FINAL EXAM

December 14, 2007, 9:00 am **Time allowed: 2 hours** **44 marks total**

Please answer all questions clearly in the booklets provided and show all your work.

$PV = NkT$ $\quad$ $U_{thermal} = \frac{1}{2}NfkT$ $\quad$ $\Delta U = Q + W$

$W = -\int_{V_i}^{V_f} P(V)dV$ $\quad$ $S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$ $\quad$ $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$ $\quad$ $VT^{f/2} = \text{constant}$ $\quad$ $PV^{(f+2)/f} = \text{constant}$

$\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}$ $\quad$ $\Omega = \Omega_A\Omega_B$ $\quad$ $S = k\ln\Omega$

$\Omega(N,n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}$ $\quad$ $F = U - TS$ $\quad$ $H = U + PV$

$R_{gas} = 8.315$ J/molK $\quad$ $N_A = 6.022 \times 10^{23}$ mol^{-1} $\quad$ $e = 1.602 \times 10^{-19}$ C

$\Delta S = \frac{Q}{T}$ $\quad$ $dU = TdS - PdV + \mu dN$ $\quad$ $dG = -SdT + VdP + \mu dN$

$0\ ^\circ\text{C} \equiv 273$ K

QUESTION 1. [16 marks] Consider an Einstein solid with q units of energy and N oscillators. The total energy is $U = q\epsilon$. Both q and N are large. Here, we will consider the high T limit, i.e. $q >> N$.

(a) [**5 marks**] Using Stirling's approximation, $\ln N! = N \ln N - N$, and relevant simplifications involving $q >> N$, obtain an expression for the multiplicity Ω in terms of N and q.

(b) [**2 marks**] Find entropy S as a function of U.

(c) [**4 marks**] Find U as a function of temperature T.

(d) [**2 mark**] Obtain an expression for the heat capacity C_V for this system.

(e) [**3 marks**] Obtain an expression for the chemical potential for this system, in terms of N, q and T. Upon adding one oscillator to the system while keeping the volume fixed, how much energy must be added or removed in order to keep the entropy unchanged?

QUESTION 2. [20 marks] The Helmholtz free energy is defined as $F = U - TS$.

(a) [**4 marks**] Find the thermodynamic identity for F, and find related formulas for the partial derivatives with respect to T, V, and N.

(b) [**2 marks**] Derive a Maxwell relation based on F.

(c) [**4 marks**] A system with fixed N and V is in contact with a reservoir with which it can exchange only energy. The reservoir's temperature T is constant. Using the Second Law, show that F for the system tends to decrease.

(d) [**5 marks**] At room temperature and atmospheric pressure, kyanite is the stable phase of aluminum silicate, Al_2SiO_5. At a higher T but still at ambient P, another form of the material, andalusite, becomes more stable. Calculate the transition temperature by assuming that the difference in molar entropy and volume between the two phases does not change with temperature. Below are some molar data at standard conditions. You can leave an unsimplified numerical expression as your answer.

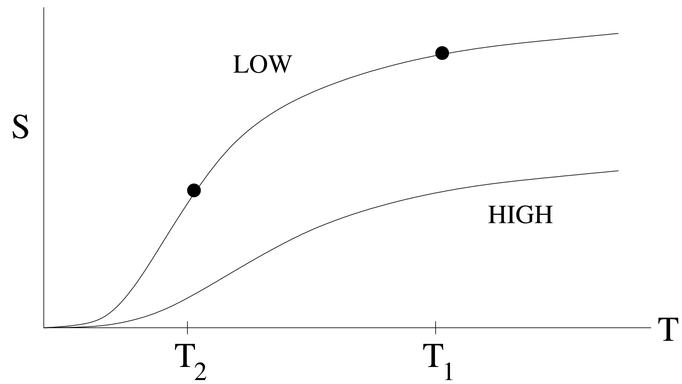
	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
kyanite	-2594.29	-2443.88	83.81	121.71	44.09
andalusite	-2590.27	-2442.66	93.22	122.72	51.53

(e) [**3 marks**] Derive the Clausius-Clapeyron relation, i.e. an expression for the slope $\frac{dP}{dT}$ of the coexistence line in terms of thermodynamic properties of the two phases. (Hint: At coexistence the two phases have the same value of G. Changing T and P will change G for both phases. To stay on the coexistence line, the change in G must be the same for both phases.)

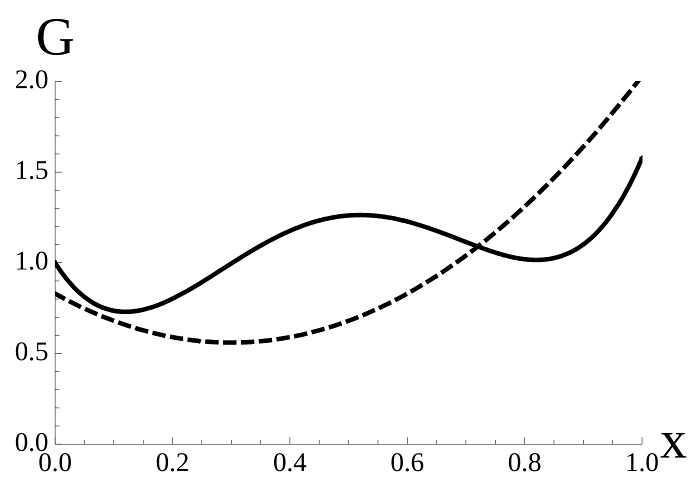
(f) [**2 marks**] Using the Clausius-Clapeyron relation, and the numbers from the above table, write down a numerical expression for the the slope of the coexistence line (in Pa/K) at the transition point found in part (d). You do not need to simplify your answer.

QUESTION 3. [8 marks] Answer **any four** of the following six questions.

(a) [**2 marks**] The figure below shows two $S(T)$ curves for a paramagnet, one at low external magnetic field, the other at a high value of the external field. To understand the relative positions of the curves, consider that a higher field will tend to align the dipoles more strongly, and hence a higher T is needed to disorder (increase the entropy of) the system. Assuming that the system starts off at temperature T_1 in a low external field, how might you cause the paramagnet to end up at the lower temperature T_2 also at low external field? T_1 is the lowest temperature you can achieve with your other lab equipment.

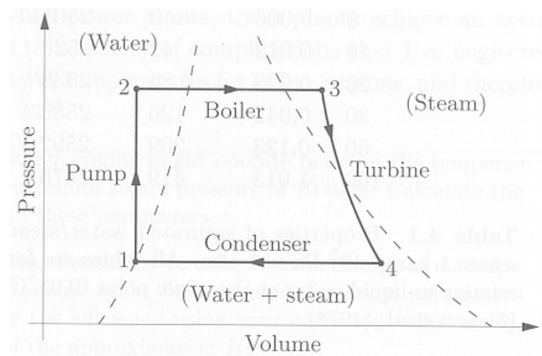


(b) [**2 marks**] Consider a system composed of type A and B particles, and let x be the fraction of particles that are of type B. At $x \approx 0$ the mixture consists almost purely of A particles. At a particular temperature and pressure, the Gibbs free energy as a function of x for the vapour phase of the mixture is plotted with a dashed line in the figure below. At the same conditions, the Gibbs free energy as a function of x for the liquid phase of the mixture is plotted with a solid curve and shows a miscibility gap. Describe the thermodynamic ground state of the system if the overall composition is $x = 0.65$, in terms of what phases are present and at what approximate compositions.



(c) [2 marks] Give an example in which the entropy of a system increases without the addition of heat. Use equations to help illustrate your point.

(d) [2 marks] Below is a PV diagram for a steam engine. Sketch and label a similar diagram for a refrigerator. The COP for a refrigerator is Q_c/W, where Q_c is the heat removed from the cold interior, and W is the work required to run the compressor. Using the First Law, write down the COP in terms of enthalpies relevant to the refrigeration cycle and assume that a throttle is used in the refrigerator.



(e) [2 marks] Two identical bubbles of gas form at the bottom of a lake, than rise to the surface. Because the pressure is much lower at the surface than at the bottom, both bubbles expand as they rise. However, bubble A rises very quickly, so that no heat is exchanged between it and the water. Meanwhile, bubble B rises slowly (impeded by a tangle of seaweed), so that it always remains in thermal equilibrium with the water. Assume that the lake has the same temperature everywhere. Which of the two bubbles is larger at the surface? Explain your reasoning fully.

(f) [2 marks] A snowflake in the sunlight sublimates directly to water vapour at -1 °C. The heat of sublimation is L per gram, and the snowflake has a mass of 0.02 g. Write down an expression for the factor by which the multiplicity of the universe has increased.