Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x
Second Exam
October 24, 2002

Total Points: 150

2002
George Flynn
75 Minutes

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

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Print your first name:

Signature:____

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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a	2a	3a	4a
1b	2b	3b	4b
1c		3c	4c
1d		3d	4d
			4e
			4f
		Total Score:	

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Problem 1 (Points 35) [Oxtoby problem 13.7]. In a study of the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) in a benzene solution, the following set of initial reaction rates was measured at 25 degrees centigrade for different initial concentrations of the two reactants:

$[C_5H_5N]$(mol/L)	$[CH_3I]$(mol/L)	Initial Rate r_0(mol/L-s)
1.00×10^{-4}	1.00×10^{-4}	7.5×10^{-7}
2.00×10^{-4}	2.00×10^{-4}	3.0×10^{-6}
2.00×10^{-4}	4.00×10^{-4}	6.0×10^{-6}

a) (10 points) Determine the order of the reaction with respect to the species methyl idodide, CH_3I. Show all reasoning clearly.

b) (10 points) Determine the order of the reaction with respect to the species pyridine, C_5H_5N. Show all reasoning clearly.

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c) (10 points) Determine the kinetic rate constant for the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) at T= 25 C. Show all reasoning clearly.

d) (5 points) Predict the initial reaction rate for a solution in which $[C_5H_5N] = 5.0 \times 10^{-5}$ mol/L and $[CH_3I] = 2.0 \times 10^{-5}$ mol/L. Show all reasoning clearly.

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Problem 2 (Points 15) [Oxtoby problem 13.39]. The activation energy for the isomerization reaction:

$$CH_3NC \rightarrow CH_3CN$$

is 161 kJ mol^{-1}. The reaction rate constant at 600 K is 0.41s^{-1}.

a) (5 points) Determine the Arrhenius factor, A, for this reaction at 600 K. Show all reasoning clearly.

b) (10 points) Determine the kinetic rate constant for this reaction at T=1000 K assuming that the Arrhenius factor, A, is independent of temperature. Show all reasoning clearly.

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Problem 3 (50 points) Propionic Acid is a weak acid:

$CH_3CH_2COOH + H_2O = CH_3CH_2COO^- + H_3O^+$ $\qquad$ $K_a = 1.34 \times 10^{-5}$

Phenolphthalein is an indicator with a pK_a of 8.0:

PhenH(colorless) + H_2O = $Phen^-$(red) + H_3O^+

A solution is prepared by dissolving 0.50 moles of sodium propionate $Na(CH_3CH_2COO)$ in one liter of water. This salt completely dissociates in solution to Na^+ and $CH_3CH_2COO^-$. A drop of phenolphthalein is added to follow the solution pH. The phenolphthalein does not affect the concentration of H_3O^+ because there is such a small amount of it. However, the color of phenolphthalein is, of course, affected by the concentration of H_3O^+.

a) (15 points) What is the pH of this solution? Show reasoning clearly.

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b) (10 points) What is the color of the solution? Show all reasoning clearly.

c) (10 points) What is the pH for this mixture if 0.3 moles of HCl (a strong acid) is added to the solution without changing the volume? Show reasoning clearly.

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d) (15 points) What is the pH for this mixture if another 0.2 moles of HCl (a strong acid) is added to the solution of part c without changing the volume? Show reasoning clearly.

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Problem 4 (50 points) The excitation of a molecule M by light to produce an excited molecule M* can be treated by the techniques of chemical kinetics even though there need not be any chemical change taking place in these photo-initiated events. The entire process can be described by three elementary kinetic steps:

$M + h\nu_a \rightarrow M^*$	Rate = I_{abs}	(Absorption)
$M^* \rightarrow h\nu_f + M$	Rate constant = k_f	(Fluorescence)
$M^* + Q \rightarrow M + Q$	Rate constant = k_q	(Quenching)

ν_a is the frequency of light absorbed by the molecule and ν_f is the frequency of light emitted by the molecule in a process called fluorescence. Generally, ν_a and ν_f are different from each other, and the light emitted by the excited M* molecules at frequency ν_f can be used in the laboratory to detect the presence of M* and measure its concentration. I_{abs} is the **rate** (not the rate constant) of absorption of light by the molecule M (in units of moles of photons per second per liter). It is also equal to the rate of production of M* in just the first step above. k_f is the rate constant (not the rate) for the fluorescence step and k_q is the rate constant (not the rate) for the quenching step. Q is a quencher molecule that converts M* back to M via a collision, thereby preventing re-emission of light as fluorescence.

a) (5 points) Using this elementary kinetic scheme, express the rate for each of the elementary steps and d[M*]/dt, the rate of change of [M*], the concentration of excited M. Show all reasoning clearly.

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b) (5 points) In many experiments a light of constant intensity is shined on the sample so that the rate of absorption of photons I_{abs}, is a contant. Under these conditions, make an appropriate approximation and find [M*] as a function of I_{abs}, [Q], and the kinetic rate constants. Show reasoning clearly.

c) (5 points) The rate of emission of photons in step 2 is symbolized by I_f (in units of moles of photons per second per liter). Express I_f as a function of I_{abs}, [Q], and the kinetic rate constants. Show all reasoning clearly.

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d) (10 points) Unfortunately, it is very difficult to measure the absolute number of photons emitted. It is however, relatively easy to measure the relative number of photons emitted (I_{f0}/I_f) where I_{f0} is the photon emission rate in the absence of quencher, Q. Describe a plot of I_{f0}/I_f vs [Q] and tell what information about the kinetic scheme above can be obtained from such a plot (called a Stern-Volmer plot after the scientists who first used this approach). Show all reasoning clearly.

e) (15 points) Suppose now that the light shining on the sample consists of a single short pulse (e.g. from a laser) that instantaneously produces a concentration of [M*] = $[M^*]_0$ and then shuts itself off so there is no further excitation of M by the light in the first step above. You may assume that no fluorescence or quenching takes place while the light pulse is on (because it is so short) and that [M*] = $[M^*]_0$ at time t =0, the moment that the light pulse shuts off. Using your vast knowledge of chemical kinetics, derive an expression that gives [M*] as a function of time. (Begin with a kinetic scheme like that above, develop a differential equation for [M*], and integrate this equation to find [M*] vs t.) Show all reasoning clearly.

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f) (10 points) Assuming that you could measure [M*] as a function of time, what kind of plots would you make to obtain both k_f and k_q? Show all reasoning clearly.

The End