Chemistry 361
FINAL EXAM
Friday 17 December, 2004

Name ____

Full credit will be given to correct answers only when ALL the necessary steps are shown.

DO NOT GUESS THE ANSWER.

This is a close book exam, and you are responsible to be sure that your exam has no missing pages (7 pages).

If you consider that there is not enough information to solve a problem you have to specify the missing information and describe the problem solving procedure.

Honor Statement
I have neither give nor received aid in this examination.

Full signature ________________________________

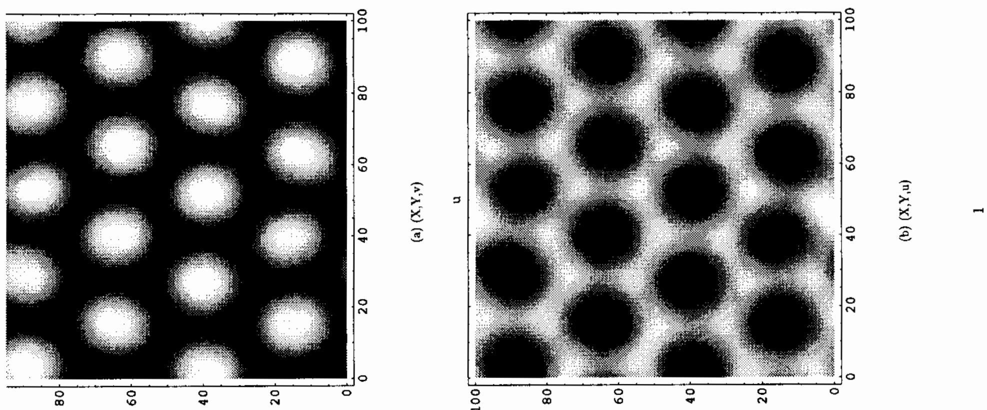

Figure 1: Spots from the Templator's RD equation

Problem 1 (25 points)

To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equal spaced lines, separated by 6.26 x 10^{11} Hz. Calculate the bond length of $H^{35}Cl$.

ENERGY BETWEEN LINES = 2B

$$2B = \frac{h}{4\pi^2 I} = 6.26 \times 10^{11}\ Hz$$

Solving for $I = \frac{(6.626 \times 10^{-34}\ J \cdot s)}{4\pi^2 (6.26 \times 10^{11} s^{-1})} = 2.68 \times 10^{-47}\ Kg\ m^2$

Reduced mass $\mu = \frac{(1.00)(35.00)}{36.00} 1.66 \times 10^{-27} kg = 1.61 \times 10^{-27} kg$

$$I = \mu r^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.68 \times 10^{-41}\ Kg\ m^2}{1.61 \times 10^{-27}\ Kg}}$$

$$\boxed{r = 1.29 \times 10^{-10} m = 129\ pm}$$

Problem 2 (25 points)

Use the trial function of the form

$$\phi(x) \;=\; e^{-\alpha\, x^2/2} \tag{1}$$

to calculate the ground-state energy of a quartic oscillators, whose potential is

$$V(x) \;=\; c\, x^4 \tag{2}$$

and $-\infty < x < \infty$

You may need to use the following integrals

$$\int_0^\infty e^{-a\, x^2}\, dx \;=\; \frac{1}{2}\sqrt{\frac{\pi}{a}} \tag{3}$$

$$\int_0^\infty x^{2n}\, e^{-a\, x^2}\, dx \;=\; \frac{1\cdot 3\cdot 5\,\cdots\,(2n-1)}{2^{(n+1)}\, a^n}\sqrt{\frac{\pi}{a}} \tag{4}$$

for n a positive integer.

Remember to calculate first E_ϕ and, second, find the value of α that minimizes the nergy.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + c x^4$$

$$\hat{H}\phi = -\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + c x^4\phi = -\frac{\hbar^2}{2m}\left[\frac{d}{dx}\left(-\alpha x e^{-\frac{\alpha x^2}{2}}\right)\right] + c x^4\phi$$

$$= -\frac{\hbar^2}{2m}\left[-\alpha e^{-\frac{\alpha x^2}{2}} + \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}\right] + c x^4\phi(x)$$

$$= \frac{\hbar^2}{2m}\left[\alpha\,\phi - \alpha^2 x^2\phi\right] + c x^4\phi$$

$$\langle\phi|\hat{H}\phi\rangle = \int_{-\infty}^{\infty}\phi(x)\left\{\frac{\hbar^2}{2m}\alpha\phi - \frac{\hbar^2}{2m}\alpha^2 x^2\phi + c\, x^4\phi\right\}dx$$

$$= \frac{\hbar^2}{2m}\alpha\int_{-\infty}^{\infty}\phi^2 dx - \frac{\hbar^2}{2m}\alpha^2\int_{-\infty}^{\infty} x^2\phi^2 dx + c\int_{-\infty}^{\infty} x^4\phi^2 dx$$

$$\langle\phi|H\phi\rangle = \frac{\hbar^2}{2m}\alpha\sqrt{\frac{\pi}{\alpha}} - \frac{\hbar^2}{2m}\alpha^2\frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}} + c\,\frac{1\cdot 3}{2^2\alpha^2}\sqrt{\frac{\pi}{\alpha}}$$

$$= \frac{1}{2}\,\frac{\hbar^2\alpha}{2m}\sqrt{\frac{\pi}{\alpha}} + \frac{3c}{4\alpha^2}\sqrt{\frac{\pi}{\alpha}}$$

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \sqrt{\frac{\pi}{\alpha}}$$

$$E_\phi = \frac{\langle\phi|H\phi\rangle}{\langle\phi|\phi\rangle} = \frac{1}{2}\,\frac{\hbar^2}{2m}\alpha + \frac{3c}{4\alpha^2}$$

$$\frac{\partial E_\phi}{\partial\alpha} = \frac{1}{2}\frac{\hbar^2}{2m} - \frac{6c}{4\bar\alpha^3} = 0 \Rightarrow \bar\alpha^3 = \frac{m}{\hbar^2}6c$$

$$\boxed{\bar\alpha = \frac{m^{1/3}\,2^{1/3}\,3^{1/3}\,c^{1/3}}{\hbar^{2/3}}}$$

$$E_\phi = \sqrt[3]{\frac{81\hbar^4 c}{256\,m^2}}$$

$$E_\phi = \frac{1}{2}\frac{\hbar^2}{2m}\frac{m^{1/3}\,2^{1/3}\,3^{1/3}\,c^{1/3}}{\hbar^{2/3}} + \frac{3c}{2^2}\frac{\hbar^{4/3}}{m^{2/3}\,2^{2/3}\,3^{2/3}\,c^{2/3}}$$

$$= \frac{\hbar^{4/3}\,3^{1/3}\,c^{1/3}}{m^{2/3}\,2\,2^{2/3}} + \frac{\hbar^{4/3}\,3^{1/3}\,c^{1/3}}{m^{2/3}\,2^2\,2^{2/3}}$$

$$= \frac{\hbar^{4/3}\,3^{1/3}\,c^{1/3}}{m^{2/3}\,2\,2^{2/3}}\,\frac{3}{2} = \boxed{\frac{3^{4/3}\,\hbar^{4/3}\,c^{1/3}}{2^{8/3}\,m^{2/3}} = E_\phi}$$

Problem 3(25 points)

For the following data determine the activation energy.

Effect of temperature on rate constant		
	Experimental value	
Tempeature	$90\ °C$	$130\ °C$
k	$4.53\ x\ 10^{-8}\ s^{-1}$	$6.13\ x\ 10^{-6}\ s^{-1}$

$$k_1 = A\, e^{-Ea/RT_1} \qquad k_2 = A\, e^{-Ea/RT_2}$$

$$\frac{k_2}{k_1} = \frac{e^{-Ea/RT_2}}{e^{-Ea/RT_1}} = e^{\frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\,\frac{T_2 - T_1}{T_1 T_2}$$

$$\boxed{E_a = \frac{R T_1 T_2}{T_2 - T_1} \ln\left(k_2/k_1\right)}$$

$$E_a = \frac{R\,(273+90)(273+130)\,K^2}{\underbrace{40}_{\text{2 sig figs}}\,K} \ln\left(\frac{613}{4.53}\right)$$

$$\boxed{E_a = 150\ \frac{kJ}{mol}}$$

Problem 4 (25 points)

For the following overall reaction, find the rate of the reaction associated with the mechanism.

$$O_3(g) + O_3(g) \xrightarrow{k^{obs}} 3\ O_2(g) \tag{5}$$

Mechanism

$$O_3(g) + O_3(g) \xrightarrow{k_1^+} O_3(g) + O_2(g) + O(g) \tag{6}$$

$$O_3(g) + O_2(g) + O(g) \xrightarrow{k_1^-} O_3(g) + O_3(g) \tag{7}$$

$$O_3(g) + O(g) \xrightarrow{k_2} O_2(g) + O_2(g) \tag{8}$$

$$\frac{d[O]}{dt} = k_1^+[O_3][O_3] - k_1^-[O_3][O_2][O] - k_2[O_3][O] \simeq 0$$

$$[O] = \frac{k_1^+[O_3]^2}{k_1^-[O_3][O_2] + k_2[O_3]} = \frac{k_1^+[O_3]}{k_2 + k_1^-[O_2]}$$

$$\text{rate} = \frac{1}{3}\frac{d[O_2]}{dt} = \left[\underbrace{k_1^+[O_3]^2 - k_1^-[O_3][O_2][O]}_{k_2[O_3][O]} + 2\,k_2[O_3][O]\right]\frac{1}{3}$$

$$\boxed{\text{rate} = k_2[O_3][O] = \frac{k_2\,k_1^+[O_3]^2}{k_2 + k_1^-[O_2]}}$$

Problem 5 (25 points)

For the following overall reaction, find the rate of the reaction associated with the mechanism.

$$RX + Y^- \xrightarrow{k^{obs}} RY + X^- \tag{9}$$

Mechanism

$$RX \xrightarrow{k_1^+} R^+ + X^- \tag{10}$$

$$R^+ + X^- \xrightarrow{k_1^-} RX \tag{11}$$

$$R^+ + Y^- \xrightarrow{k_2} RY \tag{12}$$

a) Assume that Eq.(10) and Eq.(11) achieve equilibrium and find the rate of the reaction in Eq. (9).

b) Now use the Steady State Approximation for the intermediates and find the rate of the reaction in Eq.(9).

c) Under which conditions rates in a) and b) are equal.

a) $K_1 = \dfrac{[R^+][X^-]}{[RX]} \Rightarrow [R^+] = \dfrac{K_1 [RX]}{[X^-]}$

$\text{rate} = \dfrac{d[RY]}{dt} = k_2 [R^+][Y^-] = \dfrac{k_2 K_1 [RX][Y^-]}{[X^-]}$

b) $\dfrac{d[R^+]}{dt} = k_1^+ [RX] - k_1^- [X^-][R^+] - k_2 [Y^-][R^+] \simeq 0$

$[R^+] = \dfrac{k_1^+ [RX]}{k_1^- [X^-] + k_2 [Y^-]} \Rightarrow \text{rate} = \dfrac{k_2 k_1^+ [RX][Y^-]}{k_1^- [X^-] + k_2 [Y^-]}$

c) $k_1^- [X^-] >> k_2 [Y^-]$

Problem 6 (75 points)

The following mechanism first suggested by Se'lkov (1962), used by Gierer and Meinhardt in development, Schankenberg in chemical systems and Grey and Scott in contimous stir tank reactors (CSTR), is now widely know as the Autocatalator

$$Ao \xrightarrow{k_o} A \tag{13}$$
$$A + 2B \xrightarrow{k} 3\ B \tag{14}$$
$$B \xrightarrow{k_d} \phi \tag{15}$$

Using the mass action laws we get the following ODEs:

$$\frac{d[A]}{d\,t} = r_\circ - k\,[A]\,[B]^2 \tag{16}$$
$$\frac{d[B]}{d\,t} = k\,[A]\,[B]^2 - k_d\,[B] \tag{17}$$

where $r_\circ = k_\circ\, A_\circ$. For Eqs. (16, 17):

a) (10 points) Scale time (τ) and concentrations (X, Y) such that the new k and k_d are equal to unity.

b) (10 points) Find the steady states $(\bar{X}, \bar{Y})$ and any constraints in the parameter values

c) (10 points) Calculate the relaxation matrix as a function of the steady states $(\bar{X}, \bar{Y})$.

d) (10 points) Calculate the relaxation matrix as a function of the rescaled r_o.

e) (35 points) Find an analytical expression for the bifurcation relation for the **rescaled** r_o that separates homogeneous stable steady state and oscillatory solutions.

a) $\dfrac{dX}{d\tau} = \dfrac{s r_0}{m} - (s k m^2) X Y^2$

$\dfrac{dY}{d\tau} = (s k m^2) X Y^2 - (s k_d) Y$

$s = \dfrac{1}{k_d}$

$m^2 = \dfrac{k_d}{k} \Rightarrow m = \sqrt{\dfrac{k_d}{k}}$

$\tilde{r}_0 = \dfrac{r_0 k^{1/2}}{k_d^{3/2}}$

$\dfrac{dX}{d\tau} = \tilde{r}_0 - XY^2$

$\dfrac{dy}{d\tau} = xy^2 - y$

b) $\bar{y} = \tilde{r}_0$

$\bar{X} = \dfrac{1}{\tilde{r}_0}$

$\Rightarrow \bar{X}\,\bar{Y} = 1$

$\tilde{r}_0 \geq 0$

c) $R = \begin{pmatrix} -\bar{y}^2 & ; & -2\bar{x}\bar{y} \\ \bar{y}^2 & ; & 2\bar{x}\bar{y}-1 \end{pmatrix}$

d) $R = \begin{pmatrix} -\tilde{r}_0^2 & ; & -2 \\ \tilde{r}_0^2 & ; & 1 \end{pmatrix}$ $\det R = \tilde{r}_0^2 > 0$

e) $\operatorname{tr} R = 1 - \tilde{r}_0^2 \leq 0$

$1 \leq \tilde{r}_0^2$

$1 \leq \tilde{r}_0$ stable

$1 \geq \tilde{r}_0$ UNSTABLE