

**DEPARTMENT OF PHYSICS AND PHYSICAL OCEANOGRAPHY**  
**MEMORIAL UNIVERSITY OF NEWFOUNDLAND**  
**Final Exam** **Physics 3400** **December 10, 2008**  
**Fall 2008** **Time: 2 hours**

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**INSTRUCTIONS:**

1. There are **two** parts to this exam. A complete paper consists of **four (4)** questions from part I (questions 1-6) and **two (2)** questions from part II (questions 7-9).
2. Write your answers in the booklets provided. Indicate **CLEARLY** which answer corresponds to a particular question.
3. Consider weighting of each question when budgeting time.
4. Don't panic.

**POTENTIALLY USEFUL INFORMATION:**

$$PV = NkT \quad (\text{ideal gas law})$$

$$U_{\text{thermal}} = N \frac{f}{2} kT \quad (\text{equipartition theorem})$$

$$\Delta U = Q + W \quad (\text{first law of thermodynamics})$$

$$W = - \int_{V_i}^{V_f} P(V) dV \quad (\text{quasistatic expansion/compression work})$$

$$dU = TdS - PdV + \mu dN \quad (\text{thermodynamic identity})$$

$$VT^{f/2} = \text{constant} \quad (\text{adiabatic process})$$

$$V^{(f+2)/f} P = \text{constant} \quad (\text{adiabatic process})$$

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} \quad (\text{for a system with } n \text{ of } N \text{ two-state particles in a specific state})$$

$$\Omega(N, q) = \frac{(q+N-1)!}{q!(N-1)!} \quad (\text{for a system with } q \text{ quanta of energy shared by } N \text{ oscillators})$$

$$dS = \frac{Q}{T} \quad (\text{quasistatic process})$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V}$$

$$\Delta S = \int \frac{C_V dT}{T}$$

$$P = T \left( \frac{\partial S}{\partial N} \right)_{U,N}$$

$$\Omega_{\text{total}} = \Omega_A \Omega_B$$

$$S = k \ln \Omega$$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

$$H = U + PV$$

$$G = U + PV - TS$$

$$F = U - TS$$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$e^x = 1 + x + \frac{x^2}{2} + \dots$$

$$(1+x)^{-1} \approx 1 - x + \dots \quad \text{for } |x| \ll 1$$

$$\ln(1+x) \approx x - \frac{x^2}{2} + \dots \quad \text{for } |x| \ll 1$$

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \quad \text{for large } N$$

$$\ln N! \approx N \ln N - N \quad \text{for large } N$$

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

$$N_A = 6.02 \times 10^{23}$$

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} = 4.136 \times 10^{-15} \text{ eV} \cdot \text{s}$$

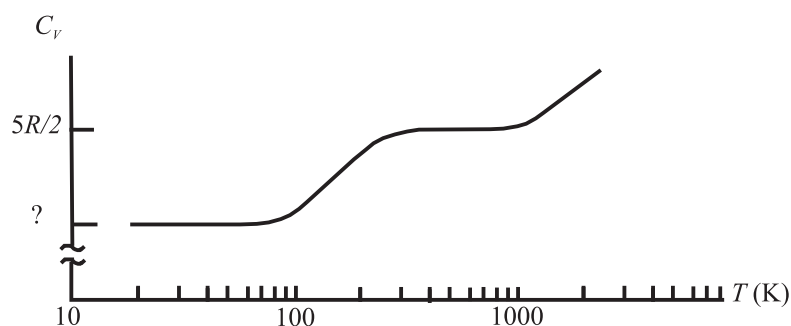
$$R = 8.315 \text{ J/mol} \cdot \text{K}$$

**Part I:** Do **four (4)** questions from the six questions (1-6) available in part I.

[5] 1. Between  $\sim 1000$  K to  $\sim 300$  K, the molar heat capacity,  $C_V$ , of  $H_2$  remains constant at  $\frac{5}{2}R$ . Upon cooling from  $\sim 300$  K to  $\sim 80$  K, the value of  $C_V$  drops from  $\frac{5}{2}R$  to a value which then remains constant from  $\sim 80$  K to  $\sim 30$  K.

(a) Briefly explain why the value of  $C_V$  for  $H_2$  above  $\sim 300$  K is different from its value below  $\sim 80$  K.

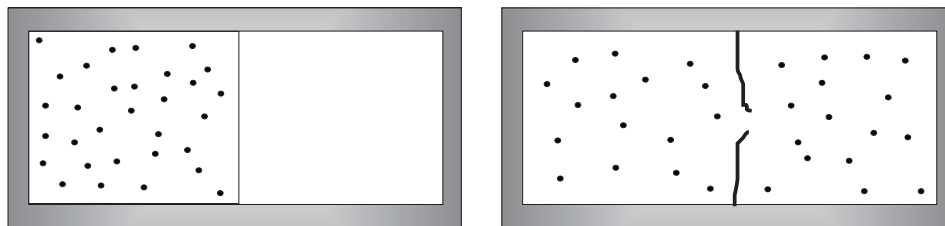
(b) What is the value of  $C_V$  for  $H_2$  between  $\sim 30$  K and  $\sim 80$  K? (Briefly justify your answer)



[5] 2. A thermally-isolated, rigid container is divided, by a thin membrane, into two spaces each of volume  $V$ . One space contains  $N$  particles of a monatomic ideal gas at temperature  $T$ . The other side is empty. The multiplicity of the gas has the form  $\Omega(U, V, N) = f(N)V^N U^{3N/2}$ . At some point, the membrane is punctured so that the gas goes from occupying volume  $V$  to occupying volume  $2V$ .

(a) What is the change in internal energy of the gas?

(b) What is the change in entropy of the gas?



[5] 3. Below 100 K, the molar heat capacity for a certain metal is  $C_V = aT + bT^3$  where  $a = 0.0014 \text{ J/K}^2$  and  $b = 2.5 \times 10^{-5} \text{ J/K}^4$  are constants specific to that metal. Calculate the entropy of this metal at 10K. To do this calculation, what assumption do you need to make about the entropy at very low temperature?

[5] 4. An ideal diatomic gas has 3 translational degrees of freedom and 2 rotational degrees of freedom.

(a) Write expressions for its internal energy,  $U$ , and its enthalpy,  $H = U + PV$ , at temperature  $T$ .

(b) If this gas is allowed to expand through a throttling valve (Joule-Thomson expansion) so that its pressure drops from 100 bar to 1 bar, what do you expect to happen to its temperature? Briefly justify your answer.

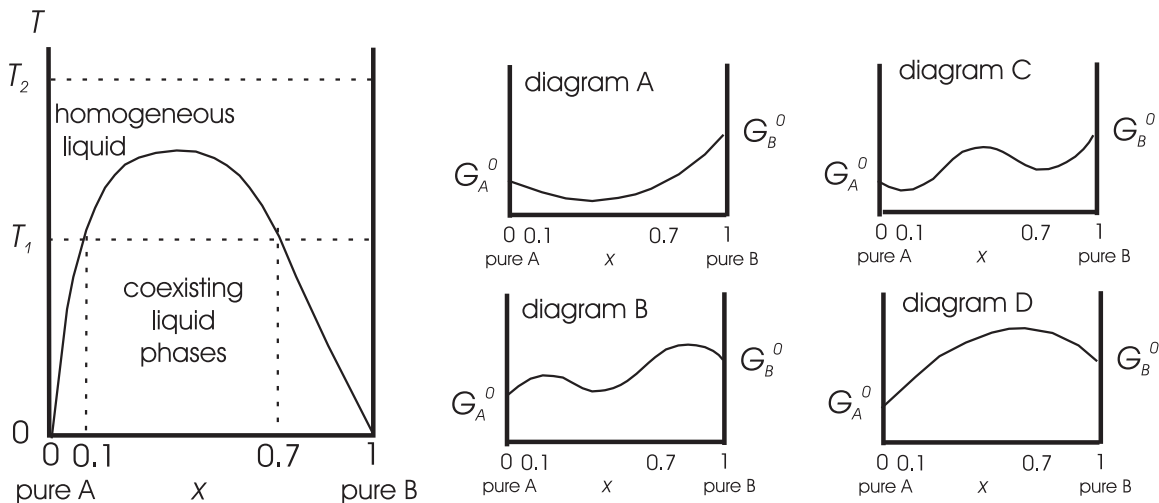
- [5] 5. An Einstein solid consisting of  $N$  harmonic oscillators contains  $q$  quanta of energy. In the low temperature limit (i.e.  $q \ll N$ ), the entropy for this system is

$$S = kq \left[ \ln \left( \frac{N}{q} \right) + 1 \right].$$

The energy per quantum is  $\varepsilon$  so that the total energy of the Einstein solid is  $U = q\varepsilon$ . Show that  $U = N\varepsilon e^{-\varepsilon/kT}$ . (Hint: start by finding  $1/T$ .)

- [5] 6. The left diagram in the group below shows a temperature-composition phase diagram, with a solubility gap, for two components, A and B, which mix non-ideally. The four diagrams on the right represent possible dependences of free energy on fraction  $x$  of component B. Which of the four  $G$  vs.  $x$  diagrams is most consistent with:

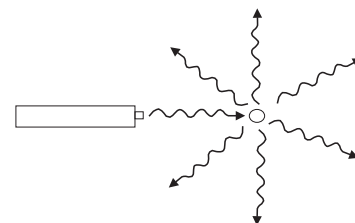
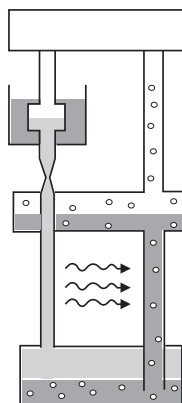
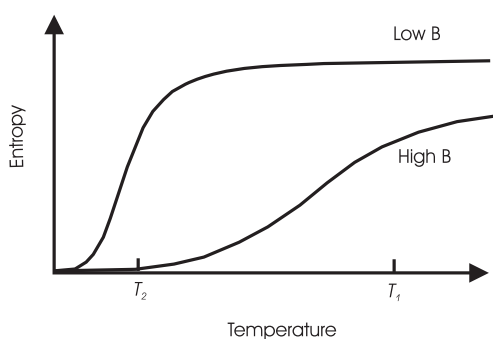
- (a)  $T = 0$  K  
 (b)  $T = T_1$  (i.e. a temperature below the critical mixing temperature)  
 (c)  $T = T_2$  (i.e. a temperature above the critical mixing temperature)



**Part II.** Do **two (2)** of the three available questions (7-9) in part II

[20] 7. Question 7 includes part (a) **and** part (b).

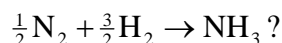
- (a) The diagrams below are relevant to three techniques used to achieve very low temperatures: magnetic cooling; helium dilution refrigeration; and laser cooling. Pick one of these cooling techniques and briefly describe the principle by which cooling is achieved in that technique. You may copy and use the relevant diagram in your description.



- (b) The table below contains some thermodynamic data for  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at atmospheric pressure (101 kPa) and 298K.

|                   | $\Delta_f G$ (kJ) | $S$ (J/K) |
|-------------------|-------------------|-----------|
| $\text{N}_2$ (g)  | 0                 | 191.61    |
| $\text{H}_2$ (g)  | 0                 | 130.68    |
| $\text{NH}_3$ (g) | -16.45            | 192.45    |

- (i) At 298K and atmospheric pressure, what is the change in Gibbs free energy,  $\Delta G$ , for the reaction



- (ii) What is the change in enthalpy,  $\Delta H$ , for this reaction?
- (iii) In this reaction, 2 moles of gas (0.5 moles of  $\text{N}_2$  and 1.5 moles of  $\text{H}_2$ ) combine to form 1 mole of gas ( $\text{NH}_3$ ) all at 101 kPa and 298 K. Calculate  $P\Delta V$  for this reaction and use your answer to find the change in internal energy,  $\Delta U$ , for this reaction.
- (iv) If this reaction were used in a fuel cell, what is the maximum amount of electrical work that could be obtained by combining nitrogen and hydrogen to form 1 mole of  $\text{NH}_3$ ?

[20] 8. The diagram represents an elastic polymer as a chain of  $N$  links, each of length  $l$ . Imagine that such a chain is hanging vertically from the ceiling with a mass  $m$  suspended from its end. We can take the energy of this system to be the gravitational potential energy of the mass,  $U = mgh$ , where  $h$  measured from the location of the mass when the chain is fully extended (i.e. when  $L = Nl$ ).

(a) Taking  $N_d$  and  $N_u$  to be the numbers of links that point down or up respectively, show that the system energy is  $U = -2mgN_d l + \text{constant}$ . (The constant is  $2mgNl$ .)

(b) Write the multiplicity of the chain in terms of factorials.

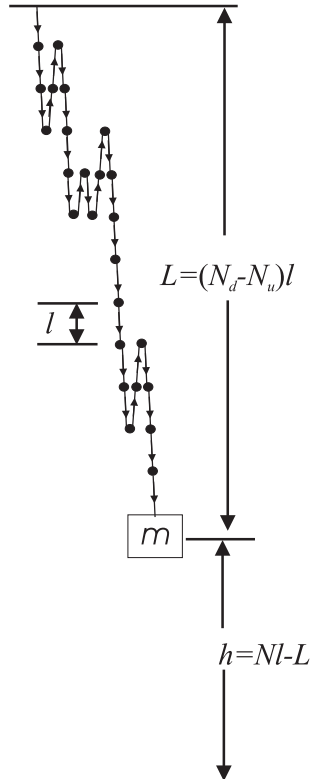
(c) Use Stirling's approximation to show that the chain entropy is

$$S = k[N \ln N - (N - N_d) \ln(N - N_d) - N_d \ln N_d].$$

(d) Use  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V}$  to obtain the result  $\frac{-2mgl}{kT} = \ln \left( \frac{N - N_d}{N_d} \right)$ .

(e) Rearrange the answer in part (d) to obtain an expression for  $N_d$ . Find the high and low  $T$  limits of  $N_d$ .

(f) What happens to the length,  $L$ , of the polymer as temperature is reduced? Comment briefly on why this does or does not seem reasonable.



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

- (a) Show that  $dG = -SdT + VdP + \mu dN$ .
- (b) Use the thermodynamic identity in part (a) to find a partial derivative that shows how  $G$  depends on  $P$ .
- (c) The table below gives some thermodynamic data (molar) for two solid phases of a substance at 298 K and atmospheric pressure. Which phase is stable under these conditions?

|         | $\Delta_f H$ (kJ) | $\Delta_f G$ (kJ) | $S$ (J/K) | $C_p$ (J/K) | $V$ (m <sup>3</sup> )  |
|---------|-------------------|-------------------|-----------|-------------|------------------------|
| phase 1 | -1206.9           | -1128.8           | 92.9      | 81.88       | $36.93 \times 10^{-6}$ |
| phase 2 | -1207.1           | -1127.8           | 88.7      | 81.25       | $34.15 \times 10^{-6}$ |

- (d) At what pressure does this substance undergo a transition from one phase to the other at 298 K?
- (e) Show that the slope of the coexistence line in a pressure temperature phase diagram is given by  $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ . In other words, derive the Clausius-Clapeyron relation, an expression for  $\frac{dP}{dT}$  along the coexistence line, in terms of thermodynamic variables of the coexisting phases. (Hint: Use the fact that as you move from one point  $(T, P)$  on the coexistence line to another point  $(T + dT, P + dP)$  on the coexistence line, the free energy for both phases must change by the same amount.)
- (f) Use your result from part (e) to calculate the pressure at which the transition between phase 1 and phase 2 occurs for  $T = 750$  K.