Chem 452 – Final Exam
December 16, 2005

Cover Sheet
Closed Book, Closed Notes, and NO Calculator

The exam consists of 14 questions.
<table>
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<th>Problem</th>
<th>Possible Score</th>
<th>Your score</th>
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1B. Consider the unimolecular isomerization of species C into D. The concentration of C is given by $[C]$ and the initial concentration is $[C_0]$. The initial concentration of D is zero. Species C decomposes by a first order process with rate constant $k$.

a. Write down the rate law.

b. Make a sketch of the concentration of C as a function of time. Be sure to label carefully your axes. The next two parts of this problem require the graph so you might want to read those before starting the sketch.
c. On the same graph, sketch the concentration of D as a function of time. Be sure to explain your logic.

d. If the rate constant is doubled, sketch the concentration of C as a function of time on the same graph. Explain your logic.
The Arrhenius equation for a rate constant, \( k \), is given by

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

A first order decomposition reaction is observed to have the following rate constants at the indicated temperatures.

<table>
<thead>
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<th>( \theta/°C )</th>
<th>p</th>
<th>q</th>
<th>r</th>
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<td>k/s(^{-1})</td>
<td>2.46</td>
<td>45.1</td>
<td>576</td>
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Assuming that the scientist took data that does, in fact, fit the Arrhenius relationship, state the procedure for taking the data and determining the activation energy, \( E_a \), graphically.

- Be sure to give what you would use for the values along the x & y axes.
- Make a sketch of the data labeling the points p, q and r. (Do not worry about actual values.)
- Denote on the graph how you would determine \( E_a \),
3B. Below is a sketch of a reaction profile from the text.

a. Sketch on the figure how the reaction profile would or would not be different if a catalyst were added to the system.

b. We discussed Activated complex theory in class. The Arrhenius equation can be written as

\[ k = A \exp\left(\frac{-E_a}{RT}\right) \]

How do A and E_a relate to thermodynamic quantities?
4B. Below is a sketch of the harmonic oscillator potential. The grid lines are a guide for graphing.

\[ \Psi_1(x) \]

\[ \Psi_2(x) \]

\begin{align*}
\text{a)} & \quad \text{Draw the first excited state (} \nu = 1 \text{) and second excited state (} \nu = 2 \text{) energy levels on the graph.} \\
\text{b)} & \quad \text{Draw the first excited} [\Psi_1(x)] \text{ and second excited} [\Psi_2(x)] \text{ state wavefunctions.}
\end{align*}
c) Give an integral that is zero because the wavefunctions are orthogonal.

d) If the system is initially in the \( v=0 \) state, what is a possible final state for an overtone?
5B. The metal sodium has a work function of 2.30 eV.

a. Make a plot of KE of emitted electron vs energy ($h\nu = \hbar \omega$) of the incident light. Use energy units of eV.

b. If the incident light has $h\nu = \hbar \omega = 1.4$ eV, what is the kinetic energy of the emitted electron?
6B. Write down the Hamiltonian for the \( \text{H}_2^+ \) molecule. Be sure to draw a sketch to show your coordinate system.
(12 points)
7B. Term symbols and angular momentum coupling. For parts a, b give whether the term symbol is right or wrong and explain your logic. Part c ask for the degeneracy.

a. \( ^5S_2 \)

b. \( ^2D_{3/2} \)

c. What is the degeneracy of the \( ^4F_{9/2} \) state of Rh?
8B. For the molecules NO and NO\(^+\), determine the bond order of each. Predict which molecule will have the smaller value of \(D_e\) (bond strength) and which one will have a shorter equilibrium bond length (\(r_e\)). Explain your logic.
9B. For the Li$^+$ ion states given below identify the exchange (permutation) symmetry (symmetric, antisymmetric, asymmetric) of both the space and spin parts of the wavefunction. Which of the states are allowed? Give your logic.

a) $\Psi = [1s(1)2s(2)] \ [\alpha(1)\beta(2)-\beta(1)\alpha(2)]/\sqrt{2}$

b) $\Psi = [1s(1)2s(2)-2s(1)1s(2)]/\sqrt{2} \ [\alpha(1)\beta(2)+\beta(1)\alpha(2)]/\sqrt{2}$

c) $\Psi = [1s(1)1s(2)] \ [\alpha(1)\beta(2)+\beta(1)\alpha(2)]/\sqrt{2}$

d) $\Psi = [1s(1)2s(2)-2s(1)1s(2)]/\sqrt{2} \ [\alpha(1)\alpha(2)]$
10B. Below is a figure of the ground state potential energy of H\(_2\) that we have seen in class. For H\(_2\), the measured value of D\(_0\) is 4.4781 eV or 36116 cm\(^{-1}\). The value of \(\omega_e\) is 4401.213 cm\(^{-1}\) and \(\omega_{ex}e\) is 121.336 cm\(^{-1}\).

For simplicity of math, assume that
\[
D_0 = 36000 \text{ cm}^{-1} \\
\omega_e = 4400 \text{ cm}^{-1} \\
\omega_{ex}e = 100 \text{ cm}^{-1}
\]

The spectroscopic equation for vibrational energy levels is given by
\[
G(v) = \omega_e (v+\frac{1}{2}) - \omega_{ex}e (v+\frac{1}{2})^2
\]
a. On the graph indicate a transition for a hot band and an overtone. Mark clearly which one is which.

b. Evaluate the energy of the first excited vibrational state using the approximate values of \( \omega_e \) and \( \omega_x e \).
(16 points)

11B. Water has three vibrational modes, a symmetric stretch at approximately 3652 cm\(^{-1}\), an antisymmetric stretch at approximately 3756 cm\(^{-1}\) and a bending mode at 1595 cm\(^{-1}\). Assume that all three modes are Raman active, that is, they can be seen in Raman spectroscopy. Make a sketch of the Raman spectrum. Be sure to label the Stokes, anti-Stokes and Rayleigh regions. Be sure to label which peaks correspond to which vibrations.
(8 points)
12B. Sketch the rotational spectrum for a heteronuclear diatomic molecule with rotational constant $B = 4 \text{ cm}^{-1}$. Plot intensity based on Boltzmann population vs energy in cm$^{-1}$. Assume that the maximum intensity occurs for the $J=2$ initial state. Plot about 7 lines.
13. Answer 4 of the following. Be sure to denote which two you do not want graded.

- State the Variation Principle.

- If the ionization energy of H from the ground state is 13.6 eV, what energy is needed to ionize it from the n=2 state?

- State the Pauli Exclusion Principle for fermions
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- Who explained the ultraviolet catastrophe of blackbody radiation. What novel assumption did he make?

- For a particle in a 1d infinite box, if the width is doubled, how does the spacing between energy levels change?

- The ground state energy of a 2-d infinite square box is 2. The energy of the first excited state is 5. What is the degeneracy of the first excited state?

(2 points) 14. Have a great break!