Chemistry 2000 Spring 2006 Test 1

Name:_____ **Student number:**_____

Time: 50 minutes

Aids allowed: Calculator

Instructions: Answer all questions in the spaces provided. You can use the backs of pages for scratch work or for extra answer space. If you do need to continue an answer on the back of a page, make sure that the continuation is clearly labeled.

Graphs should be drawn accurately on the graph paper attached to the back of this exam paper. Make sure that your graphs are clearly labeled with the question number.

Formulas and data

Order	Integrated rate law	Half-life
1	$\ln x = \ln x_0 - kt$	$\ln 2/k$
2	$\frac{1}{x} = \frac{1}{x_0} + kt$	$\frac{1}{kx_0}$

$k = Ae^{-E_a/(RT)}$ $R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$

To convert degrees Celsius to Kelvin, add 273.15.

Question	1	2	3	4	Total
Marks	/12	/13	/10	/10	/47

1. For the reaction

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)},$$

the following initial rate data have been obtained:

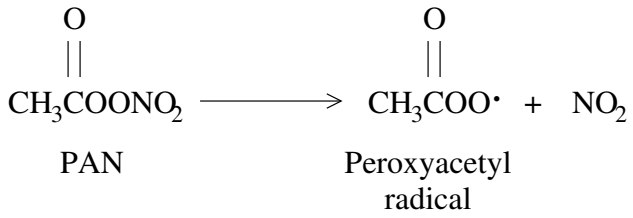
Experiment	$[S_2O_8^{2-}]$ (mol/L)	$[I^-]$ (mol/L)	v (mol $L^{-1}s^{-1}$)
1	0.038	0.060	1.4×10^{-5}
2	0.076	0.060	2.8×10^{-5}
3	0.076	0.120	5.6×10^{-5}

(a) What is the rate law for this reaction? [6 marks]

(b) Determine the value of the rate constant. [2 marks]

(c) This reaction is definitely not elementary. Give two arguments which support this conclusion, one of which is conclusive. [4 marks]

2. Peroxyacetyl nitrate (PAN) is a compound found in smog. It is very damaging to human health because it tends to break down into the peroxyacetyl and nitrogen dioxide radicals:

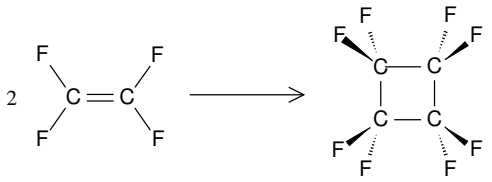


(a) At moderate pressures, this reaction obeys a first-order rate law. The frequency factor and activation energy are, respectively, $5.4 \times 10^{16}\,\mathrm{s}^{-1}$ and $114.7\,\mathrm{kJ/mol}$. What is the half-life of PAN at 20°C? [4 marks]

(b) The rate constant for the reverse (second-order) reaction is $5.74 \times 10^{9}\,\mathrm{L\,mol^{-1}s^{-1}}$ at 20°C. What is the equilibrium constant for this reaction? [5 marks]

(c) A container is filled with 0.45 bar of PAN at 20°C. If we neglect the reverse reaction, how long would it take for the partial pressure of PAN to fall to 0.05 bar? Give your answer in hours. [4 marks]

3. The following data were obtained for the gas-phase dimerization of C_2F_4 at 300°C:



t (min)	$[C_2F_4]$ (mol/L)
0	0.0500
250	0.0250
750	0.0125
1750	0.00625
3750	0.00312

Show that the data are consistent with this being an elementary reaction and calculate the rate constant. [10 marks]

4. The mechanism for the reaction

$$\mathrm{Hg}^{2+}_{2(\mathrm{aq})} + \mathrm{Tl}^{3+}_{(\mathrm{aq})} \rightarrow 2\mathrm{Hg}^{2+}_{(\mathrm{aq})} + \mathrm{Tl}^{+}_{(\mathrm{aq})}$$

is thought to be

$$\mathrm{Hg}^{2+}_{2(\mathrm{aq})} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Hg}^{2+}_{(\mathrm{aq})} + \mathrm{Hg}_{(\mathrm{aq})} \qquad \text{(fast)},$$

$$\mathrm{Hg}_{(\mathrm{aq})} + \mathrm{Tl}^{3+}_{(\mathrm{aq})} \overset{k_2}{\rightarrow} \mathrm{Hg}^{2+}_{(\mathrm{aq})} + \mathrm{Tl}^{+}_{(\mathrm{aq})} \quad \text{(slow)}.$$

(a) Identify an intermediate in the mechanism. [1 mark]

(b) What rate law would you predict based on this mechanism? [7 marks]

(c) Suppose that we carried out two initial rate experiments where, all other factors being held constant, we doubled the concentration of the mercury (II) ion from one experiment to the next. What effect would this have on the rate? [2 marks]