

Chemistry 2710 Spring 2003 Final Examination

Marks: 105

Time: 3 hours

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: Write your answers in the booklets provided. Graphs should be drawn on the graph paper distributed and clearly labeled with your name and the 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.

You have some choice in sections 2 and 3. **Answer only the required number of questions. Extra answers will not be marked.** In the event that you answer extra questions, I will arbitrarily choose which answer(s) to mark and ignore the others. If you start a problem and decide that you do not want it marked, just cross out your work. Don't let me decide for you.

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

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

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

$$N_A = 6.022142 \times 10^{23} \text{ mol}^{-1}$$

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

Conversion factors:

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

To convert degree Celsius to Kelvin, add 273.15.

SI prefixes:

$$\text{p} = 10^{-12}$$

$$\text{f} = 10^{-15}$$

Element	Molar mass (g/mol)	Atomic radius (pm)
I	126.9045	133
N	14.0067	70
O	15.9994	73

1 Answer all questions in this section.

Value of this section: 79 marks

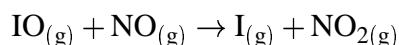
1. What is an initial rate? Describe briefly how the initial rate of a reaction can be measured. [4 marks]
2. In an initial rate experiment, it is found that increasing the concentration of a reactant by a factor of 10 increases the rate by a factor of 3.2. What is the order of the reaction? [2 marks]
3. As we saw in class, exponential growth or decay, corresponding to a first-order rate law, are commonly observed in a variety of contexts. Consider the following atmospheric CO₂ data:¹

Year	1744	1847	1943	1962	1980	2000
[CO ₂] (ppm)	276.8	286.8	307.9	317.62	336.98	367.01

Is the atmospheric CO₂ concentration growing exponentially? If so, what is the doubling time? If not, is the growth faster or slower than exponential? [6 marks]

Aside: A very deep ice core taken at the Russian Vostok research station in East Antarctica provides data for the last 400 000 years. The atmospheric CO₂ levels during this period have fluctuated quite a bit, but have never been higher (until the last few years) than 300 ppm. A single reading of 298.7 ppm was obtained for a sample corresponding to 323 000 years before the present. All the other readings are below 290 ppm. Recent CO₂ levels are therefore higher than *any* in the recent geological history of the planet, which is one of the major sources of concern about the rapid increase in atmospheric carbon dioxide concentrations in our times: We are rapidly getting away from a range of concentrations where historical trends provide any clue as to what will happen next.

4. The preexponential factor and activation energy for the reaction



have been found to be, respectively, $2.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and 3.30 kJ/mol in a series of experiments carried out over the temperature range 233–346 K.²

- (a) Do you think that this reaction is collision-limited? Support your answer with a quantitative argument. [15 marks]
- (b) It is possible to make a crude estimate of the equilibrium constant for this reaction by extrapolation from available thermodynamic data. This estimate is $K = 4 \times 10^9$ at 298 K. What would the approximate value of the rate constant for the reverse reaction be at this temperature? [4 marks]

¹The first three points are from the Antarctic ice core data of Neftel et al. (1994), available on the web at <http://cdiac.esd.ornl.gov/trends/co2/siple.htm>. The last three points are annual averages of direct atmospheric measurements taken since 1957 at the South Pole and summarized by Keeling and Whorf (2002) at <http://cdiac.esd.ornl.gov/trends/co2/sio-spl.htm>.

²D. Hölscher and R. Zellner, *Phys. Chem. Chem. Phys.* **4**, 1839 (2002).

5. The inorganic complex³ $\text{CoRu}(\text{CO})_5(\mu\text{-bma})(\mu\text{-PPh}_2)$ loses a carbonyl group to form $\text{CoRu}(\text{CO})_4(\mu\text{-bma})(\mu\text{-PPh}_2)$ in solution at moderate temperatures.

(a) The following first-order rate constants have been measured for this process:⁴

T ($^{\circ}\text{C}$)	77.2	83.0	88.0	93.2	98.1
$10^4 k$ (s^{-1})	2.37	7.3	10.1	20.4	30.3

Calculate the activation energy and preexponential factor. [8 marks]

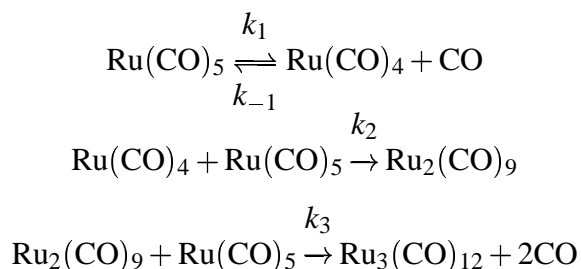
Note: No graph is required.

(b) In reactions in which a ligand is lost, there are two possibilities:

- The ligand is lost “early”, i.e. reaching the transition state mostly involves the loosening of the metal-ligand bond.
- The ligand is lost “late”, i.e. reaching the transition state involves an internal rearrangement but no significant weakening of the metal-ligand bond.

Calculate the entropy of activation at 80°C and comment on whether you think the carbonyl group leaves early or late in this reaction. [4 marks]

6. In solution under atmospheric conditions, ruthenium pentacarbonyl ($\text{Ru}(\text{CO})_5$) converts to triruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$). The mechanism is thought to be the following:⁵



(a) Apply the steady-state approximation to derive a rate law for this mechanism involving only concentrations of reactants and/or products. [12 marks]

(b) Outline an experiment or set of experiments which could be used to verify your rate law. Discuss in detail what kinetic parameters (rate constants, etc.) could be extracted from the data generated in the experiments you suggest. If appropriate, suggest a graphical method of analysis. [10 marks]

7. Discuss the relative advantages and disadvantages of pressure-jump and temperature-jump experiments. [6 marks]

8. Suppose that you want to study a relatively fast second-order reaction using ordinary lab techniques of the sort used in the laboratory of this course. Estimate the largest second-order rate constant you could measure by such methods. Explain briefly any assumptions or estimates which enter into your calculations. [8 marks]

³bma is 2,3-bis(diphenylphosphino)maleic anhydride.

⁴S. G. Bott et al., *Inorg. Chem.* **39**, 6051 (2000).

⁵W. R. Hastings et al., *J. Chem. Soc. Dalton Trans.* **1990**, 203.

2 Answer one question from this section.

Value of this section: 6 marks

1. We normally write simple integrated rate laws (e.g. the first-order equation) in terms of the concentration of a reactant. This is not the only possibility. Suppose that a reaction has the stoichiometry $A \rightarrow 2B$ and has a second-order rate law, $v = ka^2$. Derive an integrated rate law for the concentration of the product, b , assuming that $b(0) = 0$. [6 marks]
2. Fungal pellets are roughly spherical masses which sometimes form when fungi are grown in a liquid medium. The growth of the fungal population results in an increase in pellet mass which, empirically, has been found to obey the following equation:

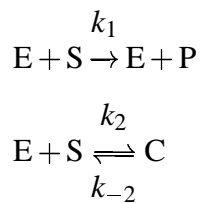
$$m^{1/3} = m_0^{1/3} + kt.$$

- (a) What is the kinetic order of this growth process? [2 marks]
- (b) Derive an equation for the doubling time. [4 marks]

3 Answer one question from this section.

Value of this section: 20 marks

1. The Michaelis-Menten mechanism isn't the only one which is consistent with the rate data obtained in simple enzyme-catalyzed reactions. In 1902, Victor Henri proposed the following alternative:⁶



Carry out a full phase-plane analysis of this mechanism, emphasizing the following points:

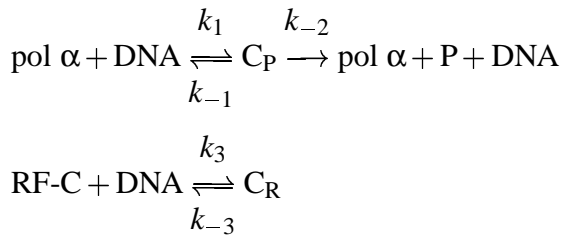
- (a) Show that there exists a slow manifold. Explain the importance of this geometric feature.
- (b) Show that at reasonably large substrate concentration s , the rate law must become identical to that of the Michaelis-Menten mechanism.

[20 marks]

⁶V. Henri, C. R. Acad. Sci. **135**, 916 (1902). Henri analyzed both this mechanism and what we now call the Michaelis-Menten mechanism. He believed that the latter was the more realistic, but wanted to point out that the kinetic data alone could not distinguish between these two possibilities.

2. DNA polymerase α (pol α) catalyzes the first step in the replication of DNA. Pol α is inhibited by replication factor C (RF-C). (RF-C is a DNA-binding protein which plays a role in helping other enzymes involved in DNA synthesis (e.g. pol δ) attach to the DNA. The complete story is too complex to explain in any detail here.) In this case, instead of having two small molecules competing for the active site of an enzyme, we have two enzymes competing for a single substrate, namely DNA.

- (a) A crude cartoon of the mechanism for this competitive process would be



Derive a rate law for this mechanism valid when the pol α concentration is much smaller than the DNA concentration, and the latter is in turn much smaller than the RF-C concentration.⁷ Show that this rate law is of identical form to that for ordinary competitive inhibition. [10 marks]

Hint: Start by writing down three conservation relations, then use the conditions given above to simplify these relations. After that, the derivation follows the normal path.

- (b) The following initial velocity data have been obtained in the presence of 0.2 μu of pol α :⁸

[RF-C] (μu)	[DNA] (g/L)			
	0.025	0.049	0.121	0.241
0	85	159	246	328
0.2	47	90	167	246

Show that these data are consistent with competitive inhibition, and calculate K_S , K_I and k_{-2} . [10 marks]

Note: Since you will have only two points, it won't be necessary to draw a graph to extract K_S and K_I .

HAVE A GOOD SUMMER!

⁷As noted in class, most enzymology textbooks disguise assumptions about the relative concentrations of inhibitor and enzyme behind formal techniques for deriving the rate laws. If you had never seen the correct derivation, it would be extremely difficult for you to complete this derivation successfully. You will no doubt find that it is difficult enough even if you have seen the proper technique! Also note that the DNA concentration might be greater than the pol α concentration in a laboratory experiment, but that this is a highly artificial situation relative to what happens in the nucleus of a cell.

⁸Maga et al., *J. Mol. Biol.* **295**, 791 (2000). A unit (u) of enzyme is an empirical unit relating the number of enzyme molecules to their catalytic activity under ideal circumstances. The precise definition of a unit is not relevant here. Just take it as a measure of concentration.