rho}{L}$$



Then pressure = $\frac{\text{weight}}{A} = \rho h g$ $\frac{\rho}{L^3} \cdot L \cdot L = \frac{\rho}{L^2}$ ✓

Work done by isothermal reversible process = $-\Delta F$

pg 120 Fermi

Free energy $F = \sum_{i=0}^2 N_i f_i(T) + RT \sum_{i=1}^2 N_i \log\left(\frac{N_i}{N_0}\right)$ } Free energy of solution

Free energy of solvent $N_0' f_0$

$$F_{\text{total}} = (N_0 + N_0') f_0 + N_1 f_1 + N_2 f_2 + RT \sum_{i=1}^2 N_i \log\left(\frac{N_i}{N_0}\right)$$

$$dF = \frac{\partial F_{\text{total}}}{\partial N_0} dN_0 + \frac{\partial F_{\text{total}}}{\partial N_0'} dN_0'$$

$$= \frac{\partial F}{\partial N_0} dN_0 - \frac{\partial F}{\partial N_0'} dN_0'$$

$$= \left(\frac{f_0}{N_0} + RT \sum_{i=1}^2 \frac{N_i}{N_0} \left(-\frac{N_i}{N_0^2} \right) \right) dN_0 - f_0 dN_0'$$

$$dF = RT \sum_{i=1}^g N_i \frac{1}{N_0} \left(\frac{N_i}{N_0} \right) dN_0$$

$$= RT \sum_{i=1}^g \frac{N_i}{N_0} dN_0 = \frac{RT}{N_0} \sum_{i=1}^g N_i dN_0$$

$$P V_0 dN_0 = \frac{RT}{N_0} \sum_{i=1}^g N_i dN_0$$

$$P V_0 N_0 = RT \sum_{i=1}^g N_i$$

$$PV = RT \sum_{i=1}^g N_i \quad \text{eq. (165)}$$

$$P = \frac{RT}{V} \sum_{i=1}^g N_i$$

Eq. 123 Form

$$1) = 10^7 \text{ ergs}$$

1 mole solute per liter H_2O

$$R = 8.314 \text{ J/mol}\cdot\text{K} =$$

$$P_{\text{normal}} = \frac{R(273.15 + 15)(1 \text{ mol})}{1000 \text{ cm}^3} = \frac{R(288.15)}{1000 \text{ cm}^3}$$

$$\{ 1 \text{ liter} = 1000 \text{ cm}^3 \}$$

$$= \frac{(8.314 \cdot 10^7)(288.15) \text{ ergs}}{10^3 \text{ cm}^3}$$

$$= 2.39 \cdot 10^7 \text{ ergs/cm}^3 = 2.39 \cdot 10^7 \frac{\text{dynes}}{\text{cm}^2}$$

$$\{ 1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa} \}$$

What is the name for the unit $\frac{\text{dyne}}{\text{cm}^2} = ?$ bar, torr?

$$1 \text{ dyne} = \frac{\text{cm}}{\text{s}^2} \text{ g} = 10^{-2} 10^{-3} \frac{\text{m kg}}{\text{s}^2}$$

$$= 10^{-5} \text{ N}$$

Then $P_{\text{normal}} = 2.39 \cdot 10^7 \cdot 10^{-5} \frac{\text{N}}{(10^{-2})^2 \text{ m}^2}$

$$= 2.39 \cdot 10^7 \cdot 10^{-5} \cdot 10^4 \text{ Pa}$$

$$= 2.39 \cdot 10^6 \text{ Pa} = 23.6 \text{ atm}$$

When energy & entropy can be written as fns of temperature only,
The equilibrium configuration is given as the minimum of the free energy

$$(157) \quad F = \sum_{i=0}^r N_i F_i + RT \sum_{i=0}^r N_i \log\left(\frac{N_i}{N_0}\right) \\ + \sum_{j=1}^s N_j' F_j' + RT \sum_{j=1}^s N_j' \log\left(\frac{N_j'}{N_0}\right)$$

$$= N_0 F_0 + \sum_{i=0}^r N_i F_i + \sum_{j=1}^s N_j' F_j' + RT \left\{ \sum_{i=0}^r N_i \log\left(\frac{N_i}{N_0}\right) + \sum_{j=1}^s N_j' \log\left(\frac{N_j'}{N_0}\right) \right\} \quad \text{eq 168}$$

$$\delta F = -k N_0 \frac{\delta F}{\delta N_0} - k \sum_{i=1}^r N_i \frac{\delta F}{\delta N_i} + k \sum_{j=1}^s N_j' \frac{\delta F}{\delta N_j'} = 0$$

$$\text{Now } \frac{\delta F}{\delta N_0} = F_0 + RT \left\{ \sum_{i=1}^r N_i \frac{1}{\left(\frac{N_i}{N_0}\right)} \left(-\frac{N_i}{N_0^2}\right) + \sum_{j=1}^s N_j' \frac{1}{\left(\frac{N_j'}{N_0}\right)} \left(-\frac{N_j'}{N_0^2}\right) \right\}$$

$$= F_0 - RT \left\{ \sum_{i=1}^r \frac{N_i}{N_0} + \sum_{j=1}^s \frac{N_j'}{N_0} \right\}$$

These terms are discarded.
As insignificant.

$$\frac{\delta F}{\delta N_i} = F_i + RT \left(\log \frac{N_i}{N_0} + N_i \frac{1}{\left(\frac{N_i}{N_0}\right)} \frac{1}{N_0} \right)$$

$$= F_i + RT \left(1 + \log\left(\frac{N_i}{N_0}\right) \right)$$

$$\frac{\delta F}{\delta N_j'} = F_j' + RT \left(1 + \log\left(\frac{N_j'}{N_0}\right) \right)$$

Thus

$$SF = -n_0(T_0)$$

$$- \sum_{i=1}^r n_i (T_i + RT + RT \log \left(\frac{N_i}{N_0} \right))$$

$$+ \sum_{j=1}^s w_j (T_j' + RT + RT \log \left(\frac{N_j'}{N_0} \right)) = 0$$

$$\Rightarrow RT \sum_{i=1}^r n_i \log \left(\frac{N_i}{N_0} \right) - RT \sum_{j=1}^s w_j \log \left(\frac{N_j'}{N_0} \right) = \sum_{j=1}^s w_j (T_j' + RT) - \sum_{i=1}^r n_i (T_i + RT)$$

$-n_0 T_0$

$$\Rightarrow \log \left[\frac{\left(\frac{N_1}{N_0} \right)^{n_1} \left(\frac{N_2}{N_0} \right)^{n_2} \dots \left(\frac{N_r}{N_0} \right)^{n_r}}{\left(\frac{N_1'}{N_0} \right)^{w_1} \left(\frac{N_2'}{N_0} \right)^{w_2} \dots \left(\frac{N_s}{N_0} \right)^{w_s}} \right] = \frac{\sum_{j=1}^s w_j (T_j' + RT) - \sum_{i=1}^r n_i (T_i + RT) - n_0 T_0}{RT}$$

$$\frac{\left(\frac{N_1}{N_0} \right)^{n_1} \left(\frac{N_2}{N_0} \right)^{n_2} \dots \left(\frac{N_r}{N_0} \right)^{n_r}}{\left(\frac{N_1'}{N_0} \right)^{w_1} \left(\frac{N_2'}{N_0} \right)^{w_2} \dots \left(\frac{N_s}{N_0} \right)^{w_s}} = K(T) \quad \text{eq 169}$$

~~If $N_0 = 0$~~ If we divide the solution \uparrow N_0

Then each fraction decreases & the total fraction increases

$$\frac{N_i}{N_0}$$

or decreases depending on $w_1 + w_2 + \dots + w_s \geq n_1 + \dots + n_r$

If $w_1 + w_2 + \dots + w_s > n_1 + \dots + n_r$ Then total fraction increases

$\Rightarrow N_1, N_2 \dots, N_r$ to decrease \Rightarrow shifts towards

or N_1', N_2', \dots, N_s' increase \rightarrow reaction shifted towards products

If $n_1 + n_2 + \dots + n_s < n_1 + n_2 + \dots + n_r$ Then total reaction decreases

$\therefore N_1, N_2 \dots, N_r$ increases

or N_1', N_2', \dots, N_s' decrease favor products

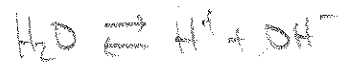
In each case we favor more moles or dissociation

M_{H_2O} atomic weight $H_2O = 16 + 2 = 18 \text{ g/mol}$

1 cc = 1 gm $H_2O \Rightarrow N_{H_2O} = \frac{1}{18}$ mol H_2O molecules

$$\frac{N_{H^+}}{N_{H_2O}} = 18 N_{H^+}$$

$$\frac{N_{OH^-}}{N_{H_2O}} = 18 N_{OH^-}$$



$$\frac{1}{18[N_{H^+}] 18[N_{OH^-}]} = K(T)$$

$$[H^+][OH^-] = \frac{1}{18^2 K(T)} \quad \text{eq 171}$$

Why do we look at \bar{F} here & not F , I think it is because for chemical equilibrium the volume & pressure will not change much as we fluxate around equilibrium. (But then I thought one uses Free energy F when we have a constant temperature situation)

~~→~~ When we dissolve solute Both volume (pressure) & temp do not fluxate. Thus we give free energy $\bar{F} = U - TS + pV$

eq (167)

$$\bar{F}_A = N_A \left\{ f_A(T) + pV_A(T) \right\} + N_1 \left\{ f_1(T) + pV_1(T) \right\} + RT N_1 \log \left(\frac{N_1}{N_A} \right) \quad \text{eq (174)}$$

$$\bar{F}_B = N_B \left\{ f_B(T) + pV_B(T) \right\} + N_1' \left\{ f_1'(T) + pV_1'(T) \right\} + RT N_1' \log \left(\frac{N_1'}{N_B} \right) \quad \text{eq (175)}$$

$$\frac{\partial \bar{F}}{\partial N_1} - \frac{\partial \bar{F}}{\partial N_1'} = 0$$

$$\frac{\partial \bar{F}}{\partial N_1} = \frac{\partial \bar{F}}{\partial N_1'}$$

$$\frac{\partial(\bar{G}_A + \bar{G}_B)}{\partial N_1} = f_1(T) + p v_1(T) + RT \log\left(\frac{N_1}{N_A}\right) + RT N_1 \frac{1}{\left(\frac{N_1}{N_A}\right)} \frac{1}{N_A} + RT$$

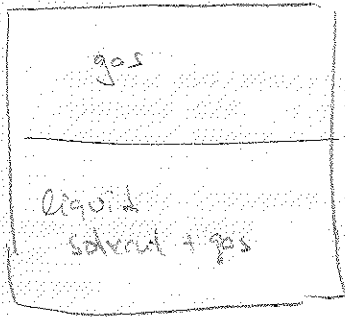
$$\frac{\partial(\bar{G}_A + \bar{G}_B)}{\partial N_1} = f_1'(T) + p v_1'(T) + RT \log\left(\frac{N_1'}{N_B}\right) + RT$$

$$\rightarrow f_1 + p v_1 + RT \log\left(\frac{N_1}{N_A}\right) + \cancel{RT} = f_1' + p v_1' + RT \log\left(\frac{N_1'}{N_B}\right) + \cancel{RT}$$

$$RT \log\left(\frac{N_1'}{N_B}\right) = f_1' + p v_1' - f_1 - p v_1$$

$$\left(\frac{N_1'}{N_B}\right) = e^{\frac{f_1' + p v_1' - f_1 - p v_1}{RT}} = e^{\frac{f_1'(T) - f_1(T) + p(v_1'(T) - v_1(T))}{RT}}$$

$$= K(T, p) \quad \text{eq 178}$$



$$F = N_0 I_0 + f_1 N_1 + RT N_1 \log \left(\frac{N_1}{N_0} \right)$$

$$N_1' (C_p T + w - T(C_p \log T - R \log p + a + R \log R))$$

$$F_{\text{system}} = N_0 I_0 + f_1 N_1 + RT N_1 \log \left(\frac{N_1}{N_0} \right)$$

$$+ N_1' (C_p T + w - T(C_p \log T - R \log p + a + R \log R))$$

$$\frac{\partial F}{\partial N_1} = \frac{\partial F}{\partial N_1}$$

$$f_1 + RT \log \left(\frac{N_1}{N_0} \right) + RT = C_p T + w - T(C_p \log T - R \log p + a + R \log R)$$

$$RT \log \left(\frac{N_1}{N_0} \right) = C_p T + w - T(C_p \log T + a + R \log R) - f_1(T) - RT + RT \log p$$

$$\log \left(\frac{N_1}{N_0} \right) = \frac{C_p T + w - T(C_p \log T + a + R \log R) - f_1(T) - RT}{RT} + \log p$$

$$\Rightarrow \frac{1}{p} \frac{N_1}{N_0} = \exp \left\{ \frac{C_p T + w - T(C_p \log T + a + R \log R) - f_1(T) - RT}{RT} \right\}$$

$$\Delta p = p' h g \quad P = p h g$$

$$\frac{\Delta p}{P} = \frac{p'}{p}$$

$$\Delta p = P \frac{p'}{p} = P \frac{V_0}{V_0'}$$

$$P = \frac{RT}{V} \sum N_i$$

$$= \frac{RT}{V} N_1 \frac{V_0}{V_0'}$$

But $V \approx N_0 V_0$ neglecting the volume occupied by the solute & the air above the liquid.

$$\Rightarrow \Delta p = \frac{RT}{N_0 V_0} N_1 \frac{V_0}{V_0'} = \frac{RT}{V_0'} \frac{N_1}{N_0} \quad \text{eq 132}$$

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$$\Phi_{sol} = ?$$

$$\Phi = U - TS + pV$$

$$U = N_0 u_0(T, p) + N_1 u_1(T, p)$$

$$V = N_0 V_0(T, p) + N_1 V_1(T, p)$$

$$S = N_0 S_0(T, p) + N_1 S_1(T, p) - k N_1 \log \left(\frac{N_1}{N_0} \right) \quad \text{eq 157}$$

$$\begin{aligned} \Phi_{sol} &= N_0 (u_0 - T S_0 + V_0 p) + N_1 (u_1 + p V_1 - T S_1) \\ &\quad + k T N_1 \log \left(\frac{N_1}{N_0} \right) \end{aligned}$$

$$= N_0 \phi_0(T, p) + N_1 \phi_1(T, p) + k T N_1 \log \left(\frac{N_1}{N_0} \right)$$

$$\Phi = N_0 \phi_0(T, p) + N_1 \phi_1(T, p) + RT N_1 \log\left(\frac{N_1}{N_0}\right) + N_0' \phi_0'(T, p)$$

$$\Delta \Phi = N_0 \frac{\Delta \Phi}{N_0} - N_0' \frac{\Delta \Phi}{N_0'} = 0$$

$$\frac{\Delta \Phi}{N_0} = \frac{\Delta \Phi}{N_0'}$$

$$\Rightarrow \phi_0(T, p) + RT N_1 \left(-\frac{1}{N_0}\right) = \phi_0'(T, p)$$

$$\Rightarrow \phi_0(T, p) - \phi_0'(T, p) = \left(\frac{N_1}{N_0}\right) RT \quad \text{eq (34)}$$

Let p_0 be vapor pressure of pure solvent at T ,

$$\phi_0(T, p_0) - \phi_0'(T, p_0) = 0$$

$$RT \frac{N_1}{N_0} = \underbrace{\phi_0(T, p_0) - \phi_0'(T, p_0)}_{=0} + \left(\frac{\partial \phi_0}{\partial p} - \frac{\partial \phi_0'}{\partial p}\right) \Delta p \Big|_{p_0}$$

$$+ \frac{\Delta p^2}{2} \left\{ \frac{\partial^2 \phi_0}{\partial p^2} - \frac{\partial^2 \phi_0'}{\partial p^2} \right\} \Big|_{p_0} + O(\Delta p^3)$$

$$= \left\{ \frac{\partial \phi_0}{\partial p} - \frac{\partial \phi_0'}{\partial p} \right\} \Delta p \Big|_{p_0} \quad \text{eq 136}$$

$$\Delta \phi = \frac{RT \left(\frac{N_1}{N_0} \right)}{v_0 - v_0'} = \frac{-RT N_1}{(v_0' - v_0) N_0} \quad \text{eq 187}$$

$$< 0$$

↓ vapor pressure is less

$$\phi_0(T, p) - \phi_0'(T, p) = \frac{RT N_1}{N_0}$$

to find explicitly about T_0

$$\phi_0(T_0, p) - \phi_0'(T_0, p + \Delta T) \left\{ \frac{\partial \phi_0}{\partial T} - \frac{\partial \phi_0'}{\partial T} \right\} = \frac{RT_0 N_1}{N_0}$$

+ ΔT^2

$$\left\{ \frac{\partial \phi}{\partial T} \right\}_p = -s \Rightarrow \frac{RT_0 N_1}{N_0} = \Delta T \left\{ -s_0 + s_0' \right\}$$

why put T_0 into R.H.S?

$$\Delta T \left\{ s_0' - s_0 \right\} = \frac{RT_0 N_1}{N_0} \quad \text{eq 189 -}$$

$$s_0' - s_0 = \frac{\Delta}{T_0}$$

$$\Delta T = \frac{RT_0^2 N_1}{N_0 (\Delta)} = \frac{RT_0^2 N_1}{\Delta N_0} \quad \text{eq 190}$$

eg 136 Form

$$\bar{\Delta} = 540 \text{ cal/gm}$$

$$\Delta = 540 \text{ cal/gm} \cdot 18 \text{ gm/mol}$$

$$Z = 8.314 \text{ J/mol}^\circ\text{K} = 1.985 \text{ cal/mol}^\circ\text{K}$$

$$T_0 = 100 + 273.15 = 373.15^\circ\text{K}$$

$$\Delta T = \frac{(1.985 \text{ cal/mol}^\circ\text{K})(373.15^\circ\text{K})^2}{(540 \cdot 18 \text{ cal/gm}) \left(\frac{1000}{18}\right) \text{ mol}}$$

$$= .512^\circ\text{K} \Rightarrow \Delta T = .512^\circ\text{C}$$

$$\Delta T = -1.85^\circ\text{K} = \Delta T = -1.85^\circ\text{C}$$

① 30 grams of NaCl is $\frac{30}{(23+35) \frac{g}{mol}} = 5.17 \cdot 10^{-1} \text{ mol}$

1 liter of $H_2O = \frac{1000 \text{ gms}}{2+16 \frac{g}{mol}} = 55.5 \text{ moles } H_2O$

Then mole fraction of NaCl

Note NaCl is a strong electrolyte & will dissociate into $2 \times$ as many moles as initially added. Moles of solute = $2(5.17 \cdot 10^{-1}) \text{ mol}$

& mole fraction is $\frac{2(5.17 \cdot 10^{-1})}{55.5} = 1.86 \cdot 10^{-2} \ll 1$

Then the osmotic pressure is given by eq 166 or

$$P = \frac{RT}{V} (N_1 + N_2 + \dots + N_j)$$

Then $N_i = \#$ of moles of solute. Assuming at room temperature

& neglecting the change in the volume due to the addition of the

Slt we get at $(8^\circ C = 291.15^\circ K)$

$$P = \frac{(8.314 \frac{J}{mol \cdot K})(291.15^\circ K)(2(5.17 \text{ mol}))}{(10^{-3} \text{ m}^3)} = 2.5 \cdot 10^6 \text{ Pa}$$

$$= 24.7 \text{ atm !! This}$$

$$1000 \text{ cm}^3 = 10^3 (10^{-2})^3 \text{ m}^3 = 10^3 10^{-6} \text{ m}^3 = 10^{-3} \text{ m}^3$$

seems

to large maybe?

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Change in boiling point is given by eq 190

$$\Delta T = \frac{RT_b^2}{\Lambda} \frac{N_1}{N_0} \quad \text{w/ } \Lambda \text{ heat of vaporization of one mole of solvent}$$

$$\Lambda = 540 \text{ cal/gm} \cdot 18 \text{ gm/mol} \\ = 9720 \text{ cal/mol}$$

$$\Delta T = \frac{(1.986 \text{ cal/mol}^\circ\text{K})(373.15^\circ\text{K})^2}{9720 \text{ cal/mol}} (1.86 \cdot 10^{-2}) = .529$$

Change in freezing point is given by eq 190 also w/ $\Lambda =$ heat of fusion per mol of solvent.

$$\Delta T = -\frac{(1.986 \text{ cal/mol}^\circ\text{K})(273.15^\circ\text{K})^2}{1440 \text{ cal/mol}} (1.86 \cdot 10^{-2}) \quad \Lambda' = 80 \text{ cal/gm} \cdot 18 \text{ gm/mol} \\ = 1440 \text{ cal/mol}$$

$$= -1.91^\circ\text{K}$$

$$(2) \quad P_{\text{total}} = \frac{RT}{V} (N_1 + \dots + N_j)$$

$$P_{\text{NaCl}} = \frac{RT}{V} N_{\text{NaCl}}$$

$$P_{\text{C}_6\text{H}_{12}\text{O}_6} = \frac{RT}{V} N_{\text{C}_6\text{H}_{12}\text{O}_6}$$

Ratio is

$$1 = \frac{N_{\text{NaCl}}}{N_{\text{C}_6\text{H}_{12}\text{O}_6}} \rightarrow N_{\text{NaCl}} = N_{\text{C}_6\text{H}_{12}\text{O}_6}$$

2 (# moles of NaCl put in solution)

How does sugar dissociate? Assume it does not

$N_{\text{C}_6\text{H}_{12}\text{O}_6} = 1$ (# moles of $\text{C}_6\text{H}_{12}\text{O}_6$ put in solid)

$$W_{\text{NaCl}} = \left(\frac{N_{\text{NaCl}}}{2} \right) M_{\text{NaCl}}$$

$$W_{\text{C}_6\text{H}_{12}\text{O}_6} = \left(\frac{N_{\text{C}_6\text{H}_{12}\text{O}_6}}{1} \right) M_{\text{C}_6\text{H}_{12}\text{O}_6}$$

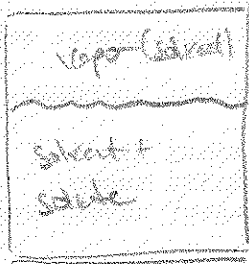
Assuming

$$\frac{W_{NaCl}}{W_{C_6H_{12}O_6}} = \frac{N_{NaCl}}{N_{C_6H_{12}O_6}} \frac{M_{NaCl}}{M_{C_6H_{12}O_6}}$$

$$= \frac{(23 + 35) \text{ gm/mol}}{2(6(12) + 12 + 6(16)) \text{ gm/mol}}$$

$$= 6.61 \cdot 10^{-1}$$

3



The phase rule

$$V = 2 + n - f$$

||

degree of variability

$$n = \# \text{ of components} \quad f = \# \text{ of phases} = \text{gas} + \text{liquid} = 2$$

that can be in both phases? No, think maximum # of components in any phase

I would say vapor has 1 component (solvent vapor)
while the liquid has 2 components (solvent + solute)

Thus liquid has 2

$$V = 2 + 2 - 2 = 2 \quad \text{This is correct (I think)}$$

we can determine 2 things 1) The temperature & the concentration of dissolved solute. Then the

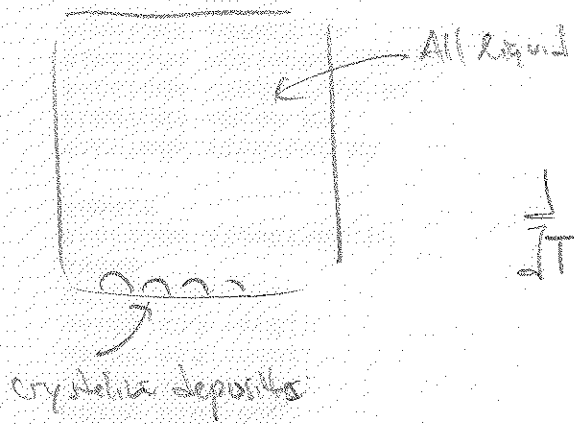
Vapor pressure follows from eq (187) + the eq for vapor

pressure eq (18) change in v.p.

4

$$\frac{N_1}{N_0} = f(T)$$

Think solute solubility means that some solid crystals remain in the tank i.e. not all the crystal can be absorbed by the liquid.



$$\int \frac{1}{T} \log f(T) = ?$$

Thus we have 3 molar terms to worry about:

- 1) # moles of solvent N_0
- 2) # moles of solute in solution N_1
- 3) # moles of solute in solid form N_1'

Following the derivation of cleoprous eq

$$V = N_0 v_0(T) + N_1 v_1(T) + N_1' v_1'(T)$$

$$U = N_0 u_0(T) + N_1 u_1(T) + N_1' u_1'(T)$$

Then if N_1 increases by ΔN_1 { so ΔN_1 moles of crystallized solvent go into Solution

$$\Delta V = v_1(T) \Delta N_1 - \Delta N_1 v_1'(T)$$

$$= (v_1(T) - v_1'(T)) \Delta N_1$$

$$\Delta U = (u_1(T) - u_1'(T)) \Delta N_1$$

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$$D(\beta) = 12 \beta^3 \int_0^{\beta} \frac{x^3 dx}{e^x - 1} - \frac{3/\beta}{e^{\beta} - 1}$$

$$= \infty \cdot 0 \text{ form} - \frac{0}{0} \text{ Both forms are indeterminate}$$

$$\lim_{\beta \rightarrow \infty} \frac{\int_0^{\beta} \frac{x^3 dx}{e^x - 1}}{\frac{1}{\beta^3}} = \frac{0}{0} \xrightarrow{\text{L'Hopital's rule}} \frac{(\beta^3)}{(e^{\beta} - 1)} \left(-\frac{1}{\beta^2} \right)$$

$$\frac{-3}{\beta^4}$$

$$= \frac{-1/\beta}{-3(e^{\beta} - 1)} \sim \frac{0}{0}$$

L'Hopital's
rule

$$\frac{-1/\beta^2}{3(e^{1/\beta})(-1/\beta^2)} = \frac{1}{3e^{1/\beta}} \rightarrow \frac{1}{3}$$

Now limit of 2nd term

$$\lim_{\beta \rightarrow \infty} \frac{3/\beta}{e^{\beta} - 1} = \frac{3 \frac{1}{\beta^2}}{e^{\beta} \frac{1}{\beta^2}} = \frac{3}{e^{\beta}} = 3$$

type 90

• when $D(\xi) = \frac{12}{3} - 3 = 4 - 3 = 1 \checkmark$

$\lim_{\xi \rightarrow 0} D(\xi) = 12\xi^3 \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{4\pi^4}{15} \xi^3$ Assume

How integrate this?

$C(T) = \frac{4\pi^4}{15} (3R) \left(\frac{T}{\theta}\right)^3 = \frac{12\pi^4}{15} R \left(\frac{T}{\theta}\right)^3$ eq 198

$S = 3R \int_0^T D\left(\frac{T}{\theta}\right) \frac{dT}{T} = 3R \int_0^{T/\theta} D(\xi) \frac{d\xi}{\xi} = 3R \int_0^{T/\theta} D(\xi) \frac{d\xi}{\xi}$ eq 199

$\xi = T/\theta \quad d\xi = dT/\theta$

Now

$\int_0^{\omega} D(\xi) \frac{d\xi}{\xi} = 12 \int_0^{\omega} \xi^3 \int_0^{1/\xi} \frac{x^3 dx}{e^x - 1} \frac{d\xi}{\xi} = 3 \int_0^{\omega} \frac{d\xi/\xi^2}{e^{\xi} - 1}$ let $v = 1/\xi$
 $dv = -\frac{d\xi}{\xi^2}$

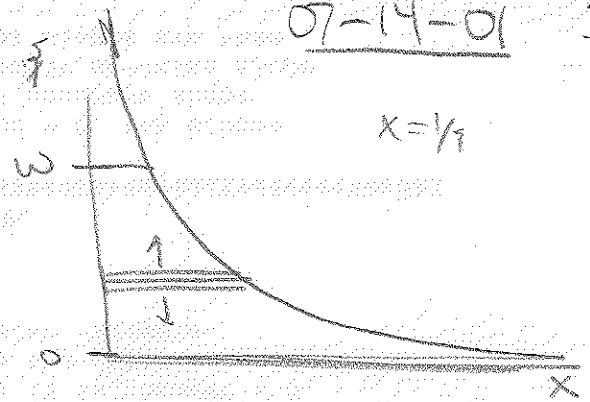
$= 12 \int_0^{\omega} \xi^2 \left(\int_0^{1/\xi} \frac{x^3 dx}{e^x - 1} \right) d\xi + 3 \int_{1/\omega}^{1/0} \frac{dv}{e^v - 1}$

Consider $\int_0^w \int_{1/x}^w f^2 df$ $\int_0^{1/w} \frac{x^3 dx}{e^x - 1}$

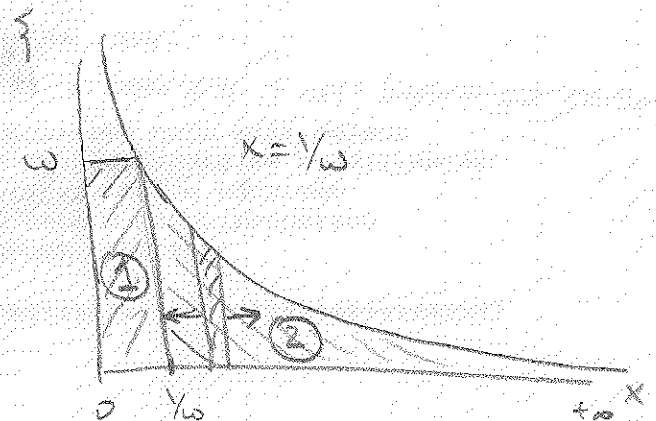
$$= \int_0^w \int_0^{1/x} f^2 \frac{x^3}{e^x - 1} dx df$$

$$= \int_0^{1/w} \frac{x^3}{e^x - 1} dx \int_0^w f^2 df$$

$$+ \int_{1/w}^{+\infty} \frac{x^3}{e^x - 1} dx \int_0^{1/x} f^2 df$$



Correct integration is horizontal strips & then moved vertically.



$$0 \leq x \leq 1/w \quad 1/w \leq x \leq \infty$$

$$0 \leq f \leq w \quad 0 \leq f \leq 1/x$$

①

②

$$\Rightarrow \int_0^w D(f) \frac{df}{f} = 12 \int_0^{1/w} \frac{x^3}{e^x - 1} dx \int_0^w f^2 df + 12 \int_{1/w}^{+\infty} \frac{x^3}{e^x - 1} dx \int_0^{1/x} f^2 df$$

$$- 3 \int_{1/w}^{+\infty} \frac{dx}{e^x - 1}$$

$$= \frac{12}{3} \omega^3 \int_0^{\omega} \frac{x^3}{e^x - 1} dx + \frac{12}{3} \int_{\omega}^{+\infty} \frac{x^3}{e^x - 1} \left(\frac{1}{x}\right)^3 dx$$

$$- 3 \int_{\omega}^{+\infty} \frac{e^{-x} dx}{1 - e^{-x}}$$

$$= 4\omega^3 \int_0^{\omega} \frac{x^3}{e^x - 1} dx + 4 \int_{\omega}^{+\infty} \frac{dx}{e^x - 1} - 3 \int_{\omega}^{+\infty} \frac{dx}{e^x - 1}$$

$$\int_{\omega}^{+\infty} \frac{dx}{e^x - 1}$$

$$\int_{\omega}^{+\infty} \frac{e^{-x} dx}{1 - e^{-x}}$$

$$+ \ln(1 - e^{-x}) \Big|_{\omega}^{+\infty}$$

$$= -\ln(1 - e^{-\omega})$$

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$$S = 3R \left[4 \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} - \log(1 - e^{-\theta/T}) \right]$$

For large $T \Rightarrow \omega \gg 1$ in

$$\int_0^{\omega} D(f) \frac{df}{f} = 4\omega^3 \int_0^{\omega} \frac{x^3 dx}{e^x - 1} - \log(1 - e^{-\omega})$$

$$= \infty \cdot 0 - 0$$

Find the asymptotic expansion for $\int_0^{\omega} \frac{x^3 dx}{e^x - 1}$ for $\omega \gg 1$

How to?

Assuming

$$S = \frac{4}{3} + \log \omega$$

$$S = 3R \int_0^{\omega} D(f) \frac{df}{f} = 3R \left[\frac{4}{3} + \log \frac{T}{\theta} + \dots \right]$$

$$= 4R + 3R \log T - 3R \log \theta + \dots \quad \text{of } 200$$

$$S = R \left\{ \frac{3}{2} \log T + \log V + \log \dots \right\}$$

(8) $S = C_v \log T + R \log V + R$

monatomic gas $C_v = \frac{3}{2}R$

$$\Rightarrow a = R \log \frac{(2\pi MR)^{3/2} \omega e^{5/2}}{h^3 A^4}$$

$$= R \left[\frac{3}{2} \log M + \log \omega + \log \left(\frac{(2\pi R)^{3/2} e^{5/2}}{h^3 A^4} \right) \right]$$

$$\frac{(2\pi(173))^{3/2} e^{5/2}}{(6.55 \cdot 10^{-27})^3 (6.03 \cdot 10^{33})^4}$$

-31.87

$$C_p = C_v + R$$

$$PV = RT$$

$$\log P + \log V = \log R + \log T$$

$$\log V = \log R + \log T - \log P$$

\Rightarrow eq 204 is

$$S = R \left\{ \frac{3}{2} \log T + \log R + \log T - \log P + \log \frac{(2\pi MR)^{3/2} \omega e^{5/2}}{h^3 A^4} \right\}$$

$$\rightarrow S = R \left\{ \frac{5}{2} \log T - \log p + \log \left(\frac{(2\pi m)^{3/2} R^{5/2} \omega e^{5/2}}{h^3 A^4} \right) \right\} \quad \text{eq (206)}$$

$$S_{\text{exp}} - S_{\text{calc}} = \frac{\Lambda}{T}$$

$$R \left\{ \frac{5}{2} \log T - \log p + \log \left(\frac{(2\pi m)^{3/2} R^{5/2} \omega e^{5/2}}{h^3 A^4} \right) \right\} - 3R \log T - 4R$$

$$+ 3R \log \theta = \frac{\Lambda}{T}$$

$$4 = \log e^4$$

$$-\frac{5}{2} \log T + \log p - \log \left(\frac{(2\pi m)^{3/2} R^{5/2} \omega e^{5/2}}{h^3 A^4} \right) + 3 \log T + 4 - 3 \log \theta = \frac{-\Lambda}{2T}$$

$$p T^{-5/2} \left(\frac{h^3 A^4}{(2\pi m)^{3/2} R^{5/2} \omega e^{5/2}} \right) T^3 e^4 \theta^{-3} = e^{-\frac{\Lambda}{2T}}$$

$$p = \frac{(2\pi m)^{3/2} R^{5/2} \omega \theta^3}{e^{5/2} h^3 A^4} \left(\frac{1}{T^{1/2}} \right) e^{-\frac{\Lambda}{2T}} \quad \text{eq 207}$$

eq 206

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$$S = R \left\{ \frac{5}{2} \log T - \log p + \log \left(\frac{(2\pi M)^{3/2} R}{h^3 A^4} w_e^{5/2} \right) \right\}$$

$T = 6309 \text{ K}$, $p = 1 \text{ atm}$, $M = 200.6 \text{ g/mol}$

What is w for Hg ?

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$$\frac{[Na]}{[Na^+][e]} = \exp \left\{ \frac{1}{R} \left[(R + C'_{Na^+} - a'_{Na^+}) + (R + C'_e - a'_e) - (R + C'_{Na} - a_{Na}) \right] \right\}$$

$\cdot \frac{1}{T} (C'_{Na^+} + C'_e - C'_{Na})$

$\cdot \exp \left\{ \frac{1}{RT} (w_{Na^+} + w_e - w_{Na}) \right\}$

w by eq a pg 153

$$= \exp \left\{ \frac{1}{R} \left[(R + \frac{3}{2}R - a'_{Na^+}) + (R + \frac{3}{2}R - a'_e) - (R + \frac{3}{2}R - a_{Na}) \right] \right\}$$

$\cdot \frac{1}{T} \left(\frac{3}{2}R \cdot 2 - \frac{3}{2}R \right) \cdot \exp \left\{ -\frac{w}{RT} \right\}$

$$\rightarrow \frac{[Na]}{[Na^+][e]} = e^{\frac{\mu}{kT}} \exp \left\{ \frac{1}{R} (-a_{Na^+} - a_e + a_{Na}) \right\} \\ \cdot T^{\frac{3}{2}} \exp \left\{ -\frac{\omega}{RT} \right\}$$

$$\frac{1}{2} (-a_{Na^+} - a_e + a_{Na}) = -\log \left[\frac{(2\pi m_{Na} R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}}{h^3 A^4} \right] - \log \left[\frac{(2\pi m_e R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}}{h^3 A^4} \right]$$

$$+ \log \left[\frac{(2\pi m_{Na} R)^{\frac{3}{2}} e^{\frac{\mu}{2}}}{h^3 A^4} \right]$$

$$= \log \left[\frac{h^3 A^4}{(2\pi m_e R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}} \cdot \frac{h^3 A^4}{(2\pi m_e R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}} \cdot \frac{(2\pi m_{Na} R)^{\frac{3}{2}} e^{\frac{\mu}{2}}}{h^3 A^4} \right]$$

$$= \log \left[\frac{h^3 A^4}{(2\pi m_e R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}} \right]$$

$$\frac{[Na]}{[Na^+][e]} = e^{\frac{\mu}{kT}} \left(\frac{h^3 A^4}{(2\pi m_e R)^{\frac{3}{2}} 2e^{\frac{\mu}{2}}} \right)^{\frac{3}{2}} \exp \left\{ -\frac{\omega}{RT} \right\}$$

=

(2) Using Debye-Hückel formal for the atomic heat

$$C(T) = 3RD\left(\frac{T}{\Theta}\right) = 3R \left[\left(\frac{T}{\Theta}\right)^3 \int_0^{T/\Theta} \frac{x^3 dx}{e^x - 1} - \frac{3(T/\Theta)}{e^{T/\Theta} - 1} \right]$$

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

$$= \int_0^1 \frac{x^3 dx}{e^x - 1} - \frac{3/2}{e^{1/2} - 1} = \frac{1}{2}$$

Solving w/ MMA gives

$$\eta =$$

$$T \quad \Theta =$$

① Gas of Na molecules at $T = 4000 \text{ K}$
 $P = 1 \text{ cm/Hg}$

Then dissociation takes place + reaction of the form



We are asking for $\frac{[\text{Na}^+]}{[\text{Na}] + [\text{Na}^+]}$ = % of ionization
 or x on page 153

But $n = [\text{Na}^+] + [\text{Na}] = \text{total \# of moles in volume per volume}$

But at pressure of 1 atm

$$N_{\text{Na}^+} = N_e$$

$$P = \underset{\substack{\uparrow \\ \text{partial} \\ \text{pressure } N_{\text{Na}^+}}}{P_{\text{Na}^+}} + P_{\text{Na}} + P_e$$

$$= \frac{N_{\text{Na}^+} RT}{V} + \frac{N_{\text{Na}} RT}{V} + \frac{N_e RT}{V}$$

$$= [N_{\text{Na}^+}] RT + [N_{\text{Na}}] RT + [N_e] RT$$

$$= 2[N_{\text{Na}^+}] RT + [N_{\text{Na}}] RT$$

2 eqs

$$2[Na^+]RT + [Na]RT = P$$

eq
$$\frac{[Na]}{[Na^+]^2} = \frac{h^3 A^3}{(2\pi m_e R)^{3/2} T^{3/2}} e^{-\frac{W}{RT}}$$

Solve for $[Na^+] + [Na]$

$$n = [Na] + [Na^+] \quad x = \frac{[Na^+]}{n}$$

$$[Na^+] = nx$$

$$[Na] = n(1-x) \quad [e] = nx$$

$$\frac{n(1-x)}{nx} = \left(\right)^{-3/2} T^{-3/2} e^{w/RT}$$

$$\frac{n \cdot x^2}{1-x} = \frac{(2\pi m_e R)^{3/2}}{h^3 \lambda^3} T^{-3/2} e^{w/RT}$$

$$U = TS$$

$$F = N \left(\frac{3}{2} RT + w \right) - NRT \left\{ \frac{3}{2} \log T + \log \frac{V}{N} + \log \frac{(2\pi m_e R)^{3/2} 2e^{w/2}}{h^3 \lambda^3} \right\}$$

$$0 = \frac{dF}{dN} = \frac{3}{2} RT + w - RT \left\{ \frac{3}{2} \log T + \log V - \log N + \log \left(\right) \right\}$$

$$- NRT \left\{ - \frac{1}{N} \right\}$$

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$$\rightarrow RT \ln\left(\frac{V}{N}\right) = \underbrace{-\frac{3}{2}RT - RT - \omega}_{-\frac{5}{2}RT} + RT \left[\frac{3}{2} \ln T + \ln\left(\frac{(2)(2\pi m_e R)^{3/2}}{h^3 A^4}\right) \right]$$

$$-\frac{5}{2}RT$$

$$\Rightarrow \ln\left(\frac{V}{N}\right) = -\frac{5}{2} - \frac{\omega}{RT} + \frac{3}{2} \ln T + \ln\left(\frac{(2)(2\pi m_e R)^{3/2}}{h^3 A^4}\right)$$

$$\frac{V}{N} = e^{-5/2} e^{-\omega/RT}$$