**CH353 – Physical Chemistry I**
Spring 2012, Unique 52135

**Exam 3**
Friday, 9 March 2012

Name: key

Useful Information:

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 8.206 \times 10^{-2}\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$1\ \text{atm} = 1.01325\ \text{bar} = 1.01325 \times 10^{5}\ \text{Pa} = 760\ \text{Torr}$

$0\ ^{\circ}\text{C} = 273.15\ \text{K}$

Always assume ideal gas unless directed otherwise.

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

Signature Date

1. (21 points) Indicate whether the following statements are true or false.

a) True **False** When the free energy of a solid material is plotted as a function of temperature (i.e. $T$ on the x-axis), the slope of the line will be steeper than when an identical plot is made for the liquid phase of the material.

b) True **False** The triple point of a phase diagram shows where $G = H = S$ for any material.

c) **True** False At $P = 1$ bar and $T = 273$ K, $\mu(H_2O(s)) = \mu(H_2O(l))$.

d) True **False** All reactions with $\Delta G < 0$ will result in complete conversion of reactants to products.

e) True **False** A reaction with an equilibrium constant $K_p > 1$ will not proceed spontaneously.

f) True **False** A phase is a material that is chemically pure and uniform in physical state.

g) True **False** Ludvig Boltzmann was a composer who lived in 19th century Vienna.

2. (20 points) Based on your general chemistry knowledge, determine whether the chemical potential of the reactants in the following balanced equations is greater than, less than, or equal to the chemical potential of the products. You may assume each reaction is taking place under standard conditions unless otherwise indicated.

a) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

NaCl dissolves spontaneously in water $\mu(\text{reactants}) > \mu(\text{products})$

b) $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

HCl is one of the "strong" acids that dissociates completely in water $\mu(\text{reactants}) > \mu(\text{products})$

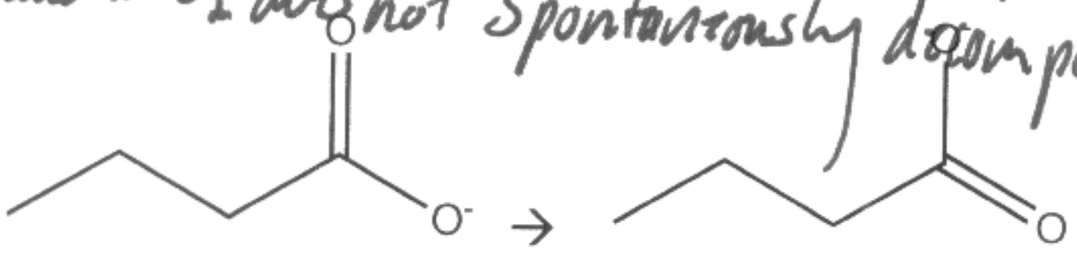
c) $H_2O(l) \rightarrow H_2O(g)$ at T = 373 K

phases are in equilibrium at T = 373 K and P = 1 bar $\mu(\text{reactants}) = \mu(\text{products})$

d) $O_2(g) \rightarrow 2\,O(g)$

$\mu(\text{reactants}) < \mu(\text{products})$

molecular $O_2$ does not spontaneously decompose into atomic O.

e) 

$\mu(\text{reactants}) = \mu(\text{products})$

resonance structures

3. (25 points) The molar enthalpy of fusion of ice at 273.15 K and 1.0 atm is 6010 J $mol^{-1}$. The change in volume caused by the fusion of ice under the same conditions is -1.63 $cm^3$ $mol^{-1}$. You may assume that these values remain constant as a function of pressure. Estimate the melting temperature of ice at 1000 atm.

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T_{fus}\,\Delta V_{fus}} \quad ; \quad \Delta T = \int_{P_i}^{P_f} \frac{dP\, T_{fus}\,\Delta V_{fus}}{\Delta H_{fus}}$$

$$\Delta T = \bar{T}_f - \bar{T}_i = \frac{T_{fus}\,\Delta V_{fus}\,\Delta P}{\Delta H_{fus}} \quad ; \quad \bar{T}_f = \frac{T_{fus}\,\Delta V_{fus}\,\Delta P_{fus}}{\Delta H_{fus}} + \bar{T}_i$$

$$\Delta T = -7.47\,K, \quad \bar{T}_f(P = 1000\,bar) = 266\,K$$

4. (14 points) Prove the following expressions are true.

a) $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$

$$dU = TdS - PdV$$

$$dS = \frac{dU + PdV}{T} = \frac{dU}{T} \quad (\text{because } \Delta V = 0)$$

rewrite: $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$

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

$$dS_P = \frac{dq_P}{T} = \frac{C_P dT}{T}$$

rewrite: $\left(\frac{\partial S_P}{\partial T}\right)_P = \frac{C_P}{T}$

5. (20 points) When a rubber band is stretched, it exerts a restoring force, $f$, which is a function of its length $L$. The work needed to stretch the rubber band is described by:

$$w = \int f(L)dL$$

a) Justify (in words) the sign of work $w$.

The rubber band is the system. It will not stretch spontaneously on its own. Work needs to be done on the rubber band. Based on our convention, because work is going into the system, $w > 0$.

b) Determine an expression for the change in internal energy of the rubber band as it is stretched. You may assume that the change in volume upon stretching the rubber band is negligible.

$w = f\Delta L$

$q = S\Delta T$

$\Delta(\text{internal energy}) = \text{heat} + \text{work}$

$\Delta U = S\Delta T + f\Delta L$

c) Extra credit (not much): Determine an expression for the change in Helmholtz energy of the rubber band as it is stretched.

$\Delta A = \Delta U - T\Delta S$