Chemistry 2850 Spring 2007 Test 3

Time: 50 min	Questions: 4	Marks: 46
Aids permitted: calculator, one 8.5 × 11-inch formula sheet		
Write all answers in the booklets provided.		

Useful data

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

$L = 6.022\,142\,0 \times 10^{23}\,\mathrm{mol^{-1}}$

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

To convert degrees Celsius to Kelvin, add 273.15.

1. Sketch a diagram of the Gibbs energy as a function of a reaction coordinate. Label your diagram with the Gibbs energies of activation for the forward and reverse reaction, as well as the overall ΔG° for the reaction. Give the mathematical relationship between these three quantities. [5 marks]

2. The radius of a hydrogen atom is 37 pm and the molar mass of H is 1.007 94 g/mol.

   (a) Predict the rate constant of the reaction $\mathrm{H + H \rightarrow H_2}$ in the gas phase at 25°C using collision theory. [5 marks]

   Hint: What is the activation energy of this reaction?

   (b) Deuterium is roughly twice as heavy as hydrogen, but is otherwise essentially identical. Without doing any calculations, what effect would replacing H by D in the above reaction have on your answer? [2 marks]

3. Describe the stopped-flow experiment and the equipment used in this experiment. Discuss in particular some of the problems which the stopped-flow experiment is designed to overcome. [10 marks]

   Note: One or more diagrams might be helpful.

4. In aqueous solution at high temperature and high acid concentrations, formic acid breaks down by decarbonylation:

$$\mathrm{HCOOH_{(aq)} \rightarrow CO_{(g)} + H_2O_{(l)}}.$$

(a) The rate of this reaction is known to depend on both the formic acid and hydrogen ion concentrations. The following initial rate data have been obtained by Yasaka and coworkers at 200°C:[1]

Experiment	$[\mathrm{HCOOH}]/\mathrm{mol\,kg^{-1}}$	$[\mathrm{H^+}]/\mathrm{mol\,kg^{-1}}$	$v/10^{-5}\mathrm{mol\,kg^{-1}\,s^{-1}}$
1	1.0	0.062	1.1
2	1.0	0.062	1.3
3	1.0	0.26	5.4
4	0.16	0.10	0.28
5	0.66	0.10	1.2
6	1.6	0.10	2.7

Determine the rate law and rate constant for this reaction. [14 marks]

Hints: You can do this question using four comparisons *or* a graphical method. Pick the whole-number partial orders which best describe these data for your final answer. Because there is considerable experimental scatter in the measurements, you must use *all* the data to calculate the rate constant.

(b) The rate constant was measured at different temperatures. The following data were obtained:

$T/°\mathrm{C}$	170	210	240	280
$k/\mathrm{kg\,mol^{-1}s^{-1}}$	1.5×10^{-5}	5.1×10^{-4}	3.7×10^{-3}	6.3×10^{-2}

Calculate the Arrhenius parameters for this reaction. [10 marks]

Note: To facilitate marking, you can *either* sketch your graph, *or* show a few sample calculations.

[1] Y. Yasaka et al., *J. Phys. Chem. A* **110**, 11082 (2006). The data given here are a subset of the data obtained by these authors. Note also the use of molality units to measure concentrations in this study.