Chemistry 311 **PHYSICAL CHEMISTRY** Fall 2004
Examination 2 Extra Credit Due: November 10, 2004

All questions are worth 10 points each. Answer all questions clearly, and show all work. Be sure to clearly number each answer and to draw lines to separate answers to different questions. If you use the back side of the paper, please clearly indicate the number of the question you are answering. Please also remember that I can only grade what I can read.

For each question, also identify the corresponding Instructional Objective(s).

---

1. Denote the entropy change for the **system**, Δ*S* as positive, negative, or zero for the following:

Process	Δ*S* (positive/negative/zero)
(a) Carnot cycle (**ideal gas**)	………………………………………
(b) **Water** boils at 100° C, 1 atm	…………………………………………
(c) **Ice** melts at 30 °C, 1 atm	…………………………………………
(d) A **gas** expands adiabatically	…………………………………………
(e) **Water** freezes at –10 °C, 1 atm	…………………………………………

2. Consider a constant pressure (1 atm) process in which one mole of supercooled water at –3 °C suddenly freezes into ice. Sketch a reversible path connecting the initial and final states along which the entropy change of the system Δ*S* may be calculated. Also show the actual path taken by the system on the same diagram.

3. Calculate the entropy change for the system ΔS for the path sketched in Q. 2.

   Given: $C_{P,m}$(water) = 75.3 J K^{-1} mol^{-1}; $C_{P,m}$(ice) = 37.7 J K^{-1} mol^{-1}; $\Delta_f H°$(ice→water) = 6.02 kJ mol^{-1}.

4. Calculate the entropy change in the surroundings, ΔS_{surr}, for the process described in Q. 2, assuming that the surroundings remain at a constant temperature of –3 °C.

5. A gas obeys the equation of state $PV_m = RT + aP^2$. Evaluate the fugacity of the gas at 500 K and 20 bar, if a = 0.00148 L bar^{-1} mol^{-1}.

6. Gibbs energies of formation for $N_2O_4(g)$ and $NO_2(g)$ are 102.00 and 51.30 kJ mol^{-1}, respectively (standard state = 1 bar, 298.15 K). What is the value of K_P for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

7. What is the free energy change for the reaction in Q. 6 if we change the standard state to 1 mol dm^{-3}?

8. At 1 bar pressure, bromine boils at 58.2 °C and at 9.3 °C, its vapor pressure is 0.1334 bar. Assuming $\Delta_{\mathrm{vap}}H$ and $\Delta_{\mathrm{vap}}S$ to be independent of temperature, calculate those quantities.

9. The K_P for the reaction $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$ at 298 K is 31.225. Calculate the the extent of reaction (amount reacted out of 1 mol) at equilibrium if we start with an equimolar mixture of CO and H_2O.

10. An industrial design problem requires that the variation of entropy with volume at constant temperature be known for a particular substance. Propose an experiment whereby this quantity could be measured in the laboratory, given that $dA = -PdV - SdT$. [Note that you must describe the experiment in one or two sentences to get full credit.]

Constants, conversion factors, and Useful Mathematical Relations:

Gas constant $R = 0.083145$ L bar K^{-1} mol^{-1} = 8.3145 J K^{-1} mol^{-1}.

1 bar = 10^5 Pa

1 L = 1 dm^3 =10^3 cm^3 = 10^{-3} m^3

- Ideal gas law: $PV = nRT$.
- Enthalpy and entropy changes for constant pressure heating or cooling if $C_{P,m}$ is independent of temperature:

$$\Delta H_m = C_{P,m}(T_f - T_i)$$

$$\Delta S_m = nC_{P,m} \ln\left(\frac{T_f}{T_i}\right)$$

- Entropy change for a phase change (pc):

$$\Delta_{pc}S = \frac{\Delta_{pc}H^\circ}{T_{pc}}.$$

- General definition of entropy change for surroundings:

$$dS_{\text{surr}} = -dq_{\text{actual}}/T,$$

  where q_{actual} is the heat absorbed or given out by the system during the actual process.
- Fugacity of a real gas:

$$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{Z-1}{P}\right) dP,$$

  where $Z = PV_m/(RT)$.
- $\Delta_r G^\circ = -RT \ln K$, where K is defined with respect to the appropriate standard state.
- Relationship between K_P and K_c:

$$K_P = K_c \left(\frac{RT}{P^\circ}\right)^{\Delta n},$$

  where Δn is the change in the number of moles of gases in going from reactants to products.
- Temperature dependence of K:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

  where K_1 and K_2 are the equilibrium constants at T_1 and T_2, respectively.