

Chemistry 2710 Spring 2003 Test 3

Marks: 40

Time: 50 minutes

Aids allowed: Calculator. One $8\frac{1}{2} \times 11$ -inch piece of paper containing any information you need. No other printed materials (e.g. periodic tables, calculator manuals) are allowed.

Instructions: Answer all questions in the spaces provided. If you run out of space for a particular question, you can use the backs of the pages but make sure to clearly label any continued work.

Graphs should be drawn on the graph paper attached and clearly labeled with the corresponding question number. You can use a graphing calculator instead of hand-drawn graphs, but you should in these cases provide a clearly labeled and reasonably accurate sketch of the graph. This sketch need not be presented on the graph paper.

Clarity may be considered in evaluating your answers. Make sure to explain in detail the procedures used to obtain the answers you present.

Useful data

$$h = 6.6260688 \times 10^{-34} \text{ J/Hz}$$

$$k_B = 1.3806503 \times 10^{-23} \text{ J/K}$$

$$R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ bar} = 100000 \text{ Pa}$$

$$1 \text{ m}^3 = 1000 \text{ L}$$

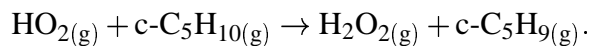
Question	1	2	3	4
Mark				

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. The development of transition-state theory starts with one key approximation. What is it? Discuss briefly. [4 marks]

2. The reaction $A_{(aq)}^{2+} + B_{(aq)} \rightarrow C_{(aq)}^{2+}$ has a rate constant of $2.9 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ at a temperature of 295 K and an ionic strength of $1.6 \times 10^{-4} \text{ mol/L}$. The permittivity of water at this temperature is $7 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$. What rate constant does Brønsted-Bjerrum theory predict at an ionic strength of $2.6 \times 10^{-3} \text{ mol/L}$? Discuss briefly. [4 marks]

3. Reactions of the hydroperoxy radical (HO_2) with hydrocarbons are important in combustion processes. The rate constant has been measured as a function of temperature for the elementary reaction



(c-C₅H_{10(g)} is cyclopentane.) The following data were obtained:¹

T (K)	673	713	753	783
$10^{-4}k$ (L mol ⁻¹ s ⁻¹)	2.95	5.55	12.3	18.4

- (a) Calculate the preexponential factor and activation energy. [8 marks]

Note: It is not necessary to draw a graph.

- (b) Calculate the entropy of activation at 298 K. What does the value of the entropy of activation tell us about the transition state? [10 marks]

¹S. M. Handford-Styring and R. W. Walker, *Phys. Chem. Chem. Phys.* **4**, 620 (2002).

4. Microorganisms are increasingly being used to degrade pollutants. Accordingly, the kinetics of these processes are of considerable interest. Because biochemical degradation pathways often have a rate-limiting enzyme-catalyzed step, it is often (but not always) the case that biodegradation obeys simple Michaelis-Menten kinetics. Consider the following initial rate data obtained for the degradation of phenol by *Pseudomonas putida* immobilized on 2.5 mm calcium alginate beads:²

[phenol] (mmol/L)	1.01	2.67	5.29	7.94	10.4
v ($\mu\text{mol L}^{-1}\text{h}^{-1}$)	3.1	6.4	10	12	14

- (a) Does this reaction follow Michaelis-Menten kinetics? Explain briefly. [8 marks]

- (b) Regardless of your answer to part a, provide estimates of the Michaelis constant and maximum reaction rate. [6 marks]

²K. Bandhyopadhyay et al., *Biochem. Eng. J.* **8**, 179 (2001).