Chemistry 2710 Spring 2001 Final Examination

Name: ______________________________________

Student number: ___________________

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) are allowed.

Instructions: Answer all questions in the spaces provided. Use the backs of the printed pages for rough work or for extra space. Graphs should be drawn on the graph paper attached and clearly labeled with the corresponding question number.

Make sure to explain in detail the procedures used to obtain the answers you present. For instance, if you get a slope by performing a linear regression on your calculator, say so. If you determined something from a graph, refer to the graph in explaining your answer.

In the event that you use a graphing calculator instead of hand-drawn graphs, show at least a sketch of your graph with your answer. Be aware however that it is sometimes difficult to assign part marks if your sketch does not correspond to the expected graph.

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

$R = 8.314\,510\,\mathrm{J\,K^{-1}mol^{-1}}$

$k_B = 1.380\,658 \times 10^{-23}\,\mathrm{J/K}$

$h = 6.626\,069 \times 10^{-34}\,\mathrm{J/Hz}$

$1\,\mathrm{m^3} = 1000\,\mathrm{L}$

$1\,\mathrm{bar} = 100\,000\,\mathrm{Pa}$

To convert degrees Celsius to Kelvin, add 273.15.

Substance	$\Delta\bar{E}_f^\circ$ (kJ/mol)
$CH_{3(g)}$	146.9268
$CH_{4(g)}$	−72.3941
$H_{(g)}$	216.759
$H_{2(g)}$	0

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. The following initial data have been obtained for the reaction

$$2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}$$

at 700°C:

$[H_2]$ (mol/L)	[NO] (mol/L)	v (mol L^{-1}s^{-1})
0.0050	0.025	1.2×10^{-6}
0.010	0.025	2.4×10^{-6}
0.010	0.0125	6.0×10^{-7}

Determine the rate law and rate constant. [6 marks]

2. In the laboratory, you studied the acid-catalyzed hydrolysis of sucrose. The experiment involved only two solutions, namely a sucrose solution and an HCl solution which were mixed in varying proportions to obtain different initial concentrations. At any given H^+ concentration, the reaction displays apparent first-order kinetics. However, the rate constant increases with $[H^+]$, indicating that the reaction is only a pseudo-first-order process. Typically in these cases, the pseudo-first-order rate constant is directly proportional to the catalyst concentration, i.e. $k_{\text{observed}} = k[H^+]$. In this case however, if we calculate the second-order rate constant k, the values increase as the acid concentration increases. Based on mechanistic studies, it is thought that the reaction really is a second-order process depending on the sucrose and hydrogen ion concentrations. Why then are the calculated second-order rate constants not consistent from one acid concentration to the next? [2 marks]

3. The reaction $2Fe(CN)_{6(aq)}^{3-} + 2S_2O_{3(aq)}^{2-} \rightarrow 2Fe(CN)_{6(aq)}^{4-} + S_4O_{6(aq)}^{2-}$ displays first-order kinetics. Measurements of the rate constant at different temperatures are given below:[1]

T (°C)	20	30	40	50	60	70
$10^4 k$ (min^{-1})	1.52	2.13	3.28	5.29	9.31	14.06

(a) Calculate the activation energy and preexponential factor for this reaction. [10 marks]

(b) Predict the value of the rate constant at 0°C. [2 marks]

[1] Y. Li et al., J. Phys. Chem. B **104**, 10956 (2000).

4. The phenomenological equilibrium constant of the reaction

$$CH_3COOH_{(aq)} \underset{k_a}{\overset{k_d}{\rightleftharpoons}} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

has the value 1.8×10^{-5} mol/L at 25°C. The relaxation time measured at this temperature in a 0.100 mol/L solution of acetic acid is 8.3 ns. What are the values of the two rate constants? [9 marks]

Hint: You will need the equilibrium concentrations of acetate and of protons. These can be calculated straightforwardly from the equilibrium condition using the approximation that very little of the acetic acid dissociates.

5. $\pi - \pi$ interaction in molecules with several double or triple bonds often result in the formation of loosely bound dimers or, in extreme cases, of stacks of molecules. Butadiene dimerizes in this way in the gas phase, i.e. it undergoes the reaction $2\,\text{butadiene} \rightarrow \text{dimer}$. The following data were obtained in a reaction vessel held at 326°C which originally contained pure butadiene:

t (min)	P (torr)
0	632.0
20.78	556.9
49.50	498.1
77.57	464.8
103.58	442.6

Note that the pressure measured is the total pressure.

(a) Could this reaction be elementary? If so, what would the order of the reaction be? [3 marks]

(b) Are the data consistent with the order of reaction you predicted above? If so, what is the rate constant? [10 marks]

6. All stars contain traces of metals which can be detected by analyzing their spectra. The heavier metals are almost exclusively made during extremely violent events such as supernova explosions. The debris from a supernova is widely scattered and is incorporated into other stellar bodies (stars and planets) during their formation. Some of the very heavy metals are (relatively) stable while others are not. If we know the ratio in which these heavy metals are initially present and the half-life of an unstable metal, we can estimate the average ages of the supernovas which contributed to the sample. Since young galaxies have many more supernova explosions than older galaxies, this gives a rough idea of the age of the galaxy. The initial ratios are only known from theoretical calculations, so their values are a source of considerable uncertainty which must be taken into account in deriving these estimates.

^{232}Th has a very long half-life and can be taken to be stable for the purpose of these calculations. ^{238}U has a much shorter half-life of about 4.5 Gy. According to stellar nucleosynthesis models, the initial ratio of ^{238}U to ^{232}Th was between 0.56 and 0.79. The currently observed ratio of these two isotopes in star CS31082-001 is 0.18. Using these data, determine a range of possible ages for our galaxy. [6 marks]

7. Obtain an integrated rate law for the concentration of A in the parallel reaction mechanism

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B},$$

$$2\mathrm{A} \xrightarrow{k_2} \mathrm{C}.$$

Your final expression should be written in the form $a = f(t)$. [10 marks]

Useful fact:

$$\int \frac{dx}{x(\alpha+\beta x)} = -\frac{1}{\alpha}\ln\left(\frac{\alpha+\beta x}{x}\right)$$

8. In 1902, Victor Henri studied two mechanisms which might account for the rate data from enzyme-catalyzed reactions. One was the now-familiar Michaelis-Menten mechanism. The other was the following, sometimes called the nuisance mechanism since the enzyme-substrate complex plays no productive role:

$$\begin{aligned} \mathrm{E} + \mathrm{S} \ &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\ \mathrm{C} \\ \mathrm{E} + \mathrm{S} \ &\overset{k_2}{\rightarrow}\ \mathrm{E} + \mathrm{P} \end{aligned}$$

Show that this mechanism gives exactly the same rate law as the Michaelis-Menten mechanism. [10 marks]

9. Consider the reaction

$$H_{(g)} + CH_{4(g)} \to H_{2(g)} + CH_{3(g)}.$$

(a) The preexponential factor for this reaction is $1.25 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}$ over the temperature range 372–1290 K. Estimate the collision efficiency of this reaction given that the radius of a hydrogen atom is $3.7 \times 10^{-11}\,\mathrm{m}$ and the radius of a methane molecule is about $1.9 \times 10^{-10}\,\mathrm{m}$. The molar masses of hydrogen and of carbon atoms are, respectively, 1.0079 and 12.011 g/mol. [10 marks]

Note: You will have to choose a reasonable temperature for your calculations in this and the following part of this question.

(b) Calculate the entropy of activation for the reaction. Discuss (briefly) the physical interpretation of the value calculated. [8 marks]

(c) The activation energy for the reaction is 49.8 kJ/mol. Calculate the activation energy for the reverse reaction. [4 marks]

10. Compare and contrast the continuous flow and stopped flow methods. [10 marks]

Note: You are encouraged to sketch diagrams of the equipment.