PHYS 3400 Physics & Physical Oceanography, Memorial University of Newfoundland Fall 2006

FINAL EXAM

December 14, 2006, 3:00 pm **Time allowed: 2 hours** **44 marks total**

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

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

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

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

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

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

$$\Delta S = \frac{Q}{T} \qquad dU = TdS - PdV + \mu dN \qquad dF = -SdT - PdV + \mu dN$$

QUESTION 1. [16 marks] A peculiar kind of chain has oval links of length l and negligible width. Furthermore, the links can be in one of two states: lying parallel to the length of the chain, or perpendicular. Let's say there are N links in the chain, and n links that are in the perpendicular configuration. The length of the chain is then $L = (N - n)l$. Additionally, the links interact with a constant external field in such a way that the perpendicular links have energy μ, and the parallel links have energy 0, i.e. the energy of the entire chain is $U = n\mu$, where $\mu > 0$ is a constant. A sample chain is shown below.

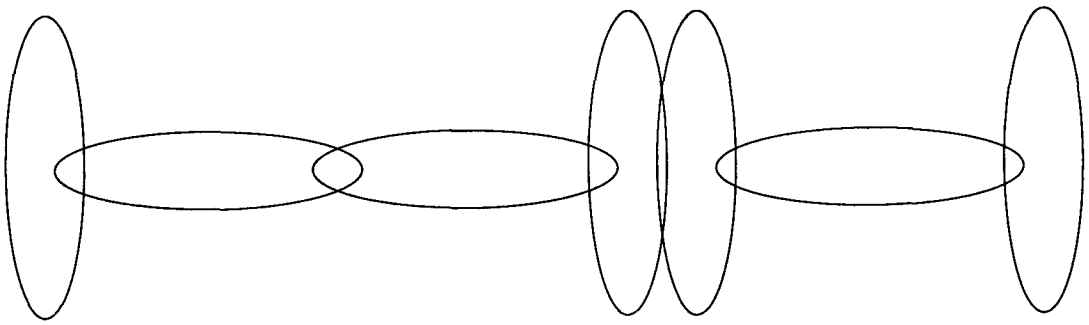


Figure 1: Chain with $N = 7$, $n = 4$, $L = (7 - 4)l = 3l$, and $U = n\mu = 4\mu$.

(a) [2 marks] Write down a formula in terms of factorials for the multiplicity Ω of a chain in terms of N and n. At what value of n is Ω the biggest?

(b) [3 marks] For the case where N and n are large, use Stirling's approximation ($\ln N! = N \ln N - N$) to find an expression for the entropy S as a function of n. Draw a rough sketch of $S(n)$.

(c) [4 marks] Find U as a function of temperature T, which we define here by $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$.

(d) [2 mark] Write L as a function of T.

(e) [2 marks] What is L in the limits $T \to 0$ and $T \to \infty$?

(f) [3 marks] A gremlin prepares a chain with $L = Nl/4$ and brings it into thermal contact with a chain at $T \approx \infty$. Qualitatively, what should happen to the lengths of the chains if energy cannot escape into the surroundings? What will happen to the temperature of the chain originally at $T = \infty$? (Hint: consider your graph in part b.)

QUESTION 2. [20 marks] The Gibbs free energy is defined as $G = U - TS + PV$.

(a) [3 marks] Find the thermodynamic identity for G, and find related formulas for the partial derivatives with respect to T, P, and N.

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

(c) [4 marks] A system with fixed N is placed in contact with a reservoir with which it can exchange only energy and volume. The reservoir keeps T and P constant. Using the Second Law, show that G for the system tends to decrease (thus showing that the system is equilibrated when G is minimized).

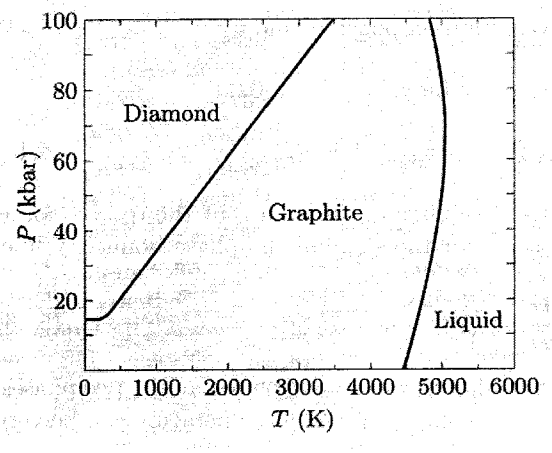
(d) [4 marks] At room temperature, find the pressure (in pascals) at which diamond becomes more thermodynamically stable than graphite, assuming that the difference in molar volume between the two phases does not change with pressure. Below are some molar data at standard conditions. You can leave an unsimplified numerical expression as your answer.

	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
graphite	0	0	5.74	8.53	5.30
diamond	1.895	2.90	2.38	6.11	3.42

(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.

(g) [2 marks] Below is the experimental phase diagram for carbon. At the melting temperature of graphite at 100 kbar, which is more dense, the liquid or graphite? Also, use the Third Law to explain why the graphite-diamond coexistence boundary becomes horizontal as $T \to 0$.

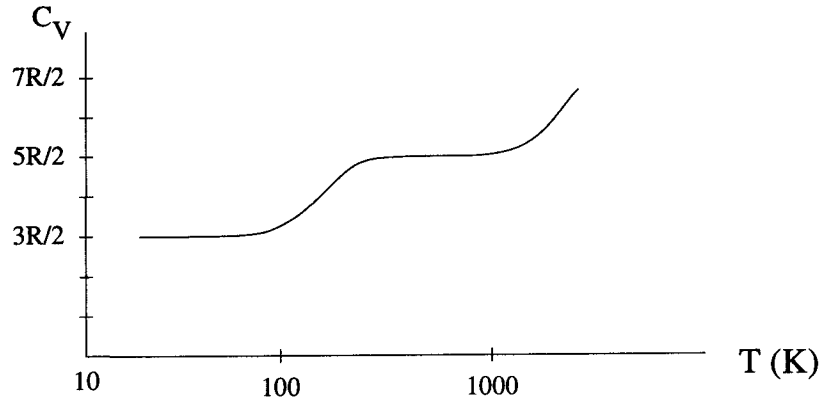


QUESTION 3. [8 marks] Short answer.

(a) [2 marks] Answer **ONE** of the following 2 questions.

(1) The fundamental assumption of statistical mechanics states: In an isolated system in thermal equilibrium, all accessible microstates are equally probable. What do we mean by the "most probable state"?

(2) Below is a sketch of C_V for 1 mole of H_2 gas as a function of T (with T on a log scale). Explain the jump in heat capacity that occurs from $T = 100$ K to $T = 1000$ K.



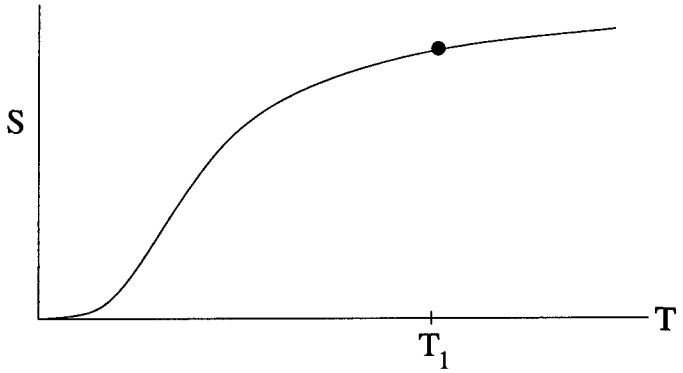
(b) [2 marks] Answer **ONE** of the following 4 questions.

(1) Fundamentally, why are diesel engines more efficient than gasoline engines?

(2) Why can't helium be cooled from room temperature by throttling?

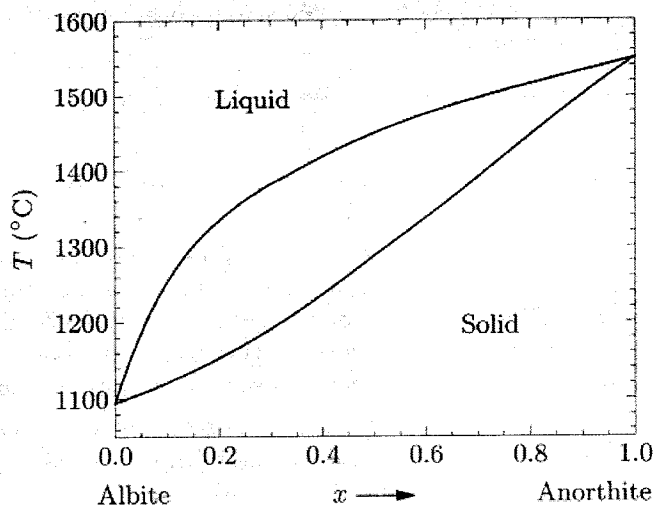
(3) List three interesting facts about the MUN cryogenic facility.

(4) The figure below shows $S(T)$ for a paramagnet at a given value of the external magnetic field. By changing the external field, explain how you might obtain a lower temperature of a system initially at T_1 and a low external field.

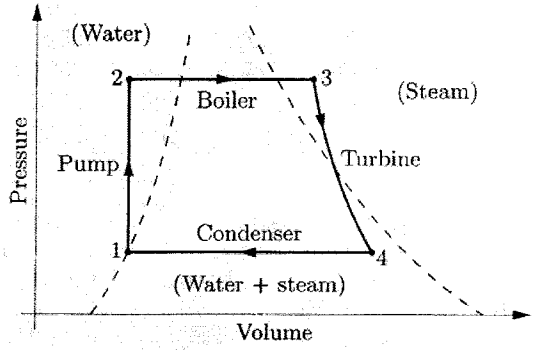


(c) [2 marks] Answer **ONE** of the following 2 questions.

(1) Below is a phase diagram for feldspar. Feldspar is a miscible mixture of two minerals, Albite and Anorthite. In stage 1 of a process, liquid feldspar with 20% Anorthite is cooled to 1300 °C. The resulting solid feldspar is removed from the system and taken to stage 2. In stage 2, the solid is reheated to 1400 °C. The resulting solid portion is removed and analyzed. Approximately, what should the compositions be of the solid portions of feldspar after stage 1 and after stage 2?



(2) Below is a PV diagram for a steam engine. Write down an equation that determines the composition of the steam + water mixture at 4. You can assume to know the P and T at 3 and 4, and also that you have access to steam tables. What other important assumption or approximation do you make?



(d) [2 marks] Answer **ONE** of the following 2 questions.

(1) In a hydrogen fuel cell, the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ occurs in a controlled way, and ΔG, ΔS, ΔU and ΔH are known. Write down an expression for the maximum voltage of the cell, in volts. At the electrodes, the following reactions take place.

(at negative electrode) $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

(at positive electrode) $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

(2) In the van der Waals equation of state, $P = \dfrac{NkT}{V - Nb} - \dfrac{aN^2}{V^2}$, what is the physical meaning behind the terms containing the parameters a and b?