The University of Waterloo
Chemistry 254 Elementary Thermodynamics
April 16, 1992

FINAL EXAMINATION
NOW, CHEMISTRY 452D — ASSIGNMENT #1 [DUE: Sept 20, 2005]
DO #2 to #6

NAME .... I.D. ....
(surname first)

Instructions

(1) Answer ALL six questions.
(2) A standard, non-programmable calculator is allowed.
(3) Total time permitted for this examination is THREE hours.

Some (*possibly* useful) Equations and Constants

The gas constant: $R = 1.99$ cal/mol/K = 0.082 ℓ-atm/mol/K = 8.3 J/mol/K

Internal Energy:
$dU = (\partial U/\partial T)_V\, dT + (\partial U/\partial V)_T\, dV$
$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$

For an ideal gas:
$P = nRT/V$
$(\partial U/\partial V)_T = 0$
$C_p/n - C_v/n = R$

For a van der Waals gas:
$P = nRT/(V-nb) - n^2a/V^2$
$(\partial U/\partial V)_T = n^2a/V^2$

Gibbs Free Energy: $\Delta G^\Theta = -RT \ln K$

Gibbs-Helmholtz equation: $[\partial(G/T)/\partial T]_P = - H/T^2$

PLEASE SUBMIT BOTH THE EXAM PAPER (*this paper*) AND THE BOOKLET.

QUESTION	SCORE	MAXIMUM
1		20%
2		10%
3		20%
4		15%
5		15%
6		20%
TOTAL		100%

[1] Briefly discuss and/or define the following concepts in thermodynamics.

a. Phase equilibrium and reaction equilibrium. (Be sure to define all variables).
[5%]

b. Intensive and extensive properties. (Give an example for each).
[5%]

c. The second law of thermodyanmics, from the system's point of view.
[5%]

d. The use of van't Hoff equation to determine thermodynamics quantities.
[5%]

[2] During a Grey Cup game, a football official inflated a football to the required pressure of 191 kPa prior to the game. The football had an volume of 2.65 ℓ and the air was at room temperature (25°C) when the football was first inflated. The ball was then taken onto the field. By kick-off time, the air temperature had dropped to 0°C.

How much heavier would the football be if the official now had to re-inflate the football to the required pressure of 191 kPa? Hint: Molar mass of air is 28.97g/mol. We can assume air as a monatomic ideal gas.
[10%]

[3] One mole of a monatomic ideal gas expands isothermally at 300 K into an evacuated vessel so that the total pressure drops from 10 atm to 1 atm. i.e. It expands from a vessel of 2.463 ℓ into a connecting vessel such that the total volume becomes 24.63 ℓ.

a. Calculate w, q, ΔU and ΔH.
[10%]

b. Now, calculate ΔS, ΔA and ΔG. Is this a spontaneous process?
[10%]

[4] Given the following data for H_2O:

$C_P(l) = 75.3$ J/K/mol ; $C_P(s) = 2.05$ J/K/mol ;
$\Delta H_{vap} = 40670$ J/mol ; $\Delta H_{fus} = 6008$ J/mol .

Calculate S (of the system) for the following reaction.

$$H_2O(g)_{100°C} \rightarrow H_2O(s)_{-100°C}$$

[15%]

[5]a. The Gay-Lussac-Joule experiment indicates that the internal energy of an ideal gas is a function of temperature only. Use the appropriate Maxwell relation(s) to give a mathematical proof of this statement.
[10%]

b. By considering the temperature dependence of the Gibbs free energy and one of the six basic equations, derive the Gibbs-Helmholtz equation.
[5%]

[6] Suppose we put 0.3 mol of H_2 and 0.1 mol of D_2 into a 2.0 ℓ flask at 25°C with a catalyst to promote the following isotope-exchange reaction:

$$H_2\,(g) + D_2\,(g) = 2\,HD\,(g)$$

For this reaction, $\Delta G° = -2.928$ kJ/mol.

a. Determine the equilibrium constant, K.
[10%]

b. Determine the amount (in mol) of HD produced.
Hint. For a quadratic equation $ax^2 + bx + c = 0$, the roots are given by the following:

$$x = [-b \pm (b^2 - 4ac)^{1/2}]/[2a].$$

[10%]