Chemistry 2850 Spring 2007 Final Examination

Instructions

Time: 3 h

Marks: 110

Aids permitted: graphing calculator, one 8.5 × 11-inch formula sheet

Write all answers in the booklets provided.

In section 2, you have a choice of questions to answer. **Do not** answer more than the required number of questions. Extra answers will not be marked. If you start a question and decide that you would rather complete a different one, cross out the one that you don't want marked.

Useful data

$F = 96\,485.3383\,\mathrm{C/mol}$

$h = 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz}$

$k_B = 1.380\,650\,3 \times 10^{-23}\,\mathrm{J/K}$

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

To convert degrees Celsius to Kelvin, add 273.15.

Reduction process	$\mathcal{E}^\circ$/V
$\mathrm{Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}}$	1.498
$\mathrm{NO^-_{3(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow HNO_{2(aq)} + H_2O_{(l)}}$	0.934

1 Answer *all* questions in this section.

Value of this section: 95

1. In its most general form, the ideal gas law can be written

$$PV = nR(\theta + c)$$

where θ is the temperature measured on any reasonable scale (e.g. Celsius) and c is a constant. Explain how this equation can be used to derive a value for the absolute zero of temperature in the temperature scale chosen. [3 marks]

2. For the reaction $Cl_2 + h\nu \rightarrow 2Cl$, what is the quantum yield of chlorine atoms? [1 mark]

3. How is a transition state different from an intermediate of a chemical mechanism? [4 marks]

4. What information does each of the following observations give you? [2 marks each]

   (a) The rate constant of a reaction decreases as the pressure is increased.

   (b) The rate constant of a reaction increases as the ionic strength is increased.

   (c) The equilibrium constant of a reaction increases as the temperature is increased.

5. Describe (possibly using diagrams) the equipment used in the bomb calorimetry experiment. Explain briefly how this equipment is used. [10 marks]

6. Describe briefly the flash photolysis experiment. To what kind(s) of reactions can this technique be applied? [8 marks]

7. A textbook gives the following initial rate data for the reaction $OCl^-_{(aq)} + I^-_{(aq)} \rightarrow OI^-_{(aq)} + Cl^-_{(aq)}$:

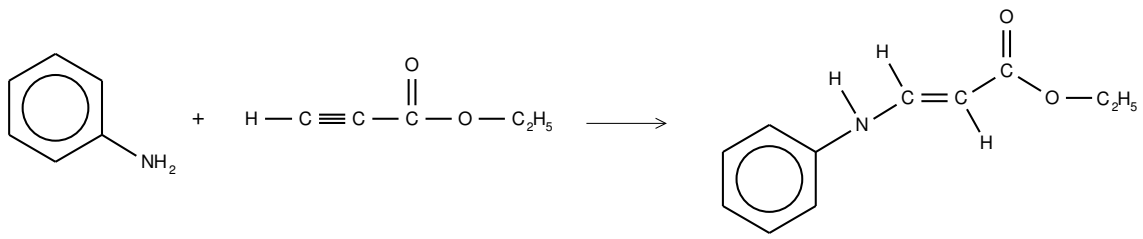
Experiment	$[OCl^-]/\text{mol L}^{-1}$	$[I^-]/\text{mol L}^{-1}$	$[OH^-]/\text{mol L}^{-1}$	$v/10^{-4}\text{L mol}^{-1}\text{s}^{-1}$
1	0.0040	0.0020	1.00	4.8
2	0.0020	0.0040	1.00	5.0
3	0.0020	0.0020	1.00	2.4
4	0.0020	0.0020	0.50	4.6
5	0.0020	0.0020	0.25	9.4

   Determine the rate law and the value of the rate constant. [13 marks]

   Bonus: There's something suspicious about these data. What is it?

8. The solubility of barium fluoride in water at 25°C is 6.8×10^{-3} mol/L. Using Debye-Hückel theory, calculate the solubility product of this compound. [11 marks]

9. For the reaction of aniline with ethyl propiolate in solution in the solvent DMSO,



the following second-order rate constants have been obtained:[1]

T/K	318	323	328	333	338
$k/10^{-3}\,\mathrm{L\,mol^{-1}s^{-1}}$	1.44	2.01	2.71	3.73	4.87

Calculate the activation energy, preexponential factor, enthalpy and entropy of activation at 25°C. [16 marks]

Note: It is not necessary to sketch your graph in this question. If you prefer, you can just show some sample calculations and describe briefly the graphical procedure used.

10. The oxidation of indole by $\mathrm{HSO_5^-}$ in acidic solution is thought to proceed by the following mechanism:[2]

$$\text{indole} + \mathrm{HSO_5^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \overset{k_2}{\rightarrow} \text{oxindole} + \mathrm{HSO_4^-}.$$

(a) Derive a rate law for this mechanism. [6 marks]

(b) Experimentally, it is found that the rate depends on the concentrations as follows:

$$v = k[\text{indole}][\mathrm{HSO_5^-}].$$

How is the experimental rate constant k related to the elementary rate constants? [2 marks]

(c) At 293 K in a 20:80 (by volume) mixture of acetonitrile and water, $k = 4.0 \times 10^{-3}\,\mathrm{L\,mol^{-1}s^{-1}}$. If we start the reaction with $[\text{indole}] = [\mathrm{HSO_5^-}] = 0.030\,\mathrm{mol/L}$, how long would it take before 90% of the indole was oxidized under these reaction conditions? [3 marks]

[1] D. Nori-Shargh et al., Int. J. Chem. Kinet. **38**, 144 (2006).

[2] S. Meenakshisundaram and N. Sarathi, Int. J. Chem. Kinet. **39**, 46 (2007).

11. Gold is often known as a noble metal because it is highly unreactive under most conditions. For instance, most acids won't dissolve gold. Gold can however be dissolved by aqua regia, a mixture of concentrated nitric and hydrochloric acid. When nitric acid reacts with gold, the following reaction occurs:[3]

$$2\mathrm{Au}_{(\mathrm{s})} + 3\mathrm{NO}^{-}_{3(\mathrm{aq})} + 9\mathrm{H}^{+}_{(\mathrm{aq})} \rightarrow 2\mathrm{Au}^{3+}_{(\mathrm{aq})} + 3\mathrm{HNO}_{2(\mathrm{aq})} + 3\mathrm{H_2O}_{(\mathrm{l})}.$$

(a) Calculate the equilibrium constant for this reaction at 25°C. From the result of your calculation, argue that this reaction alone won't dissolve much gold. [9 marks]

(b) The hydrochloric acid provides chloride ions which go on to react with the gold (III) ions:

$$\mathrm{Au}^{3+}_{(\mathrm{aq})} + 4\mathrm{Cl}^{-}_{(\mathrm{aq})} \rightleftharpoons \mathrm{AuCl}^{-}_{4(\mathrm{aq})}.$$

Explain qualitatively why this reaction could help dissolve gold. [3 marks]

[3]This is a bit of a cartoon. The reaction generates a range of nitrogen oxide products, including the brown gas $\mathrm{NO_2}$.

2 Answer *one* question from this section.

Extra answers will **not** be marked.

Value of this section: 15 marks

1. One recipe for ice cream calls for 480 mL of "half-and-half" (cream with a 12% fat content by weight, density 1.027 kg/L), and 130 g of sugar (i.e. sucrose, molar mass 342.300 g/mol), among other ingredients. The molar mass of water is 18.0153 g/mol, and its enthalpy of fusion (melting) is 6.007 kJ/mol.

   (a) Assuming that most of the non-fat portion of the half-and-half is water, what is the weight of water in this recipe? [3 marks]

   (b) Assuming that sugar is the main solute in this recipe, what percentage of the total water would be in the liquid phase at a serving temperature of −8°C? [12 marks]

2. Recent spectroscopic evidence suggests that nitrate ions exist in two forms in solution, α nitrate and β nitrate.[4] The equilibrium constant for the conversion

$$\alpha\text{-}NO^-_{3(aq)} \rightleftharpoons \beta\text{-}NO^-_{3(aq)}$$

   has been measured as a function of temperature in aqueous potassium nitrate solution:

T/°C	10	25	40	50	60	70
K	0.082	0.113	0.151	0.180	0.212	0.248

   Calculate ΔH° and ΔS° from the data. In the discussion section of their paper, Simeon and coworkers argue that the equilibrium they studied involves the breaking of a hydrogen bond between nitrate and water, i.e.

$$[NO_3(H_2O)_n]^- \rightleftharpoons [NO_3(H_2O)_{n-1}]^- + H_2O.$$

   Are the values of ΔH° and ΔS° you calculated consistent with this hypothesis? Typical hydrogen bond enthalpies are in the range of 15–40 kJ/mol. [15 marks]

[4] V. Simeon et al., Phys. Chem. Chem. Phys. **5**, 2015 (2003).