Chemistry 549
Hour Exam
March 15, 2004

1. (25 points). The following mechanism has been proposed for the thermal decomposition of acetaldehyde:

$$CH_3CHO \xrightarrow{k_1} \cdot CH_3 + CHO$$
$$\cdot CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \cdot CH_2CHO$$
$$\cdot CH_2CHO \xrightarrow{k_3} \cdot CH_3 + CO$$
$$\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3CH_3$$

A. Write down the differential equations describing the reaction rates of the following species: CH_3CHO, $\cdot CH_3$, $\cdot CH_2CHO$, CH_4

B. Make the appropriate steady state approximations to simplify the previous rate equations. You may assume that the concentration of acetaldehyde (CH_3CHO) is constant for the duration of the measurement. (In other words, perform your analysis for the early stages of the reaction.)

C. Using the previous result, express the rate of production of methane (CH_4) in terms of the concentration of acetaldehyde and the various rate constants.

In order to simplify the notation, please use the following symbols:

A = acetaldehyde, M = methane, y = $\cdot CH_3$, and z = $\cdot CH_2CHO$.

2. (25 points) Suppose the potential energy of a diatomic molecule is given by the Lennard-Jones function, $V(r) = 4e\left[\left(\frac{s}{R}\right)^{12} - \left(\frac{s}{R}\right)^{6}\right]$,
where R is the bond length and s and e are constants (the "potential parameters").

A. What is the equilibrium bond length, R_e, of the molecule? What is the potential energy at that value of R?

B. Define a new distance variable, $x = R - R_e$, and express the potential energy as a function of x. Next, expand $V(x)$ as a Taylor series to second order about the point x = 0.

C. Determine the force constant of the molecule and express it in terms of the potential parameters.

3. (25 points) Consider the collinear reaction, $H + I_2 \rightarrow HI + I$. The bond energies of HI and I_2 are 3.054 and 1.542 eV, respectively.

A. Where do you expect the transition state for this reaction to lie, in the entrance valley or the exit valley of the potential energy surface? Why?
B. Based on Polanyi's analysis of different types of potential energy surfaces, which form of energy do you expect to be more effective in promoting the reaction, translation or vibration? Why?
C. How do you expect the available energy to be released, primarily as translation or as vibration? Why?

4. (25 points) A certain molecule, *A*, has an extinction coefficient of 1,000 liter mol^{-1} cm^{-1} (base e) at a wavelength of 400 nm. The molecule undergoes the photochemical reaction

$$A + hn \rightarrow products.$$

A laser at this wavelength has a power of 0.1 Watts and is shined into a vessel containing a 0.3 molar solution of compound *A*. The volume of the vessel is 0.02 liters, and the path length of the laser is 0.5 cm.

A. What is the initial number of moles in the vessel?
B. How many photons per second are initially absorbed by the solution?
C. How many moles per second of the compound react initially?
D. Write down an expression for the number of moles in the vessel at time t.
E. How long will it take for the concentration in the vessel to decline to 1/e of its initial value?

Table 3. Energy conversion factors (approximate)[a]

	erg	J	cal	eV	au	cm^{-1}	Hz	K	kJ mol^{-1}	kcal mol^{-1}
1 erg =	1	1.0000(−7)	2.390(−8)	6.241(+11)	2.294(+10)	5.034(+15)	1.5092(+26)	7.243(+15)	6.022(+13)	1.4393(+13)
1 joule (J) =	1.0000(+7)	1	2.390(−1)	6.241(+18)	2.294(+17)	5.034(+22)	1.5092(+33)	7.243(+22)	6.022(+20)	1.4393(+20)
1 cal =	4.1840(+7)	4.1840	1	2.611(+19)	9.597(+17)	2.106(+23)	6.315(+33)	3.031(+23)	2.520(+21)	6.022(+20)
1 eV =	1.6022(−12)	1.6022(−19)	3.829(−20)	1	3.675(−2)	8.065(+3)	2.418(+14)	1.1605(+4)	9.648(+1)	2.306(+1)
1 hartree (au) =	4.360(−11)	4.360(−18)	1.0420(−18)	2.721(+1)	1	2.195(+5)	6.580(+15)	3.158(+5)	2.626(+3)	6.275(+2)
1 cm^{-1} =	1.9865(−16)	1.9865(−23)	4.748(−24)	1.2399(−4)	4.556(−6)	1	2.998(+10)	1.4388	1.1963(−2)	2.859(−3)
1 Hz =	6.626(−27)	6.626(−34)	1.5837(−34)	4.136(−15)	1.5198(−16)	3.336(−11)	1	4.799(−11)	3.990(−13)	9.537(−14)
1 °K (K) =	1.3807(−16)	1.3807(−23)	3.300(−24)	8.617(−5)	3.167(−6)	6.950(−1)	2.084(+10)	1	8.314(−3)	1.9871(−3)
1 kJ mol^{-1} =	1.6606(−14)	1.6606(−21)	3.969(−22)	1.0364(−2)	3.809(−4)	8.359(+1)	2.506(+12)	1.2027(+2)	1	2.390(−1)
1 kcal mol^{-1} =	6.948(−14)	6.948(−21)	1.6606(−21)	4.337(−2)	1.5936(−3)	3.498(+2)	1.0486(+13)	5.032(+2)	4.184	1

[a] Numbers in parentheses denote powers of 10 by which the entry is to be multiplied.