MatE 251
Fall 2010

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Midterm Examination

This examination is Open Book, Open Notes. You may use your class notes and homework solutions from this semester, and any other reference texts that you might have brought with you. However, <u>you cannot share any of your materials with anybody else in the class</u>.

There are five questions. Each question is worth 20 points, for a total of 100 points. There is one Bonus Question, worth 5 points.

You may attempt, and prepare your answer in any order you wish. However, when you turn in the examination, **the answers must be arranged sequentially**. Please begin each question on a fresh sheet of paper, and make sure that your working of the problem is arranged in a neat and logical manner that will enable the reader to follow your logic. Please note that correct grammar is essential for the reader to be able to follow your logic. Random scribblings will not be taken into account and will not be credited. All chemical reactions should include the phase of the species. All YES/NO or one-word answers must be substantiated with valid reasons - otherwise they will receive no credit. The number of points for each question is shown at the end of the question, in *italics*.

If you feel that you have insufficient information to answer any of the questions, please identify the information that you need, and how you would use this information to arrive at an answer.

This examination will be graded only if you sign the following Honor Code statement:

I, ____________________________, do hereby attest that I have neither received aid from anybody else, nor given aid to anybody else, in answering the questions contained in this examination.

Signed: ____________________________ Date: ________________

Name: (Print): ________________________________
Student ID #: ________________________________

In taking this examination, you accept that the slightest suspicion of the above "Honor Code" not being followed will result in an "F", and that the burden of proof that the Honor Code was not violated is on you.

1a. A student attempts to apply the phase rule to a 5%Si-95%Al alloy in the α + L region. She sees that she is in a two-phase region, and at a pressure of 1 atm the Gibbs Phase Rule yields: F = C – P + 1, or, F = 2 – 2 + 1 = 1. She says that since this is an area where there are two variables, i.e., composition and temperature, the phase rule is incorrect in yielding F = 1. Do you agree? *(10 points)* 5 + 5

1b. Another student applies the phase rule to the eutectic temperature for the aluminum-silicon system. She says quite correctly that there are three phases and two components; hence F = 0. She then says that three phases will be in equilibrium from 1.6% to 99% silicon, at 577°C, so there is still a variable to be fixed if she is to describe the system to another student. Can you help her? *(10 points)* 10

2. The rate of a chemical reaction can be expressed in the following form:

$$\text{Rate} = v \exp(-\Delta G^*)/RT,$$

where v is a frequency factor, and ΔG* is the activation free energy. Derive an expression for the change in rate with change in pressure such that it can be represented in terms of physically measurable quantities. *(20 points)*

10 10

3. Calculate the final temperature and the entropy produced when 1500 g of Pb at 100°C is placed in 100 g of adiabatically contained water, the initial temperature of which is 25°C. You are given the following information: $C_{p,H2O}$ = 18.03 cal/degree/mole and $C_{p,Pb}$ is 6.38 cal/degree/mol. The molecular weights of H_2O and Pb are 18 and 207 g, respectively.

4. The expression below shows the temperature-dependence of the free energy change of a reaction.

$$\Delta G = -1{,}750{,}000 - 15.7\, T \log T + 370\, T \quad (\text{J/mol})$$

4a. Will this reaction occur spontaneously at 227°C? 7
4b. Calculate ΔS for this reaction at 227°C. 7
4c. Calculate ΔH for this reaction at 227°C. 6

5. Calculate the enthalpy of reaction for:

$$NH_3 + 5/4\, O_2 = NO + 3/2\, H_2O(g)$$

You may find the following data useful:

$\frac{1}{2} N_2 + 3/2\, H_2 = NH_3$	ΔH_1 = -46,190 J/mol
$NO = \frac{1}{2} N_2 + \frac{1}{2} O_2$	ΔH_2 = -90,370 J/mol
$H_2 + \frac{1}{2} O_2 = H_2O$ (liq)	ΔH_3 = -285,840 J/mol
H_2O (g) = H_2O (liq)	ΔH_4 = -44,000 J/mol

MatE251 Fall 2010

Midterm Solutions

#1a (10) Under the stated conditions there is only 1 degree of freedom in the 2-phase region. This means you can either:

(i) Fix the temperature ⇒ then the composition of the phases are fixed. (NOT the overall composition)

(ii) Fix the composition of one phase ⇒ then the composition of the other phase and the temperature will be fixed.

#1b (10) At 577°C the compositions of each of the three phases are fixed. Varying the concentration of Si from 1.6 to 99% will vary the amount of each phase, but not the composition of each phase.

#2 (20)

$$\text{Rate} = \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \quad \text{where } \nu \text{ is a constant}$$

$$\ln \text{Rate} = \ln \nu - \Delta G^*/RT$$

$$\frac{\partial \ln \text{Rate}}{\partial P} = -\frac{1}{RT}\frac{\partial \Delta G^*}{\partial P}$$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \qquad \frac{\partial \ln \text{Rate}}{\partial P} = -\frac{1}{RT}\cdot \Delta V^*$$

#3 1500 g Pb at 100°C → 100 g H_2O at 25°C

$C_{P,H_2O} = 18.03$ cal/deg/mol

$C_{P,Pb} = 6.38$ cal/deg/mol

# of moles of Pb $= \frac{1500}{207} = 7.24$

# of moles of $H_2O = \frac{100}{18} = 5.56$

Let the final temp be t

$7.24 \times 6.38 (100 - t) = 5.56 \times 18.03 (t - 25)$

(10) $t = 48.5°C = 321.5$ K

$\Delta S = n C_p \frac{dT}{T} = n C_p \ln\left[\frac{T_2}{T_1}\right]$

$\Delta S_{Pb} = 7.24 \times 6.38 \times 2.303 \log \frac{321.5}{373}$

$= -6.93$ eu

$\Delta S_{H_2O} = 5.56 \times 18.03 \times 2.303 \log \frac{321.5}{298}$

$= +7.53$ eu

(10) $\Delta S_{Tot} = \Delta S_{Pb} + \Delta S_{H_2O} = 0.60$ eu

#4 $\Delta G = -1,750,000 - 15.7\, T \log T + 370\, T$ J/mol

$227°C = 500K$.

(7) 4a. $\Delta G = -1,750,000 - 15.7 \times 500 \times \log 500 + 370 \times 500$ J/mol

$= -1,586,000$ J/mol.

$\therefore$ Reaction is spontaneous.

(7) 4b. $dG = -S\,dT + V\,dP$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{\partial}{\partial T}(+1,750,000) + \frac{\partial}{\partial T}(15.7\,T \log T) - \frac{\partial}{\partial T}(370\,T)$$

$$= 0 + \left[15.7\,T \frac{d}{dT}(\log T)\right] + \log T \frac{d}{dT}(15.7\,T) - 370$$

$$= 0 + 15.7\,T \cdot \frac{\log_{10} e}{T} + 15.7 \log T - 370$$

$$= 15.7 \log_{10} e + 15.7 \log T - 370$$

$\simeq -320$ J/mol.

(6) 4c.

$$dG = dH - TdS$$
$$\Delta G = \Delta H - T\Delta S$$
$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S.$$

Differentiate with respect to $\frac{1}{T}$

$$\Delta H = d\left(\tfrac{1}{T}\right)\left(\frac{\Delta G}{T}\right)$$
$$= d\left(\tfrac{1}{T}\right)\left[-\frac{1,750,000}{T} - 15.7 \times 2.303 \ln T + 370\right]$$
$$= -1,750,000 - 15.7 \times 2.303 T$$
$$= -1,732,000.$$

#5

$$\Delta H_{rxn} = \sum_{products} \nu_i \Delta H_i - \sum_{reactants} \nu_i \Delta H_i$$

$$\Delta H_{rxn} = \Delta H_{f,NO} + \frac{3}{2}\Delta H_{f,H_2O,g} - \Delta H_{f,NH_3} - \cancel{\Delta H_{f,O_2}} \to 0$$

$$\Delta H_{f,H_2O,g} = \Delta H_{f,H_2O,liq} + \Delta H_{evap,H_2O}$$
$$= -285,840 + 44,000 = -241,840 \text{ J/mol}$$

$$\therefore \Delta H_{rxn} = +90,370 + \tfrac{3}{2}(-241,840) - (-46,190)$$
$$= -226,200 \text{ J/mol}$$