

Physics 360 – Winter 2006  
Exam #3

Instructor: Lawrence Rees

CID: \_\_\_\_\_

Score: \_\_\_\_\_

- Calculators are not permitted
- Nothing written on the colored cover sheet from the testing center will be graded.
- Be sure your test has seven pages excluding the colored cover sheet.
- Each problem is worth 10 points

**Possibly Useful Information**

$$F = U - TS, \quad H = U + PV, \quad G = U + PV - TS$$

$$\left( P + \frac{aN^2}{V^2} \right) (V - Nb) = NkT$$

$$e = 1 - \frac{T_C}{T_H}$$

At constant energy and volume,  $S$  tends to increase.

At constant temperature and volume,  $F$  tends to decrease.

At constant temperature and pressure,  $G$  tends to decrease.

$$\mu(P, T) = \mu^\circ(T) + kT \ln \left( \frac{P}{P^\circ} \right), \quad \mu_A(P, T) = \mu^\circ(P, T) - \frac{N_B kT}{N_A}, \quad \mu_B(P, T) = f(P, T) + kT \ln m_B$$

$$dU = T dS - P dV + \mu dN$$

$$dH = T dS + V dP + \mu dN$$

$$dG = -S dT + V dP + \mu dN$$

## Section I. Review Questions

1. Which is larger  $C_v$  or  $C_p$ ? Use the First Law of Thermodynamics to explain why.

*$C_p$  is larger. If volume is constant, all the heat flowing in goes to internal energy and hence higher temperature. If pressure is constant, some heat goes into work.*

2. Assume that the volume of one state in phase space is  $h^3$ . Find the multiplicity for a single monatomic atom of mass  $m$  in a box of dimension  $a$  on a side and total kinetic energy  $U$ . Assume an uncertainty in energy of  $\Delta U$ . (Your answer should include only the variables defined within the problem.)

$$\Omega = \frac{a^3 4\pi p^2 \Delta p}{h^3} = \frac{a^3 4\pi 2mUm\Delta U}{h^3 \sqrt{2mU}} = \frac{4\pi a^3 m \sqrt{2mU} \Delta U}{h^3}$$

$$\text{Note: } U = \frac{p^2}{2m} \Rightarrow \Delta U = \frac{p\Delta p}{m}$$

## Section II. Qualitative Questions.

3. Describe in words Helmholtz free energy and Gibbs free energy.

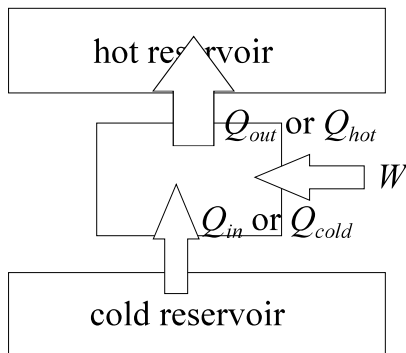
*Helmholtz free energy: create something out of nothing, but allow temperature reservoir to provide part of the necessary energy by heat flowing in.*

*Gibbs free energy: create something out of nothing and push surroundings (air) out of the way, but allow temperature reservoir to provide part of the necessary energy by heat flowing in.*

4. What does throttling mean? How is throttling used in a refrigerator?

*Allowing a fluid to pass through a porous plug from a region of high pressure to a region of lower pressure. – The expansion of the fluid causes temperature to drop.*

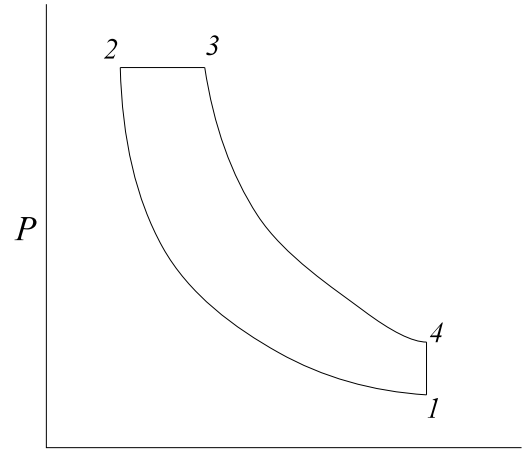
5. Sketch a diagram for a basic refrigerator. Write the equation of energy conservation involving heat and work. Define the COP.



$$COP = \frac{\text{benefit}}{\text{cost}} \text{ (half credit)} = \frac{Q_{in}}{W}$$

### Section III. Basic Problems

6. A monatomic ideal gas is used in a diesel engine that operates in the cycle illustrated in the diagram. Find an equation for the efficiency of the engine. You may leave your answer in terms of any of the pressures, temperatures, and volumes, along with  $N$  and  $k$ . Don't go to any great effort to simplify the answer.



$$Q_m = C_p(T_3 - T_2)$$

$$W = P_2(V_3 - V_2) + \frac{1}{(1-\gamma)} P_2 V_3^{\gamma} \left( \frac{1}{V_1^{\gamma-1}} - \frac{1}{V_3^{\gamma-1}} \right) + \frac{1}{(1-\gamma)} P_2 V_2^{\gamma} \left( \frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right)$$

$$e = \frac{P_2(V_3 - V_2) + \frac{3}{2} P_2 V_3^{5/3} \left( \frac{1}{V_3^{2/3}} - \frac{1}{V_1^{2/3}} \right) - \frac{3}{2} P_2 V_2^{5/3} \left( \frac{1}{V_2^{2/3}} - \frac{1}{V_1^{2/3}} \right)}{\frac{5}{2} Nk(T_3 - T_2)}$$

7. Starting from the relation  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ , find an expression for the molality of  $\text{H}^+$  that could be evaluated numerically if I gave you values for the standard change of the Gibbs free energy, the temperature, and physical constants (such as  $R$  or  $k$ ). Your derivation should include a reference to chemical potentials. (This is the same example as in the one in the text or the one we worked in class, in case you are wondering.)

$$\mu_{\text{H}_2\text{O}}^{\circ} = \mu_{\text{H}^+}^{\circ} + kT \ln m_{\text{H}^+} + \mu_{\text{OH}^-}^{\circ} + kT \ln m_{\text{OH}^-}$$

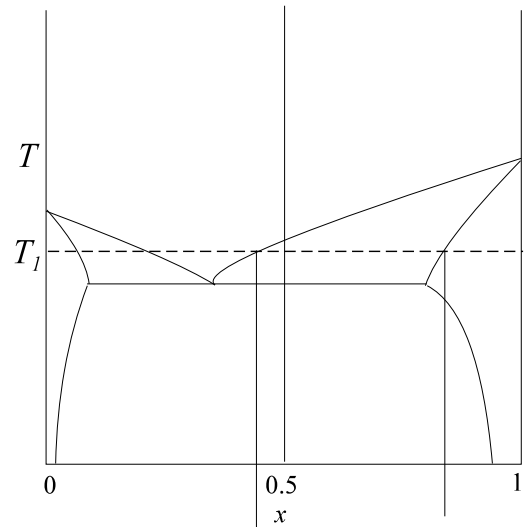
$$- N_A (\mu_{\text{H}_2\text{O}}^{\circ} - \mu_{\text{H}^+}^{\circ} - \mu_{\text{OH}^-}^{\circ}) = N_A kT \ln(m_{\text{H}^+} m_{\text{OH}^-})$$

$$- \Delta G^{\circ} = RT \ln m_{\text{H}^+}^2$$

$$m_{\text{H}^+}^2 = e^{-\Delta G^{\circ}/RT} = K$$

$$m_{\text{H}^+} = \sqrt{K}$$

8. A sample of mineral contains half type-A atoms and half type-B atoms. Let  $x$  be the fraction of **type-A** atoms, as we usually define it. The system forms solids in two different crystalline forms,  $\alpha$  and  $\beta$ . If the solid is pure A-type, it forms an  $\alpha$  crystal structure. If the temperature is  $T_l$ , of what will the sample consist ( $\alpha$ ,  $\beta$ , liquid) and what will  $x$  be for each of these components? (Estimate  $x$ , but draw lines on the graph to show how you arrived at your conclusion.) Based on your numbers, estimate the amount of each of the components that you will find at  $T_l$ .



Since numbers will not be precise, show your work so that we can determine if you understand the concepts. You do not need to evaluate the arithmetic expression for the last part of the problem.

*There will be liquid with  $x=0.4$  and  $\alpha$  solid with  $x=0.8$  (roughly)*

$$0.4 f_{\alpha q} + 0.8 f_{\beta} = 0.5$$

$$0.4 f_{\alpha q} + 0.8(1 - f_{\alpha q}) = 0.5$$

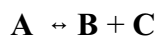
$$- 0.4 f_{\alpha q} = -0.3$$

$$f_{\alpha q} = 0.75$$

$$f_{\beta} = 0.25$$

## Section IV. Synthesis Problems

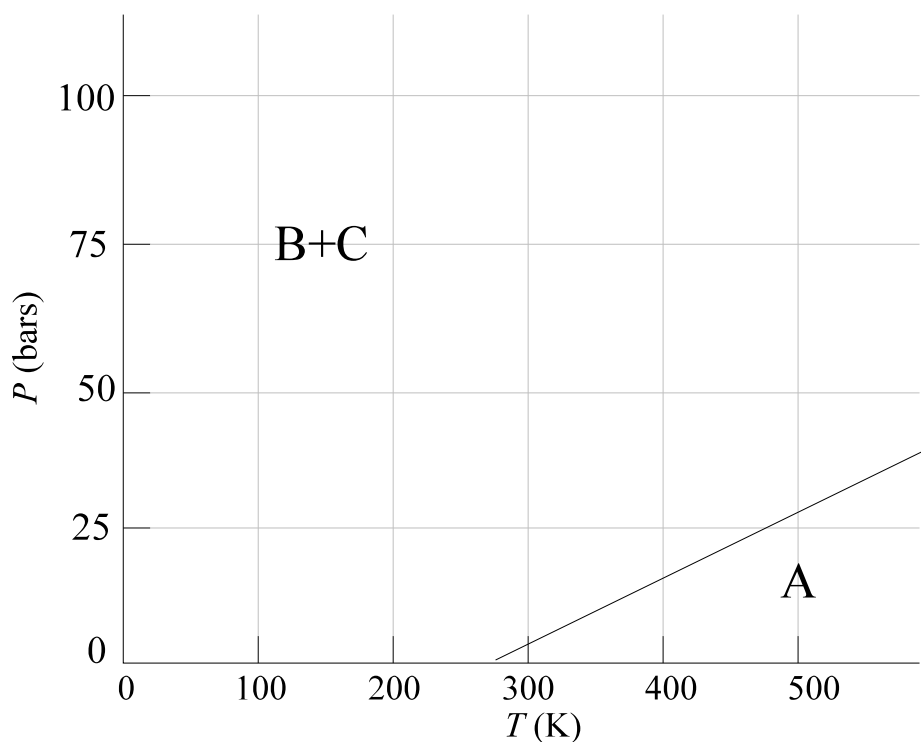
9. Geologically, mineral **A** can transform into a combination of minerals **B** and **C**.



Thermodynamic information for these minerals is listed in the table below. (Please note the units!) Also, it is useful to remember that  $dG = \mu dN - SdT + VdP$ . Given this information, make a reasonably accurate sketch of the phase diagram for these minerals. Be sure to indicate which phase (**A** or **B+C**) is on each side of the curve. Assume that the temperature and pressure dependence of  $S$  and  $V$  can be ignored.

At  $T = 300\text{K}$  and  $P = 1\text{ bar}$ , for 1 mole of material:

Mineral	$\Delta H$ (J)	$\Delta G$ (J)	$S$ (J/K)	$C_p$ (J/K)	$V$ (m <sup>3</sup> )
<b>A</b>	-5400.60	-5000.80	49.024	205.10	$96.0 \times 10^{-6}$
<b>B</b>	-2206.30	-2000.10	12.000	133.07	$52.0 \times 10^{-6}$
<b>C</b>	-3201.10	-3000.30	37.000	44.61	$42.0 \times 10^{-6}$



9. (continued)

$$G = G^o + \left( \frac{\partial G}{\partial T} \right)_{N,P} \Delta T + \left( \frac{\partial G}{\partial P} \right)_{N,T} \Delta P = G^o - S \Delta T + V \Delta P$$

The phase boundaries are given by:

$$(G_A^o - G_B^o - G_C^o) - (S_A - S_B - S_C) \Delta T + (V_A - V_B - V_C) \Delta P = 0$$

$$(G_A^o - G_B^o - G_C^o) - (S_A - S_B - S_C)(T - T_0) = -(V_A - V_B - V_C)(P - P_0)$$

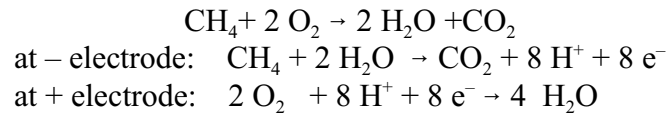
$$+ 2 \times 10^{-4}(P - P_0) = 0.40 + 0.024(T - T_0)$$

$$P - P_0 = 2.0 \times 10^5 + 1.2 \times 10^4(T - T_0)$$

$$P = 30 \times 10^5 - 36 \times 10^4 + 1.2 \times 10^4 T$$

$$P = -33 \times 10^4 + 1.2 \times 10^4 T$$

10. A fuel cell uses methane in the following reaction:



Assume that the process occurs at 300 K and 1 bar.

- (A) For one mole of methane, how much electrical work can you get out of the cell?  
 (B) For one mole of methane, how much waste heat is produced?  
 (C) What is the change in internal energy for the cell?  
 (D) What is the voltage of the cell? (You may leave  $e$ , the electron charge, and  $N_A$ , Avagadro's number, in your answer.)

Use the following data. (Note the units. These vales are actually fake and bear little resemblance to true values.)

At  $T = 300\text{K}$  and  $P = 1 \text{ bar}$ , for 1 mole of material.

	$\Delta H$ (J)	$\Delta G$ (J)	S (J/K)	$C_p$ (J/K)	V(m <sup>3</sup> )
CH <sub>4</sub>	-500	-600	0.020	35	0.0223
O <sub>2</sub> (g)	0	0	0.060	30	0.0224
H <sub>2</sub> O (g)	-425	-500	0.030	190	0.0224
CO <sub>2</sub> (g)	-262	-200	0.040	35	0.0224

- (A) This is  $\Delta G = -600 \text{ J}$   
 (B) This is  $T\Delta S = \Delta H - \Delta G = -12 \text{ J}$   
 (C)  $\Delta U = \Delta H - P\Delta V = -187 \text{ J} - 10 \text{ J} = -197 \text{ J}$   
 (D)  $-600 \text{ J}/8N_A e$  (This is just  $\Delta G$  divided by the number of electrons.)