

HW #2

Problem #1 (2.34 textbook)

- (a) Each link can point either left or right, so this system is mathematically the same as spins system.

The multiplicity.

$$g = \frac{N!}{N_L! N_R!}$$

$$\begin{aligned} \frac{S}{k} = \ln g &= N \ln N - N - N_R \ln N_R + N_R - N_L \ln N_L + N_L = \\ &= N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R) \end{aligned}$$

- (b) Each right-pointing link increases L by ℓ and each left pointing link decreases L by ℓ , so the net length is $L = \ell(N_R - N_L) = \ell(2N_R - N)$, or $N_R = \frac{1}{2}(\frac{L}{\ell} + N)$

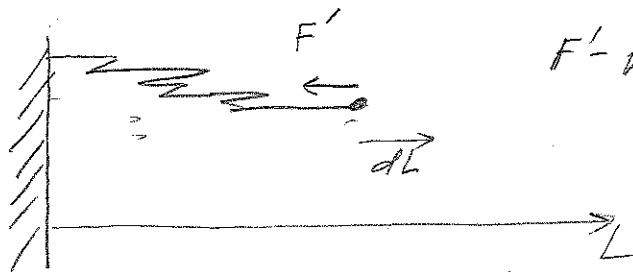
- (c) Thermodynamic identity for ideal gas.

$$dU = TdS - PdV$$

$$U = Q - W_s$$

\uparrow work done by system.

F' - force by rubber.



\downarrow work by system

$$dU = TdS - dW_s = dU = TdS - FdL = TdS + FdL$$

- (d) The internal energy of the rubber does not depend on the conformation state of the rubber. \Rightarrow

$$dU = 0. \Rightarrow F = -T \left(\frac{\partial S}{\partial L} \right)_U$$

Using the chain rule.

$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \cdot \frac{\partial N_R}{\partial L} = \frac{\partial S}{\partial N_R} \cdot \frac{1}{2e}.$$

$$F = -\frac{kT}{2e} \left[-\ln N_R - \frac{N_R}{N_R} + \ln(N - N_R) + \frac{N - N_R}{N - N_R} \right] = -\frac{kT}{2e} \ln \left(\frac{N - N_R}{N_R} \right)$$

Using $N_R = \frac{1}{2} \left(\frac{L}{e} + N \right)$

$$F = -\frac{kT}{2e} \ln \left(\frac{2}{L/Ne + 1} - 1 \right) = -\frac{kT}{2e} \ln \left(\frac{1 - L/Ne}{1 + L/Ne} \right) = \frac{kT}{e} \ln \left(\frac{1 + L/Ne}{1 - L/Ne} \right)$$

(e) When $L \ll Ne$ the argument of the logarithm is approximately

$$\frac{1 + L/Ne}{1 - L/Ne} \approx (1 + L/Ne)(1 + L/Ne) \approx 1 + \frac{2L}{Ne}.$$

$$F \approx \frac{kT}{2e} \cdot \frac{2L}{Ne} = \frac{kTL}{Ne^2} \quad \frac{kT}{Ne^2} - \text{"spring constant"}$$

(f) The tension is proportional to T so for a given force upon increasing temperature the rubber should contract.

Homework #7

Pr #2. (5.40 textbook)



1) $\Delta G = \Delta G_f(\text{products}) - \Delta G_f(\text{reagents}) = -$

$$2852.1 \text{ kJ} - 856.6 \text{ kJ} + 3711.5 \text{ kJ} = 2.8 \text{ kJ}$$

Because ΔG is positive, albite is more stable than jadeite + quartz under room temperature and atmospheric pressure. However the jadeite-quartz combination takes up considerably less volume than albite, so it should become stable at high pressure.

2) The pressure needed to conversion at room temperature, can be found as. $dG = VdP - SdT = VdP$.

$$P = \frac{\Delta G}{\Delta V} = \frac{2.8 \text{ kJ}}{\Delta V}$$

to make computation it's convenient to make a conversion

$$1 \text{ cm}^3 = 10^{-6} \text{ m}^3 = 10^{-6} \frac{\text{J}}{\text{Pa}} = 10^{-6} \cdot \frac{10^8 \text{ J}}{10^8 \text{ Pa}} = 10^{-1} \cdot \frac{\text{kJ}}{\text{kbar}}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

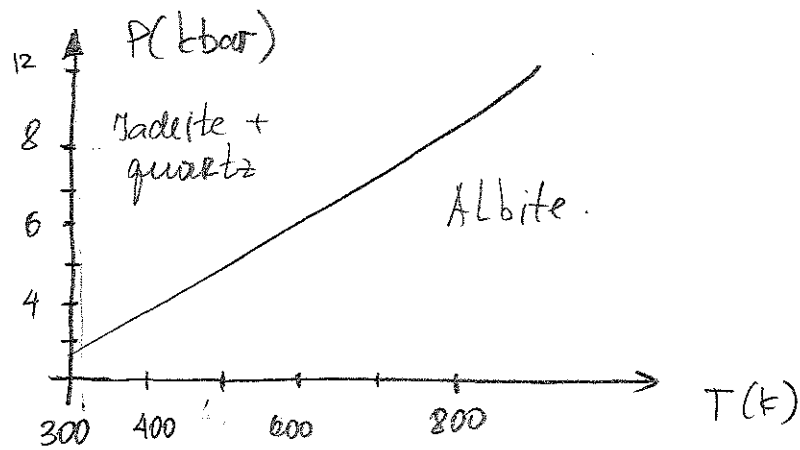
$$P = \frac{2.8 \text{ kJ}}{10. \text{ kJ/kbar} - 6.04 \text{ kJ/kbar} - 2.269 \text{ kJ/kbar}} = 1.65 \text{ kBar}$$

3) The slope of the phase boundary can be found from the Clausius-Clapeyron relation.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{207.4 \text{ J/K} - 133.5 \text{ J/K} - 41.8 \text{ J/K}}{1.7 \text{ J/bar}} = 18.9 \text{ bar/K}$$

The phase boundary is therefore given by the equation.

$$P(\text{kbar}) = 1.65 + 18.9 \cdot 10^{-3} (T - 293)$$



$$P = \frac{4 - 12}{6 - 1}$$

Homework #7

Problem #3.

definitions: P_{00} - initial pressure of water vapor.

$P_v(P)$ - pressure of water vapor after the pumping in an inert gas.

P_0 - ^{partial} pressure of inert gas that was pumped in

$P = P_0 + P_v(P)$ - total pressure.

- (a) Change of the chemical potential of ideal gas as result of increase of its partial pressure

$$\mu = \mu_0^v + kT \ln \left(\frac{P_v(P)}{P_{00}} \right) \quad \mu_{00} - \text{initial } \mu \text{ of vapor}$$

Change in the μ of liquid.

$$d\mu = VdP - SdT = VdP \quad \text{at } T = \text{const.}$$

$$\mu = \frac{G}{N} \quad \mu = \int \frac{V}{N} dP = \int V_L dP \quad V_L - \text{volume per molecule in water}$$

Liquid is not compressible $V_L = \text{const.}$

$$\mu_L = \mu_0^L + V_L \cdot (P - P_{00})$$

$$\mu_0^L = \mu_0^v$$

$$kT \ln \left(\frac{P_v(P)}{P_{00}} \right) = V_L (P - P_{00})$$

$$P_v(P) = P_{00} \cdot \exp \left[\frac{(P - P_{00}) \cdot V_L}{kT} \right]$$

For $P_0 = 1 \text{ atm}$ $P_0 \gg P_{00} = 0.03 \text{ atm.}$

$$\frac{P_v(P)}{P_v(0)} = 1.00073 \quad - \text{very small correction.}$$