

Chemistry 4000 Fall 2012 Final Examination

Time: 3 hours

Marks: 93

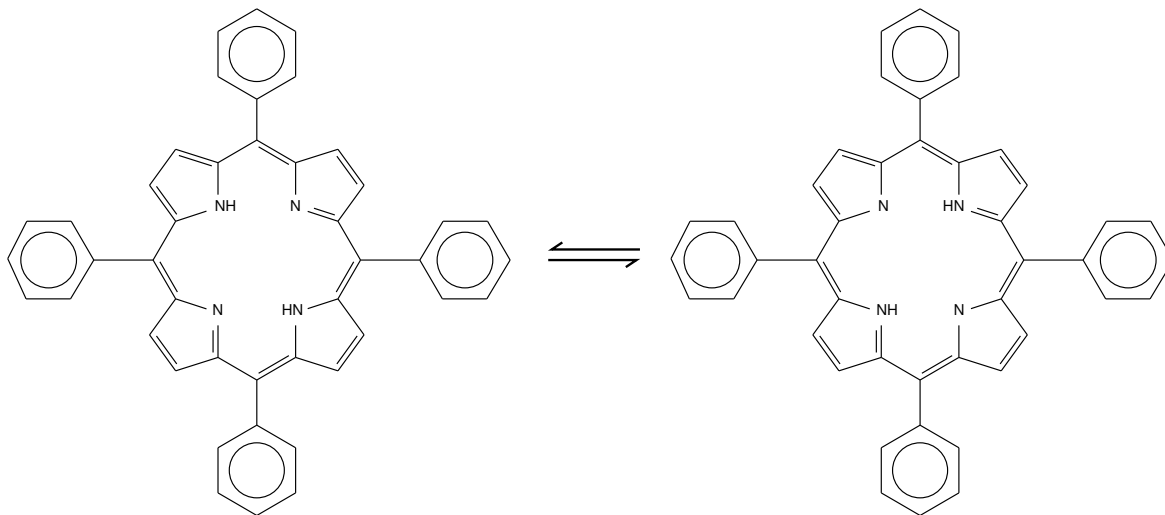
Aids allowed: calculator

Formulas and data are given on page 4.

Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).

1. How are physisorption and chemisorption distinguished? [4 marks]
2. Explain briefly where, in physical terms, the exponential term in the Arrhenius equation comes from. (No detailed mathematics need be given.) [4 marks]
3. In chemical kinetics theory, what is a cross-section? [2 marks]
4. Explain briefly the relationship between a potential energy surface, the reaction coordinate, and a reaction profile. [4 marks]
5. The free energy of activation, $\Delta^\ddagger G_m^\circ$, is a central concept in transition-state theory.
 - (a) What is the free energy of activation? [2 marks]
 - (b) What assumption of transition-state theory leads to the introduction of the free energy of activation? Explain briefly. [4 marks]
6. Describe the crossed molecular beam experiment. (A sketch would be welcome as part of your answer.) Explain what information can be obtained from this kind of experiment. [10 marks]
7. What is a transmission coefficient? What problem is the transmission coefficient intended to address? Choose one theory that deals with this problem, and explain how it does so. [10 marks]

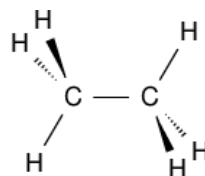
8. We can use the theory of stochastic kinetics to describe reactions at the single-molecule level. Suppose that we have a molecule with two states. An example is 5,10,15,20-tetraphenylporphyrin, which can exist in one of two protonation states:



Because of the symmetry, the forward and reverse rate constants must be identical. Let this common rate constant be k .

- (a) Let P_I be the probability of being in the first of the two protonation states, and P_{II} be the probability of being in the second. Write down the master equation for the two states of a single molecule of this substance. [3 marks]
- (b) What is the stationary probability distribution? [2 marks]
Note: It may not be necessary to do a calculation.
- (c) Sketch $P_I(t)$ assuming $P_I(0) = 1$. Label your graph as thoroughly as possible. [3 marks]
- (d) Assume that we are able to “see” which isomer is present at any given time. What data would you have to collect to verify the curve you sketched in part (c)? [4 marks]
9. (a) Sketch the reaction profile for the recombination of radicals. What is the activation energy? [4 marks]
- (b) In the reverse reaction (dissociation into radicals), what is the activation energy? You can either give your answer in words or show it on your reaction profile. [1 mark]
- (c) The products in a radical recombination reaction hold excess energy which they need to shed. Briefly explain why, with reference to your potential energy diagram. [4 marks]

- (d) How many normal modes of vibration would ethane have? [1 mark]



- (e) Radical recombination of methyl radicals (CH_3) into ethane has been thoroughly studied. Once the two radicals have recombined, we have an excited species with energy in excess of the activation energy to which RRK theory should apply. Intramolecular vibrational relaxation will rapidly move energy around the molecule. Eventually, this energy should find its way into the bond that has been formed and the molecule redissociates. Which of the rate constants from RRK theory governs the rate of redissociation? [1 mark]
- (f) For an RRK treatment of the redissociation of ethane following recombination of methyl radicals, what would be a sensible value of s ? [1 mark]
- (g) The carbon-carbon bond dissociation energy in ethane is 377 kJ mol^{-1} , and the carbon-carbon bond stretching frequency is $2.98 \times 10^{13} \text{ Hz}$. For a molecule exceeding the dissociation energy by 20 kJ mol^{-1} , estimate the rate constant for redissociation, and then the half-life of the newly formed ethane molecule. [5 marks]
- (h) Deexcitation will often occur via collision. Suppose that the recombination is studied in a helium bath gas. Calculate the collisional rate constant for helium and ethane at 300 K. The van der Waals radii of helium and ethane are, respectively, 1.4 and 4.0 Å, and their molar masses are, again respectively, 4.002 602 and 30.068 g mol^{-1} . [8 marks]
- (i) At what concentration of the bath gas would the rates of deexcitation and redissociation be equal? Give your answer in mol L^{-1} . What does your answer tell you about this system? [5 marks]
- (j) This reaction can be studied in solution using pulse radiolysis, a technique in which an intense flash of radiation causes the molecules to dissociate. The reassociation of the radicals can then be followed spectroscopically. What is the major difference between this reaction in the gas phase and in solution? [2 marks]
- (k) Assuming that the radius of a methyl radical is 2.0 Å (half that of ethane), estimate the diffusion-limited rate constant for the recombination of methyl radicals in water at 300 K. The viscosity of water at this temperature is $8.47 \times 10^{-4} \text{ Pa.s}$. The experimental value of the rate constant is $(1.24 \pm 0.20) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Would you say that this reaction is diffusion-limited? [9 marks]

Formulas and data

$$\begin{aligned}
 k_B &= 1.380\,6488 \times 10^{-23} \text{ J K}^{-1} & 1 \text{ \AA} &= 10^{-10} \text{ m} \\
 L &= 6.022\,141\,29 \times 10^{23} \text{ mol}^{-1} & 1 \text{ m}^3 &= 1000 \text{ L} \\
 R &= 8.314\,4621 \text{ J K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

$$P(\epsilon_i) = g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) / Q \quad Q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad t_{1/2} = \ln 2 / k$$

$$A_{\text{ct}} = \sigma \bar{v}_r L \quad \bar{v}_r = \sqrt{\frac{8RT}{\pi \mu_m}}$$

$$\frac{1}{\mu_m} = \frac{1}{M_A} + \frac{1}{M_B}$$

$$k_D = 4\pi L D_{AB} R_{AB} \quad D_i = \frac{k_B T}{6\pi r_i \eta}$$

$$\begin{aligned}
 k &= 4\pi L \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty \sigma_R(v_r) v_r^3 \exp\left(-\frac{\mu v_r^2}{2k_B T}\right) dv_r \\
 &= \frac{4L}{k_B T} [2\pi \mu k_B T]^{-1/2} \int_0^\infty \sigma_R(K_r) K_r \exp\left(-\frac{K_r}{k_B T}\right) dK_r
 \end{aligned}$$

$$k_1 = \frac{A_{\text{ct}}}{(s-1)!} \left(\frac{E_a}{k_B T}\right)^{s-1} \exp\left(-\frac{E_a}{k_B T}\right) \quad k_{2K} = \nu^\ddagger \left(\frac{E - E^\ddagger}{E}\right)^{s-1}$$

$$k_{\text{RRK}} = \int_{E^\ddagger}^\infty \frac{\frac{\nu^\ddagger [M]}{k_B T (s-1)!} \left(\frac{E - E^\ddagger}{k_B T}\right)^{s-1} \exp\left(-\frac{E}{k_B T}\right)}{[M] + \frac{\nu^\ddagger}{k-1} \left(\frac{E - E^\ddagger}{E}\right)^{s-1}} dE$$

$$\frac{dP(\mathbf{N}, t)}{dt} = \sum_{r \in \mathcal{R}} a_r(\mathbf{N} - \boldsymbol{\nu}_r) P(\mathbf{N} - \boldsymbol{\nu}_r, t) - \sum_{r \in \mathcal{R}} a_r(\mathbf{N}) P(\mathbf{N}, t)$$

$$k = \kappa \frac{k_B T}{c^\circ h} \frac{Q^\ddagger}{Q_X Q_Y} N \exp\left(-\frac{\Delta E_0}{RT}\right) = \kappa \frac{k_B T}{c^\circ h} \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H_m^\circ}{RT}\right)$$

$$E_a = \Delta^\ddagger H_m^\circ + RT(1 - \Delta^\ddagger n_{\text{gas}}) \quad A = \frac{k_B T}{c^\circ h} \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp(1 - \Delta^\ddagger n_{\text{gas}})$$

$$\kappa_K = \left[1 + \left(\frac{f}{2m\omega^\ddagger}\right)^2\right]^{1/2} - \frac{f}{2m\omega^\ddagger}$$

Reaction type	a	κ
$A \rightarrow$	κN_A	k
$A + B \rightarrow$	$\kappa N_A N_B$	k/LV
$A + A \rightarrow$	$\kappa N_A(N_A - 1)/2$	$2k/LV$