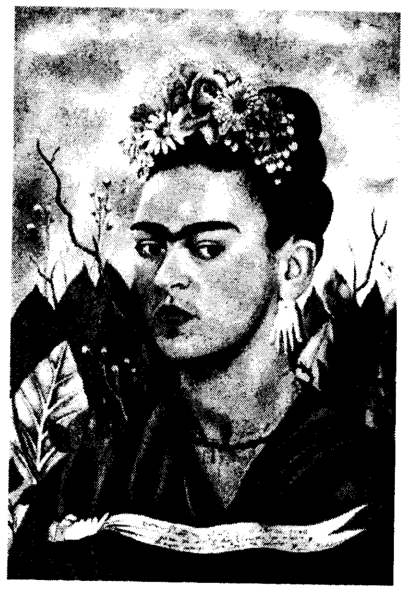
Chemistry 361
FINAL EXAM
Thursday 17 December, 2009

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.

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Problem 1 (25 points)

For the hydrogen-like wave function,

$$\Psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2} \frac{r}{a_o}\ Exp[-r/2a_o]\ Cos[\theta] \tag{1}$$

a) Calculate the average or expected value of $1/r$ ($< 1/r >$).

b) Calculate the expected value of the kinetic energy ($< E_K >$).

Hint: You could use the previous result and the Viral theorem.

$$\int_0^\infty r^n\ Exp[-\alpha\ r]\ dr\ =\ \frac{n!}{a^{n+1}} \tag{2}$$

$$\boxed{\left\langle \frac{1}{r}\right\rangle} = \int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{1}{r}\left|\Psi_{2,1,0}\right|^2 r^2 \sin\theta\, d\theta\, d\varphi\, dr = 2\pi\int_0^\pi \cos^2(\theta)\sin\theta\, d\theta \otimes$$

$$\int_0^\infty \frac{1}{\cancel{r}}\frac{1}{16(2\pi)}\frac{1}{a_o^3}\frac{r^{\cancel{2}}}{a_o^2}\, e^{-\frac{r}{a_o}}\, r^2\, dr = \cancel{2\pi}\left(\frac{2}{3}\right)\frac{1}{16(\cancel{2\pi})}\frac{1}{a_o^5}\int_0^\infty r^3 e^{-r/a_o}\, dr$$

$$= \frac{1}{3}\frac{1}{8a_o^5}\frac{3!}{(1/a_o)^4} = \frac{\cancel{3}\cdot 2a_o^4}{\cancel{3}\cdot 8a_o^5} = \boxed{\frac{1}{4a_o}}$$

FROM THE Virial THEOREM

$$\langle E_K\rangle = -\frac{1}{2}\langle E_p\rangle$$

$$\langle E_p\rangle = -\left\langle \frac{Z|e|^2}{4\pi\epsilon_0\, r}\right\rangle = -\frac{Z|e|^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle = -\frac{Z|e|^2}{16\pi\epsilon_0\, a_o}$$

$$\boxed{\langle E_K\rangle = \frac{Z|e|^2}{32\pi\epsilon_0 a_o}}$$

Problem 2 (25 points)

The gas-phase decomposition of ethyl bromide is a first-order reaction, occurring with a rate constant that demonstrates the following dependence on temperature

Effect of temperature on rate constant		
	Experimental value	
Tempeature	800 K	900 K
k	0.036 s^{-1}	1.410 s^{-1}

a) Determine the Arrhenius parameters for this reaction.
b) Using these parameters, determine $\Delta H^{\pm}$ and $\Delta S^{\pm}$ as described by the Eyring equation.

a) $k_1 = A e^{-E_a/RT_1}$ and $k_2 = A e^{-E_a/RT_2}$ CONSIDER $T_2 > T_1$

$$\frac{k_2}{k_1} = e^{-E_a/RT_2 + E_a/RT_1} \Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{E_a\, \cancel{T_2 T_1}}{R(T_1T_2)}$$

$$= \frac{E_a \Delta T}{R T_1 T_2}$$

$$\Rightarrow \boxed{E_a = \frac{R T_1 T_2}{\Delta T} \ln\left(\frac{k_2}{k_1}\right)}$$

$$= 8.314\,\text{J mol}^{-1}\text{K}^{-1} \frac{(900\text{K})(800\text{K})}{100\text{ K}} \ln\left(\frac{141.0}{3.6}\right) = \boxed{220 \frac{\text{kJ}}{\text{mol}}}$$

$$\boxed{A = k_1 e^{+E_a/RT_1} = k_1 e^{\frac{T_2}{\Delta T}\ln\left(\frac{k_2}{k_1}\right)} = k_1 \left(\frac{k_2}{k_1}\right)^{\frac{T_2}{\Delta T}}} = 3.6\times10^{-2}\,s^{-1}\left(\frac{141.0}{3.6}\right)^{9}$$

$$\boxed{A = 7.8\times10^{12}\,s^{-1}}$$

$$\boxed{\Delta H^{\#} = E_a - RT = 220\,\text{kJ mol}^{-1} - 8.314\,\text{J mol}^{-1}\text{K}^{-1}\,300\,\text{K} = 218\,\text{kJ mol}^{-1}}$$

$$\boxed{A = \frac{e k_B T}{h} e^{\Delta S^{\#}/R}} \Rightarrow \Delta S^{\#} = R \ln\left(\frac{A h}{e k_B T}\right) = \boxed{-6.5 \frac{\text{J}}{\text{K mol}}}$$

Problem 3(25 points)

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

$$S \; + \; E \xrightarrow{k^{obs}} P \; + \; E \tag{3}$$

Mechanism

$$S + E \xrightarrow{k_1^+} SE \tag{4}$$

$$SE \xrightarrow{k_1^-} S + E \tag{5}$$

$$SE \xrightarrow{k_2} P + E \tag{6}$$

but the product inhibits the active isomer of the enzyme

$$P + E \xrightarrow{k_i^+} \bar{E} \tag{7}$$

$$\bar{E} \xrightarrow{k_i^-} P + E \tag{8}$$

$$\frac{dSE}{dt} = k_1^+ S \cdot E - k_1^- SE - k_2 SE \simeq 0 \Rightarrow SE = \frac{S \cdot E}{K_M}$$

$$\frac{d\bar{E}}{dt} = k_i^+ P \cdot E - k_i^- \bar{E} \simeq 0 \Rightarrow \bar{E} = K_i P \cdot E$$

$$E_0 = E\left[1 + \frac{S}{K_M} + K_i P\right] \Rightarrow E = \frac{E_0 K_M K_i}{K_i(K_M + S)}$$

$$E = \frac{K_M E_0}{K_M + S + K_i K_M P}$$

$$\frac{dP}{dt} = rate = k_2 SE \left(- k_i^+ P \cdot E + k_i^- \bar{E}\right) \simeq 0$$

$$\boxed{rate = k_2 SE = \frac{k_2 E_0 S}{K_M + S + K_i K_M P} = \frac{V_m S}{K_M + S + K_i K_M P}}$$

Problem 4 (25 points)

My student is considering taking some time off this weekend, but before leaving he wants to start an experiment with *E. coli*. He namely needs to grow a colony starting with one bacterium. Now he wants to start the colony with one bacterium at 9:00 am this Friday and come back and check the colony on Sunday 9:00am.

a) Assuming an infinite amount of food and optimal conditions, he knows that *E. coli* reproduces every 20 min. Calculate the number of bacteria after 48 hrs.

b) If the mass of a single bacterium is $10^{-12}g$, what is the mass of the colony after 24 hrs?

c) Compare the mass in b) with the mass of an average male (70 kg), and/or the mass of the Earth ($5.98 \times 10^{24}kg$)

a) Half-Life $= \tau_{1/2} = 20$ min $\Rightarrow k = \frac{\ln 2}{\tau_{1/2}}$

$N(t) = N_0 e^{+kt}$ But $N(0) = 1$

$N(t) = e^{\ln 2 \frac{t}{20min}} = e^{\ln(2^{t/20min})} = 2^{\frac{t}{20min}}$

$48hr = 48(60)min = 2880 min$

$N(48h) = 2^{\frac{2880}{20}} = 2^{144} = 2.23 \times 10^{43}$

b) $N(24h) = 2^{72} = 4.72 \times 10^{21}$

$Mass = 4.72 \times 10^{9} g = 4.72 \times 10^{6} Kg$

c) $\frac{Mass}{70Kg} = 6.74 \times 10^{4}$ men.

Notice that the mass after $48hr = 2.23 \times 10^{28} Kg > M_{\underline{Earth}}$

Problem 5 (25 points)

Several years ago an organic synthetic chemist friend asked to help him analyze his data. He was looking at the decomposition of a couple of reagents in a particular solvent. For a fixed solvent, he found different rates of decomposition.

The problem can be reduced to the following overall reactions,

$$A + R \xrightarrow{k_1} P_1 \tag{9}$$

$$B + R \xrightarrow{k_2} P_2 \tag{10}$$

a) Find the concentrations of the reactants as function of time, assuming that the initial concentrations are A_o, and B_o, and that R is in excess, so we can consider a pseudo-first order reactions.
b) Since we know that at time t_1, only 4% of A and 80% of B are left , what is the ration of k_1/k_2.
c) If A_o and B_o are equimolal, find a relation between times t_1 and t_2 at which only 13% of A is left at time t_1 and the same percentage of B is left at t_2.

a) rate should include R!

$$\frac{dA}{dt} = -k_1[R]A \implies A(t) = A_o e^{-k_1[R]t}$$

AND $B(t) = B_o e^{-k_2[R]t}$

b) $A_1 = A_o e^{-k_1[R]t_1}$ and $B_1 = B_o e^{-k_2[R]t_2}$

$\ln\left(\frac{A_1}{A_o}\right) = -k_1[R]t_1$ and $\ln\left(\frac{B_1}{B_o}\right) = -k_2[R]t_2$; [R] dependent!

$$\frac{k_1}{k_2} = \frac{\ln(A_1/A_o)}{\ln(B_1/B_o)} = \frac{\ln(0.04)}{\ln(0.80)} = 14.4 = 14 \text{ (2 sig figs)}$$

c) Consider a t_2 for B

$\ln\left(\frac{A_1}{A_o}\right) = -k_1[R]t_1$ and $\ln\left(\frac{B_2}{B_o}\right) = -k_2[R]t_2$

BUT IN THIS CASE

$$k_1[R]t_1 = k_2[R]t_2$$

$$\boxed{\frac{t_2}{t_1} = \frac{k_1}{k_2}} = 14.4 \longrightarrow t_2 = 14.4\,t_1$$

Problem 6 (25 points)

The following mechanism, first suggested by Peacock-López, Radov and Flesner (1996), is now widely know as the Templator

$$Ao \xrightarrow{k_o} A \tag{11}$$
$$Bo \xrightarrow{k_o} B \tag{12}$$
$$A + B \xrightarrow{k_u} T \tag{13}$$
$$A + B + T \xrightarrow{k_t} T + T \tag{14}$$
$$T \xrightarrow{E} \phi \tag{15}$$

Using the mass action laws a particular definitions and scaling, we get the following dimensionless ordinary differential equations:

$$\frac{dX}{d\,\tau} = r - X^2\,Y \tag{16}$$
$$\frac{dY}{d\,\tau} = X^2\,Y - \frac{Y}{K+Y} \tag{17}$$

where X is related $(A+B)/2$, and Y to T.
For Eqs. (16, 17):
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 as a function of K that separates homogeneous stable steady state and oscillatory solutions.

b) $r = \frac{Y}{K+Y} \Rightarrow rK + rY = Y \Rightarrow \boxed{\bar{Y} = \frac{rK}{1-r}}$ $\quad r < 1$

$\boxed{\bar{X} = \sqrt{\frac{r}{\bar{Y}}} = \sqrt{\frac{1-r}{K}}}$

c) $J = \begin{pmatrix} -2\bar{X}\bar{Y} & -\bar{X}^2 \\ 2\bar{X}\bar{Y} & \underbrace{X^2 - \frac{1}{K+Y}}_{=0} + \frac{Y}{(K+Y)^2} \end{pmatrix} = \begin{pmatrix} -2\bar{X}\bar{Y} & -\bar{X}^2 \\ 2\bar{X}\bar{Y} & \frac{1}{\bar{Y}}(X^2 Y)^2 \end{pmatrix} = \begin{pmatrix} -2\bar{X}\bar{Y} & -\bar{X}^2 \\ 2\bar{X}\bar{Y} & \bar{X}^4\bar{Y} \end{pmatrix}$

d) $J = \begin{pmatrix} -2r\sqrt{\frac{K}{1-r}} & -\frac{1-r}{K} \\ 2r\sqrt{\frac{K}{1-r}} & \left(\frac{1-r}{K}\right)^2 \frac{rK}{1-r} \end{pmatrix} = \begin{pmatrix} -2r\frac{K^{1/2}}{(1-r)^{1/2}} & -\frac{1-r}{K} \\ 2r\sqrt{\frac{K}{1-r}} & \frac{(1-r)}{K}r \end{pmatrix}$

e) $\frac{(1-r)r}{K} - 2r\frac{K^{-1/2}}{(1-r)^{1/2}} = 0$ $\quad (1-r)^{3/2} = 2K^{3/2} \Rightarrow 1-r = 2^{2/3}K$

$\boxed{r = 1 - 2^{2/3}K}$