Chemistry 2740 Spring 2008 Test 2

> **Time:** $50\,\mathrm{min}$ **Questions:** 5 **Marks:** 45
> **Aids permitted:** calculator, one 8.5×11-inch formula sheet
> See reverse for useful data.

1. What effect does a catalyst have on equilibrium? [1 mark]

2. An endothermic solution-phase reaction $A + B \rightarrow P + Q$ has a very poor yield of the desired product P. List two ways that the yield could be improved significantly. [4 marks]

3. A professor has asked the following question on a test:

   Calculate the vapor pressure of bromine at $10°C$.

   One student's solution reads as follows:

   > $$Br_{2(l)} \rightarrow Br_{2(g)}$$
   >
   > $$\Delta_r \bar{G}° = \Delta_f \bar{G}°_g - \Delta_f \bar{G}°_l = 30.91\,\mathrm{kJ/mol}$$
   > $$\therefore K = \exp\left(\frac{-30.91}{8.314 \cdot 283}\right) = 0.99$$
   >
   > The vapor pressure is therefore $0.99\,\mathrm{bar}$.

   On seeing this solution, the professor experienced a moment of profound depression. Since he wanted to give the student some feedback but couldn't bear to look at this test paper, he handed it to you and asked you to explain to the student where he went wrong. Find and explain all the errors in this solution. Do *not* solve the problem for the student. Note that this student has serious problems, so we do *not* want to dwell on minor issues like significant figures. [6 marks]

4. Electrochemical cells are sometimes used to measure concentrations. Consider the cell

   $$Cu_{(s)}|CuSO_{4(aq)}(1.4 \times 10^{-3}\,\mathrm{mol/L})\|NaBr_{(aq)}(0.0085\,\mathrm{mol/L}), Br_{2(aq)}|Pt_{(s)}.$$

   Electrons flow in the external circuit from the copper to the platinum electrode. The equilibrium voltage at $25°C$ is $0.7558\,\mathrm{V}$. What is the concentration of bromine in the right half-cell? Use Debye-Hückel theory to calculate the activity coefficients of the ions. [15 marks]

5. The acid dissociation constant of uric acid[1] has been measured as a function of temperature in a solution to which NaCl had been added to maintain a constant ionic strength of $0.15\,\mathrm{mol/L}$:[2]

$T/°C$	25	32	37	42
$K_a/10^{-6}$	5.50	6.17	6.46	7.41

The calculations used in this paper to obtain these values assumed ideal behavior.

(a) Activity coefficients of ions vary weakly with temperature. Using this piece of information, explain why we should be able to get $\Delta_r \bar{H}°$ accurately from these data without considering corrections for nonideal behavior. [4 marks]

Hint: Think about using just two of the above points. What formula would you use?

(b) Calculate $\Delta_r \bar{H}°$ using *all* the data. [9 marks]

(c) Because H^+ and the conjugate base of uric acid (the hydrogen urate ion) are singly charged, their activity coefficients should be similar to the mean ionic activity coefficient of NaCl. This activity coefficient has been measured and has the value $\gamma_\pm = 0.757$ at an ionic strength of $0.15\,\mathrm{mol/L}$ at 25°C. Assuming that uric acid itself behaves ideally, correct the measured value of K_a at 25°C for the nonideal behavior of H^+ and of the hydrogen urate ion. [4 marks]

(d) Calculate $\Delta_r \bar{G}°$ at 25°C for the acid dissociation equilibrium. [2 marks]

Useful data

$\mathcal{F} = 96\,485.342\,\mathrm{C/mol}$

$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$

To convert degrees Celsius to Kelvin, add 273.15.

In the Debye-Hückel equation, $A = 1.107 \times 10^{-10}$.

For water at 25°C, $\varepsilon = 6.954 \times 10^{-10}\,\mathrm{C^2J^{-1}m^{-1}}$.

Standard thermodynamic data at 1 bar and 25°C

Species	$\dfrac{\Delta_f \bar{H}°}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\Delta_f \bar{G}°}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\bar{C}_p}{\mathrm{J\,K^{-1}mol^{-1}}}$
$Br_{2(l)}$	0	0	75.689
$Br_{2(g)}$	30.91	3.11	20.786

Standard reduction potentials at 298.15 K	
Reduction process	$\mathcal{E}°/\mathrm{V}$
$Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)}$	+1.0873
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	+0.3419

---

[1]Uric acid is diprotic, so this is actually the first dissociation constant. However, the second dissociation is of no relevance to this problem.

[2]Wang and Königsberger, *Thermochim. Acta* **310**, 237 (1998).