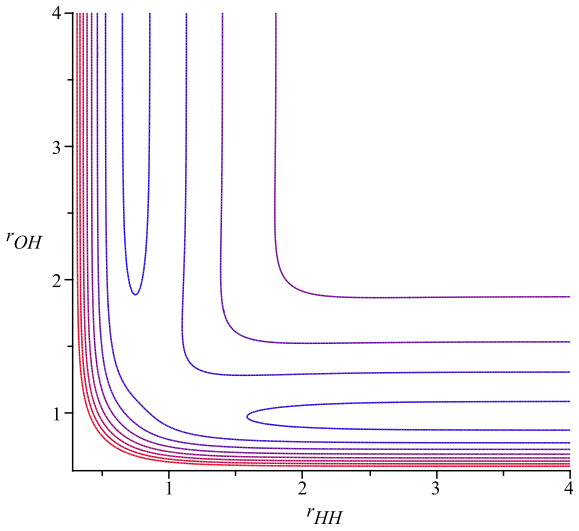
Chemistry 4000/5000/7001, Fall 2012, Assignment 5

Due: Friday, October 26, 4:00 p.m.
Total marks: 45

1. The following is a potential energy surface for a collinear reaction of an oxygen atom with a hydrogen molecule:



   The contours are drawn at intervals of $100\,\mathrm{kJ\,mol^{-1}}$, with the highest contour drawn at $300\,\mathrm{kJ\,mol^{-1}}$. Based on the shape of this potential energy surface, would you expect the product OH to carry about the same amount, more or less vibrational energy than H_2 had before passing through the transition state? Explain. [4 marks]

2. There are many variations on the Lindemann mechanism. One of the most common variations is designed to treat the case where we do a reaction without a bath gas and where A is the only significant collision partner:

$$\mathrm{A} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{A}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{product(s)}$$

   (a) You would only expect this mechanism to be valid if, for some reason, collisions with the product(s) rarely resulted in A becoming energized or in A^* becoming deenergized. Under what conditions (what experimental conditions and/or what types of reactions) would you expect this to be true? [4 marks]

   (b) Obtain a rate law for this reaction. Discuss what happens in the high- and low-pressure limits. [12 marks]

(c) An effective rate constant can be defined by $\hat{k} = v/[\mathrm{A}]$.[1] Suppose that we have a set of experimental measurements from which we calculated $\hat{k}$ at different values of [A]. Develop a graphical method for extracting the constants of this model. How many of the constants can you determine? [9 marks]

(d) For the isomerization of 3-methylcyclobutene to *trans*-1,3-pentadiene at 148.5 °C, the following data were obtained by Frey and Marshall (*Trans. Faraday Soc.* **61**, 1715, 1963):

p/torr	$\hat{k}/10^{-3}\,\mathrm{s}^{-1}$	p/torr	$\hat{k}/10^{-3}\,\mathrm{s}^{-1}$
32.3	1.50	0.365	1.14
11.0	1.47	0.148	0.969
6.49	1.46	0.086	0.841
3.42	1.43	0.061	0.762
1.13	1.32	0.029	0.594
0.634	1.22	0.012	0.429

Apply the graphical method you derived in the previous part of this question. If the graph is linear, use all the data to extract the parameters. Otherwise, extract only k_∞ by finding the linear part of the graph at high pressures and extrapolating to find the intercept. [10 marks]

3. Suppose that we have a unimolecular reaction for which the collision-theory estimate of the preexponential factor for the energization step is $2 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}$ at 500 °C, the activation energy is $100\,\mathrm{kJ\,mol^{-1}}$, and the reactant has 24 normal modes. Calculate k_1 using both the simple Lindemann theory and the Hinshelwood theory. [6 marks]

[1] Because of the dependence of the rate on $[\mathrm{A}]^2$, this is a funny thing to do, and the resulting quantity isn't a rate constant in quite the same way as for the case where there is a bath gas, which is why I am denoting this quantity by $\hat{k}$ rather than just k.