For instructor's use only

1	1b bonus	2	3	4	Si. D.	Total: /15

Name: **Student ID:**

UNIVERSITY OF MANITOBA, DEPARTMENT OF CHEMISTRY
Chemistry 2290, Winter 2012, Dr. H. Georg Schreckenbach

Second Midterm Examination March 11, 2012

This exam has **4** (four) pages. *READ the question carefully*! Answer **ALL** questions, except possibly 1b, which is a bonus question that may earn you one extra mark. Most questions have *multiple* parts. Note that the questions aren't necessarily ordered by difficulty or by any other criteria.

If you use *pencil*, your exam will not be remarked! For numerical problems, all mathematical steps must be shown. Please answer all questions *on* the question sheets. Use *reverse* side or extra paper if more space is needed. On any extra sheet, please indicate your name and student ID number, please.

1. Third Law **2 marks (part a; 1.5 bonus mark (part b)**

(a) Provide a concise verbal statement of the Third Law of Thermodynamics.

(b Bonus) Provide an alternative statement of the Third Law *and* prove that your two formulations are equivalent.

(i) It is impossible to reach the absolute zero in temperature (0 K)

— or —

(ii) At 0K, all perfectly crystalline substances have the same entropy.

(b) (ii) → (i) differences in S can be used to lower the T of the substance with the lower entropy

(i) → (ii) related: if we could reach 0K, there would be no reason for (ii)

(Details see text)

2. Phase and phase equilibrium **5 marks**

(a) In the context of the "phase rule", what are "thermodynamic degrees of freedom"? (Definition.)

(b) If two phases are in equilibrium with each other, what follows for the chemical potentials?

(c) Determine the number of the thermodynamic degrees of freedom for the following system:

A closed bottle of carbonated water. (Assume that carbonated water contains CO_2 dissolved in pure water. Assume further that some gas has collected at the top of the bottle.)

(a) least # of intensive variables that can be varied independently without changing the # of phases in the system.

(b) For each component i: $\mu_i^\alpha = \mu_i^\beta$ where α and β are the 2 phases in equilibrium

(c) 2 phases (ℓ, g)

2 components (H_2O, CO_2)

$F = C - P + 2 = 2$ (T, P)

3. Free energies **5 marks**

Consider 1.50 mol of an ideal gas at 400.K and 1.00 atm pressure. This gas is compressed reversibly and at constant temperature to a final pressure of 2.00 atm. For this process, calculate the Helmholtz free energy (ΔA) and Gibbs free energy (ΔG).

$T = 400.\,K$ $= \text{const}$

$P_i = 1.00$ atm

$P_f = 2.00$ atm

$$dG = -S\,dT + V\,dP$$

$$dA = -S\,dT - P\,dV$$

($-S\,dT = 0$ (isothermal))

$$dG = V\,dP \qquad dA = -P\,dV$$

$$\Delta G = \int_1^2 V\,dP \qquad \Delta A = -\int_1^2 P\,dV$$

(ideal gas)

$$= \int_1^2 \frac{nRT}{P}\,dP \qquad = -\int_1^2 \frac{nRT}{V}\,dV$$

$$\overset{\text{const } T}{=} nRT \ln\frac{P_2}{P_1} \qquad = -nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{V_1}{V_2}$$

but $\frac{P_1}{P_2} = \frac{V_2}{V_1}$ (ideal gas)

$$\Rightarrow \Delta A = nRT\ln\frac{P_2}{P_1}$$

$$\Delta G = \Delta A = 3.46 \text{ kJ}$$

4. Thermochemistry **3 marks**

The hydrolysis of adenine triphosphate (ATP) to give adenine diphosphate (ADP) and phosphate (P) can be represented by:

$$ATP \leftrightarrow ADP + P$$

The following values have been obtained for the reaction at 37.0°C (standard state, 1M):

$$\Delta G^0 = -31.0 \text{ kJ mol}^{-1}$$
$$\Delta H^0 = -20.1 \text{ kJ mol}^{-1}$$

(a) Calculate ΔS^0 at 37.0°C.

(b) Calculate the equilibrium constant at 25°C, assuming that ΔS^0 and ΔH^0 are independent of temperature.

(a) const T: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

T = 37.0°C = 310.15 K

$$\Rightarrow \Delta S^\circ = \frac{1}{T}(\Delta H^\circ - \Delta G^\circ)$$
$$= 35.1 \text{ J K}^{-1} \text{mol}^{-1}$$

(b)

$$\Delta G^\circ (25°C) = \Delta H^\circ - T\Delta S^\circ \quad (T = 298.15 \text{ K})$$
$$= -30.6 \text{ kJ mol}^{-1}$$

$$\ln K = -\frac{\Delta G^\circ}{RT} = 12.3$$

$$K = 2.27 \times 10^5$$

Total marks in this exam: 15 (regular questions); bonus marks: 1.5 (question 1b)

--- END OF EXAM ---