

Chemistry 553, Heat and work

Final exam

14 June 2006, High noon room 104 Gilbert
Rules: books ... OK; human resources ...not OK

1. Suppose that the single particle partition function is

$$q_T(N, V, T) = \frac{V - Nb}{\Lambda^3} \quad (1)$$

where b is a constant.

- (a) What is the accompanying pressure (or equation of state) of this fluid; and
(b) what physics does this representation of q_T attribute to the system?
2. Derive the T-dependence of the equilibrium constant for the gas phase dimerization of water in the temperature range $\Theta_R \ll T \ll \Theta_v$. Write the result in the form

$$K_d(T) \simeq T^a e^{-b/T} \quad (2)$$

Give a precise value for a and the interpretation of b in terms of molecular properties.

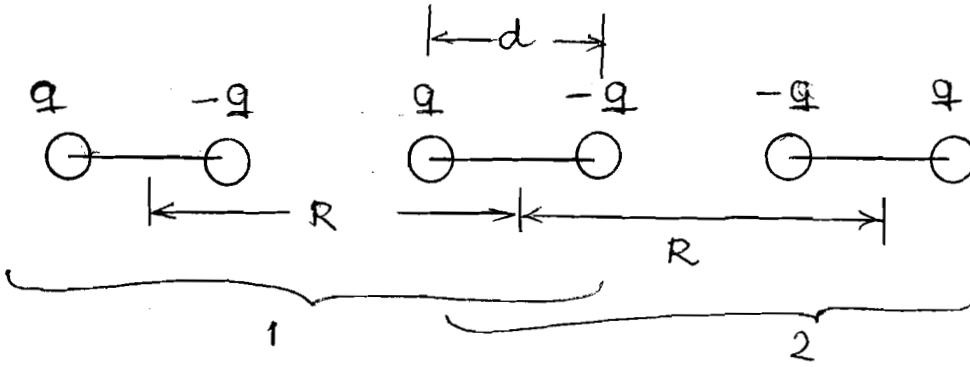
3. In the treatment of boiling point elevation and freezing point depression, conditions must to be satisfied for equilibrium to be established between the frozen phase or gas phase with its liquid mixture. What are the conditions?
4. Hildebrand's theory of Regular Solutions is a theory of non-ideal liquid mixtures. a) Derive the Henry's law constant in terms of χ_{12} as implemented in the lattice theory presented by Dill and Bromberg. b) Using a graphics package, plot $A(N_1, N_2, T)$ for a two component fluid

$$\frac{A(N_1, N_2, T)}{Nk_B} = T[x_1 \ln(x_1) + x_2 \ln(x_2)] + u_1 x_1 + u_2 x_2 + u_{12} x_1 x_2 \quad (3)$$

and locate coexisting phases using the common tangent construction discussed in the text, Eq(25.8). Select the temperatures $u_1 \neq u_2, U_{12}$ and T in any way you see fit that gives rise to two-phase equilibria. Hint: start with $u_1 = 1$, select u_2 either slightly greater or less than u_1 and pick a temperature and u_{12} so that $T < T_c$.

5. Derive the potential energy function for two dipoles in the two linear geometries given below. Compare your results with the dipole-dipole interaction energy

$$U(\mathbf{R}, \mathbf{e}_1, \mathbf{e}_2) = -\mu_1 \cdot \mathbf{T} \cdot \mu_2, \quad \mathbf{T} = \frac{3\mathbf{R}\mathbf{R} - \mathbf{I}R^2}{R^5} \quad (4)$$



6. Using the definition of $g(r)$,

$$\frac{g(r_1, r_2)}{V^2} = \frac{\int dr_3 \cdots dr_n e^{-\beta U}}{\int dr_1 dr_2 \cdots dr_N e^{-\beta U}} \quad (5)$$

derive the expression for the energy

$$\frac{E}{Nk_B T} = \frac{3}{2} + \frac{\rho}{2k_B T} \int u(r) g(r) dr \quad (6)$$

starting from

$$A = -k_B T \ln Q_N(V, T), \quad Q_N(V, T) = \frac{1}{N! h^{3N}} \int dr_1 dr_2 \cdots dr_n dp_1 \cdots dp_N e^{-\beta(T+U)} \quad (7)$$

7. The Helmholtz energy for a fluid comprised of hard rods is given by the Landau expansion

$$A(S) = A(0) + 2S^2(1 - a\rho^*) + S^3 + 4S^4 \quad (8)$$

where S is the alignment order parameter, $\langle P_2(\cos \theta) \rangle$. Here a is a measure of the shape anisotropy of the rod, $a \simeq (L_{long} - L_{short})^2 / L_{short}^2$, where L is the length along a long or short axis.

Find the lowest density at which an orientationally ordered phase can form. This density corresponds to the liquid crystal transition and is an example of spontaneous alignment induced by molecular shape not by outside forces.

Final exam.

1. $q_T(N, V) = (V - Nb) / \Lambda^3$

a)

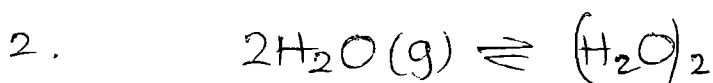
$$A = -k_B T \ln(q_T^N / N!)$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = k_B T N \frac{\partial \ln q_T}{\partial V} = \frac{k_B T N}{V - Nb}$$

or

$$P = \rho k_B T / (1 - b\rho)$$

b) This is a vdW theory without attractive forces, in other words, hard sphere fluid.



$$K_d = \frac{q_{(\text{H}_2\text{O})_2} / V}{(q_{\text{H}_2\text{O}} / V)^2} = \frac{\rho_{\text{dimer}}}{\rho_{\text{mono}}^2}$$

$$q_{(\text{H}_2\text{O})_2} \approx T^{3/2} T^{3/2} e^{\beta D_0(\text{dimer})}$$

\uparrow trans \leftarrow rot

$$q_{\text{H}_2\text{O}} = T^3 \exp(\beta D_0(\text{H}_2\text{O}))$$

∞

$$K_d \approx \frac{T^3 \exp(\beta [D_0(\text{dimer}) - 2D_0(\text{mono})])}{(T^3)^2}$$

$$\approx \frac{1}{T^3} \exp(\beta [\quad \quad \quad])$$

$a = -3, b = -\frac{1}{k_B} \left\{ \text{dissociation energy of the dimer} \right\}$

$$3. \quad \mu_1(T, P, x_1) = \mu_1(T, P)$$

chem pot'l of the solvent in the liquid mixture = chem pot'l of ^{solvent of} pure solid or pure vapor

$$4. \quad A = Nk_B T \{x_1 \ln x_1 + x_2 \ln x_2\} + Nk_B [U_1 x_1 + U_2 x_2 + U_{12} x_1 x_2]$$

a) Henry's law $P = x_1 p_1$

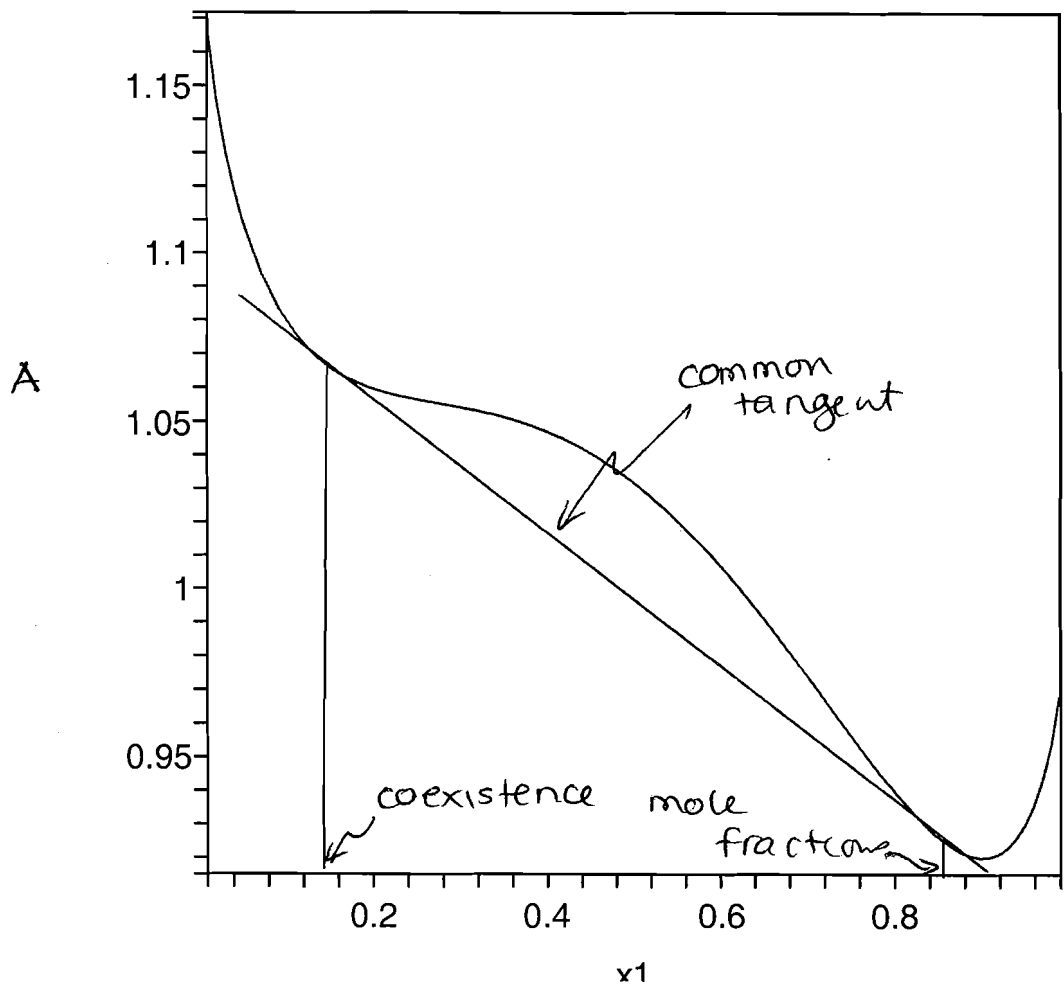
Plan: derive $\mu_1 = \left(\frac{\partial A}{\partial N_1} \right)_{N_2, V, T} = k_B T \ln(x_1 \delta_1 p_1^0)$

↑
activity coef

$$\left(\frac{\partial A}{\partial N_1} \right)_{N_2} = k_B T \ln x_1 + k_B U_1 + x_2^2 U_{12} k_B$$

$$= k_B T \ln \left\{ x_1 \underbrace{\exp(U_1/T)}_{\text{include in } p_1^0} \underbrace{\exp(x_2^2 U_{12}/T)}_{\text{as } x_2 \rightarrow 1 \Rightarrow e^{U_{12}/T}} \right\}$$

$$\therefore p_1 = p_1^0 e^{U_{12}/T}$$



$$A = T(x_1 \ln x_1 + x_2 \ln x_2) + U_1 x_1 + U_2 x_2 + U_{12} x_1 x_2$$

selected $U_1 = 1$
 $U_2 = 1.2$
 $U_{12} = 2.5$
 $T = 1$

5. Geometry 1

$$U = \frac{q^2}{R} + \frac{q^2}{R} - \frac{q^2}{R-d} - \frac{q^2}{R+d} = \frac{q^2}{R} \left\{ 2 - \frac{1}{1-\frac{d}{R}} - \frac{1}{1+\frac{d}{R}} \right\}$$

$$U_1 = \frac{q^2}{R} \left\{ 2 - \left(1 + \frac{d}{R} + \frac{d^2}{R^2} + \dots \right) - \left(1 - \frac{d}{R} + \frac{d^2}{R^2} \right) \right\}$$

$$= \frac{q^2}{R} \left(-\frac{2d^2}{R^2} \right) = -\frac{2(qd)^2}{R^3} = -2\mu^2/R^3$$

$$U_2 = -\frac{q^2}{R} - \frac{q^2}{R} + \frac{q^2}{R+d} + \frac{q^2}{R-d} = -U_1 = \frac{2\mu^2}{R^3}$$

whereas,

$$U_1 = \mu_1 \cdot T \cdot \mu_2$$

and for geometry 1

$$\mu_1 = -q\hat{z}d, \quad \mu_2 = -q\hat{z}d$$

$$U_1 = q^2 d^2 \hat{z} \cdot \underline{T} \cdot \hat{z}, \quad \hat{z} \cdot \underline{T} \cdot \hat{z} = \frac{3(R \cdot \hat{z})^2 - R^2}{R^5}$$

$$R \cdot \hat{z} = R \quad \text{and}$$

$$\hat{z} \cdot \underline{T} \cdot \hat{z} = 2R^2/R^5 = 2/R^3$$

$$\therefore U_1 = 2\mu^2/R^3 \Rightarrow \text{sign on } T \text{ is wrong}$$

U_2 has the opposite sign as U_1 owing to the reversal of the dipole moment.

$$\therefore T = \left(\frac{11R^2 - 3RR}{R^5} \right)$$

$$6. A = -k_B T \ln Q_N$$

$$E = -T^2 \left(\frac{\partial (A/T)}{\partial T} \right)_{N,V} = k_B T^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_{N,V}$$

$$Q_N(V,T) = \frac{1}{N! h^{3N}} \left[\int dp_1 e^{-\beta p_1^2 / 2M} \right]^N \underbrace{\int dr_1 \dots dr_N e^{-\beta U}}_Z$$

$$Q_N = \frac{1}{N!} \frac{1}{\Delta^{3N}} Z_N$$

$$\frac{\partial \ln Q_N}{\partial T} = \frac{\partial \ln(1/N!)}{\partial T} + \frac{\partial 3N \ln T^{1/2}}{\partial T} + \underbrace{\frac{\partial \ln Z_N}{\partial T}}_{\text{next}}$$

\uparrow
 ≈ 0

\uparrow
 $\approx \frac{3N}{2T}$

at this stage we have

$$E = \frac{3}{2} N k_B T + k_B T^2 \frac{\partial \ln Z_N}{\partial T}$$

$$\frac{\partial \ln Z_N}{\partial T} = \frac{1}{Z_N} \int dr_1 \dots dr_N e^{-\beta U} \frac{U}{k_B T^2}$$

$$k_B T^2 \frac{\partial \ln Z_N}{\partial T} \Rightarrow \frac{1}{Z_N} \int dr_1 \dots dr_N e^{-\beta U} U$$

$$= \frac{1}{Z_N} \frac{N(N-1)}{2} \int dr_1 \dots dr_N U_{12} e^{-\beta U}$$

$$= \frac{N(N-1)}{2} \int dr_1 dr_2 U_{12} \left(\frac{\int dr_3 \dots dr_N e^{-\beta U}}{Z_N} \right)$$

$\leftarrow \int dr_{12} / V^2$

so

$$k_B T^2 \frac{\partial \ln Z_N}{\partial T} = \frac{N(N-1)}{2V^2} \underbrace{\int dr_1 dr_2 g(r_{12}) U(r_{12})}_{V \int dr g(r) U(r)}$$

$$= \frac{N^2}{2V} \int dr g(r) U(r) \quad \text{ad}$$

$$E = \frac{3}{2} N k_B T + \frac{N^2}{2V} \int dr g(r) U(r)$$

7. $A(s) = A(0) + 2s^2(1 - a\rho^*) + s^3 + 4s^4$

$$\left(\frac{\partial A}{\partial s}\right) = 0 = 4s(1 - a\rho^*) + 3s^2 + 16s^3$$

$$\therefore s=0 \quad \text{or} \quad 4(1 - a\rho^*) + 3s + 16s^2 = 0$$

solve the quadratic eq

$$s = -3 \pm \sqrt{9 - 64 \cdot 4(1 - a\rho^*)}$$

$$= (-3 \pm \sqrt{9 - 256(1 - a\rho^*)}) / (2 \cdot 16)$$

so when $9 - 256(1 - a\rho^*) = 0$

$$\text{or} \quad \frac{9}{256} = 1 - a\rho^*$$

$$a\rho^* = 1 - 9/256 = \frac{247}{256}$$

$$\rho^* \geq \frac{247}{256} \frac{1}{a}$$

For densities such that

$$\rho^* \geq \frac{247}{256} a$$

$$S \sim -\frac{3}{2 \cdot 16}$$

and there is spontaneous alignment.