NAME: ________________________________ **CHEMISTRY 444, SPRING, 2012(12S)**

Circle Section Number: 10 11 80 **Final Examination, May 23, 2012**

*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (10 points) Calculate the average speed for each of the three isotopomers of water, H_2O, HDO, and D_2O (where D is the deuterium nucleus) in water vapor at 300 K as precisely as you can. [HINT: Assume that the oxygen atoms are all ^{16}O.]

The average speed is given by the formula: $v_{ave} = \sqrt{\frac{8RT}{\pi M}}$

From Table 12.2, the exact masses of the atoms are:

M_H = 1.007825 gm/mole
M_D = 2.0140 gm/mole
M_O = 15.99491 gm/mole

To get precise values, one must use these exact masses, not rounded or average masses.

The total mass of each molecule is then:

$$M_{H_2O} = 18.01061\, gm/mole$$
$$M_{HDO} = 19.016735\, gm/mole$$
$$M_{D_2O} = 20.02291\, gm/mole$$

Substitution into the equation above, using precise numbers for the fundamental constants, gives

$$v_{H_2O} = 593.858\, m/s$$
$$v_{HDO} = 577.935\, m/s$$
$$v_{D_2O} = 563.227\, m/s$$

DO NOT WRITE IN THIS SPACE
p. 1________/10
p. 2________/10
p. 3________/10
p. 4________/15
p. 5________/10
p. 6________/10
p. 7________/15
p. 8________/10
p. 9________/10
p. 10_______/10
p. 11_______/15
p. 12_______/10
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p. 13_______/10 (Extra credit)
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TOTAL PTS (out of 135)

2. (10 points) Assuming that the interior of a cell is primarily a water solution, how long – on average – does it take a rabbit papilloma virus to move from one side of cell to another at 293.15 K, assuming the cell is 1 micrometer in diameter?

This is a three-dimensional diffusion problem for which

$$\delta r = \sqrt{6Dt}$$

Using the diffusion coefficient of rabbit papilloma virus in water that is reported in the handbook:

$$t = \frac{(\delta r)^2}{6D} = \frac{(1\times10^{-6}\,m)^2}{6\left(0.006\times10^{-9}\,m^2 s^{-1}\right)} = 2.8\times10^{-2}\ s$$

Of course, the cell has a very complex geometry which must be modeled more completely (for example, including reflections off walls), but this simple calculation gives an order of magnitude for the time to travel across this distance.

Score for Page

3. (10 points) The reduction of methylene blue by ascorbic acid has been studied by observing the color disappear from a solution containing both materials. The initial rate of disappearance of methylene blue is reported for a series of solutions as a function of ascorbic acid concentration in the table. Estimate the initial order of reaction with respect to ascorbic acid from these data. Confirm your answer with a plot or a calculation.

Ascorbic Acid Concentration (M)	Rate of Disappearance of Methylene Blue (Absorbance loss s^{-1})
0.0050	0.0115
0.0150	0.034
0.0250	0.057
0.0350	0.077

One can note that the rate should be proportional to the concentration by the following formula:

$$v = kC_{AA}^{n}.$$

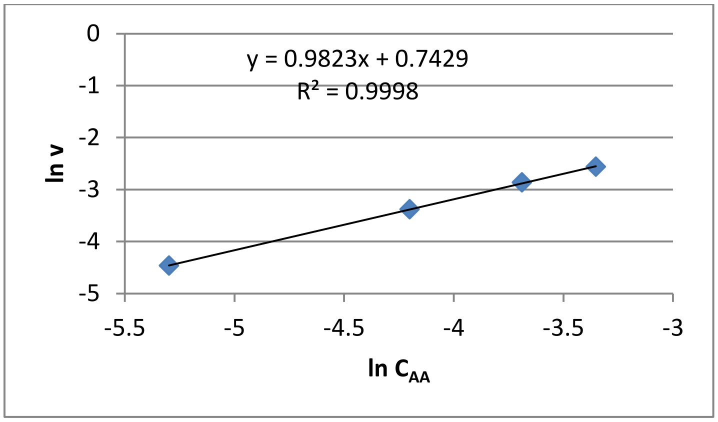
This equation can be rewritten as:

$$\ln v = \ln k + n \ln C_{AA}$$

A plot of the logarithm of the rate versus the logarithm of the concentration will have a slope that is the order.

$\ln C_{AA}$	ln(v)
-5.298	-4.465
-4.200	-3.381
-3.689	-2.865
-3.352	-2.564

The graph is shown below. The slope indicates that the order is close to 1.



One could also show that the ratio of the rates among ALL the different experiments is the same as the ratio of the respective initial concentrations, but that would require a large number of calculations.

Score for Page

4. (15 points) Bromination of a hydrocarbon (*RH*) occurs by the process

$$RH + Br_2 \rightarrow RBr + HBr$$

which is thought to proceed by the following mechanism:

$$(1)\quad Br_2 \xrightarrow{k_1} 2\,Br\cdot$$
$$(2)\quad Br\cdot + RH \xrightarrow{k_2} R\cdot + HBr$$
$$(3)\quad \mathrm{R}\cdot + Br_2 \xrightarrow{k_3} Br\cdot + RBr$$
$$(4)\quad \mathrm{R}\cdot + Br\cdot \xrightarrow{k_4} RBr$$

Derive the steady-state rate expression for this mechanism.

The rate law is given by the rate of formation of the RBr.

$$\frac{d[RBr]}{dt} = v_3 + v_4$$

At steady state, the rates of formation of intermediates are zero:

$$\frac{d[Br\cdot]}{dt} = 2v_1 - v_2 + v_3 - v_4 = 0$$
$$\frac{d[R\cdot]}{dt} = v_2 - v_3 - v_4 = 0$$

Summing these two equations gives:

$$v_1 = v_4 \qquad or \qquad k_1[Br_2] = k_4[Br\cdot][R\cdot]$$

Subtracting these two equations gives:

$$v_2 = v_3 \qquad or \qquad k_2[Br\cdot][RH] = k_3[R\cdot][Br_2]$$

Substitution for the radical $[R\cdot]$ from this second equation into the first gives

$$k_1[Br_2] = k_4[Br\cdot]\left(\frac{k_2[Br\cdot][RH]}{k_3[Br_2]}\right) = \frac{k_2k_4}{k_3}\frac{[RH]}{[Br_2]}[Br\cdot]^2$$

Solving this for the bromine radical concentration gives:

$$[Br\cdot] = \sqrt{\frac{k_1k_3}{k_2k_4}}\frac{[Br_2]}{\sqrt{[RH]}}$$

Because of the two relationships we derived,

$$\frac{d[RBr]}{dt} = v_2 + v_1 = k_2[Br\cdot][RH] + k_1[Br_2]$$
$$= k_2\sqrt{\frac{k_1k_3}{k_2k_4}}\frac{[Br_2][RH]}{[RH]^{1/2}} + k_1[Br_2]$$
$$= \sqrt{\frac{k_1k_2k_3}{k_4}}[Br_2][RH]^{1/2} + k_1[Br_2]$$

Score for Page

5. (10 points) Calculate the speed of an electron with a wavelength of 300 nm.

By DeBroglie's relation, one can find the momentum of the electron from the wavelength.

$$p = \frac{h}{\lambda} = \frac{6.6260693 \times 10^{-34}\, J\, s}{300 \times 10^{-9}\, m} = 2.2086898 \times 10^{-27}\, \frac{kg\, m}{s}$$

Using this result, one can find the speed from the definition of the momentum.

$$v = \frac{p}{m_e} = \frac{2.2086898 \times 10^{-27}\, kg\, m\, s^{-1}}{9.1093826 \times 10^{-31}\, kg} = 2.4246317 \times 10^{3}\, m\, s^{-1}$$

Even though this is quite a speed, it is still much less than the speed of light, so using nonrelativistic definitions is appropriate.

Score for Page

6. (10 points) Calculate the **second** ionization potential (in eV) of the helium atom.

This problem is the ionization of a hydrogen-like atom with nuclear charge of 2. The ionization takes an electron from the lowest-energy orbital to a state with an infinite principal quantum number. The energy change is found from an equation on page 11.4 of your Handbook:

$$\begin{aligned}
\Delta E &= E_\infty - E_1 \\
&= -\frac{Z^2 E_h}{2}\left(\frac{1}{\infty^2} - \frac{1}{1^2}\right) \\
&= \frac{2^2 E_h}{2} = 2E_h = 2\times\left(27.2114 eV\right) = 54.4228 eV
\end{aligned}$$

Score for Page

7. (15 points) In the following, carry out the mathematics requested as completely as possible.

(a) Find the constant, *A*, that normalizes the radial part of the wave function of the hydrogen atom with n=3 and l=2:

$$R_{32} = A_{32}\left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right)$$

$$\int_0^\infty R_{32}^2(r) r^2 dr = 1 = A^2 \int_0^\infty \left(\frac{r}{a_0}\right)^4 r^2 \exp\left(-\frac{2r}{3a_0}\right) dr = A^2 a_0^3 \int_0^\infty \left(\frac{r}{a_0}\right)^6 \exp\left(-\frac{2r}{3a_0}\right) d\left(\frac{r}{a_0}\right) = A^2 a_0^3 \frac{6!}{\left(\frac{2}{3}\right)^7}$$

$$A = \sqrt{\frac{\left(\frac{2}{3}\right)^7}{6\times5\times4\times3\times2\times1}}\left(a_0\right)^{-3/2} = \frac{4}{81\sqrt{30}}\left(a_0\right)^{-3/2}$$

(b) Determine the simplest form of the commutator: $\left[x\frac{d}{dx}; x^2\frac{d^2}{dx^2}\right]$

$$\left[x\frac{d}{dx}; x^2\frac{d^2}{dx^2}\right] f(x) = x\frac{d}{dx}\left(x^2\frac{d^2}{dx^2} f(x)\right) - x^2\frac{d^2}{dx^2}\left(x\frac{d}{dx} f(x)\right) =$$

$$x\left(2x\frac{d^2 f(x)}{dx^2} + x^2\frac{d^3 f(x)}{dx^3}\right) - x^2\frac{d}{dx}\left(\frac{d}{dx}\left(x\frac{d}{dx} f(x)\right)\right) = 2x^2\frac{d^2 f(x)}{dx^2} + x^3\frac{d^3 f(x)}{dx^3} - x^2\left(\frac{d}{dx}\left(\frac{df(x)}{dx} + x\frac{d^2 f(x)}{dx^2}\right)\right) =$$

$$2x^2\frac{d^2 f(x)}{dx^2} + x^3\frac{d^3 f(x)}{dx^3} - x^2\left(\frac{d^2 f(x)}{dx^2} + \frac{d^2 f(x)}{dx^2} + x\frac{d^3 f(x)}{dx^3}\right) = 0$$

Whadoyouknow! Those two commute and the simplest form of the commutator is 0

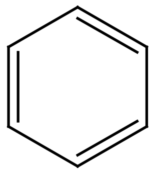
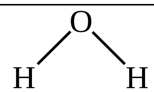
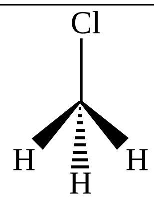
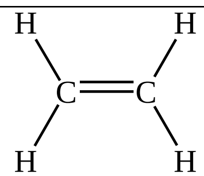
Score for Page

8. (10 points) Match the statements/equations in part A with the names/answers in part B by inserting the appropriate letter next to the statement.

Part A	Part B
Emission of electrons from solids under illumination is the origin of _______h_______	a. Motion
The number of ways that a system represented by different wave functions can have the same energy is called ________e______	b. Photoelectronic effect
According to the QM postulates, to every _____d___ there is a corresponding operator in quantum mechanics	c. Single-valuedness criteria
Set of functions such that $\oint_{all\ space} \psi_i^* \psi_j d\tau = 0 \ and \ \oint_{all\ space} \psi_j^* \psi_j d\tau = 1$ is called ______g_______	d. Observable
$Equation: \psi(0) = \psi(a) = 0$ states _________j__________ that any well-behaved state function for a particle in a one-dimensional box of length a must satisfy	e. Degeneracy
	f. Orthopedic
	g. Orthonormal
	h. Photoelectric effect
	i. Boundary conditions
	j. Orthorhombic
	k. Probability
	m. Functional restrictions

Score for Page

9. (10 points) For each molecule below, give the point group in the box to its right.

Molecule	Point group
 Benzene	D_{6h}
 Water	C_{2v}
 Chloroform	C_{3v}
 Ethene	D_{2h}
Carbon monoxide	$C_{\infty V}$

Score for Page

10. (10 Points) A pure rotational spectrum of a diatomic molecule NaCl is complicated by the presence of two different isotopes of chlorine. A paper by M. Caris, F. Lewen, and G. Winnewisser (*Z. Naturforsch*., **2002**, *57a*, 663-668) reported 189 newly recorded rotational lines of NaCl. The predicted equilibrium bond length of $^{23}Na^{35}Cl$, to maximum precision, is 2.3598 A. (a) The derived rotational constant for $^{23}Na^{37}Cl$ is 6397.28111 MHz. Calculate the equilibrium bond length in $^{23}Na^{37}Cl$ based on this value, as precisely as you can. (b) Compare your result to that for $^{23}Na^{35}Cl$.

(a) The

$B_e = \frac{h}{8\pi^2 I}$, where $I = \mu R_e^2$ and the units of B_e are s^{-1} = Hz:

$$B_e = \frac{h}{8\pi^2 \mu R_e^2} \text{ or } R_e = \sqrt{\frac{h}{8B_e\pi^2\mu}}$$

$$\mu(^{23}Na^{37}Cl) = \frac{22.9898 \times 36.9659}{22.9898 + 36.9659} g/mol = 14.1744 g/mol$$

$$R_e(^{23}Na^{37}Cl) = \sqrt{\frac{6.6260755\times 10^{-34} J \times s \times 6.022\times 10^{23} \frac{1}{mol}}{8\pi^2 \times 14.1744 g/mol \times 10^{-3} \frac{kg}{g} \times 6397.28111 \times 10^6 Hz}} = 2.3608\times 10^{-10} m = 2.3608 \text{ A}$$

(b) The bond length is slightly longer than that of $^{23}Na^{25}Cl$. The likely cause is the slight centrifugal distortion of the molecule due to the heavier chlorine-37 atom.

Score for Page

11. (15 Points) Determine ground state (unless indicated otherwise) configurations, bond order, total orbital angular momentum, total spin angular momentum, and the terms corresponding to the lowest-energy state arising from these configurations (indicate the symmetry under inversion (g vs. u) **only for the ground state species with Σ terms** and symmetry under reflection through the mirror plane σ (+ vs -) **only for $^1\Sigma$ terms of the ground state species**) for the following diatomic homonuclear molecules and ions:

Molecule	Configuration	BO =	Λ =	S =	Term
H_2	2e: $(\sigma_g 1s)^2$	½*(2-0) = 1	0	0	$^1\Sigma_g^+$
H_2^- in its **first excited state**	3e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^0$ $(\sigma_g 2s)^1$	½*(3-0) = 1.5	0	½	$^2\Sigma$
He_2^-	5e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^2$ $(\sigma_g 2s)^1$	½*(3-2) = 0.5	0	½	$^2\Sigma_g$
O_2	16e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^2$, $(\sigma_g 2s)^2(\sigma_u{*}2s)^2(\sigma_g 3s)^2(\pi_u)^4(\pi_g^*)^2$	½*(10-6) = 2	2 or 0	1 or 0	$^3\Sigma_g^-$
F_2^{2+}	16e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^2$, $(\sigma_g 2s)^2(\sigma_u{*}2s)^2(\sigma_g 3s)^2(\pi_u)^4(\pi_g^*)^2$	½*(10-6) = 2	2 or 0	1 or 0	$^3\Sigma_g^-$

Score for Page

12. (10 Points). Using data provided in Table 12.1, calculate the energy of the n = 0, J = 1 to n = 2, J = 2 transition for $^{127}I^{35}Cl$, in cm^{-1}, as accurately as these data allow you to.

Data from Table 12.1. ω_e = 384.18 cm^{-1}; $x_e\omega_e$ = 1.465 cm^{-1}; B_e = 0.114162 cm^{-1}; α_e = 0.000536 cm^{-1}.
Using the equation on page 12-5 of the handbook, one can calculate the centrifugal distortion coefficient, D_c:

$$D_c = 4\frac{B_e^3}{\varpi_e^2} = 4\frac{\left(0.114162\ cm^{-1}\right)^3}{\left(384.18\ cm^{-1}\right)^2} = 4.032\times10^{-8} cm^{-1}$$

Then use of the equation on page 12-5 gives the energy level difference:

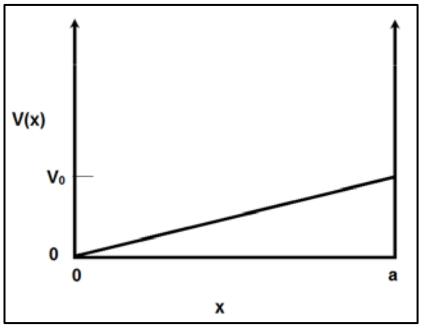
$$\frac{E_{n,J}}{hc} = \left(n+\frac{1}{2}\right)\varpi_e - \left(n+\frac{1}{2}\right)^2 \varpi_e x_e + J(J+1)B_e - J(J+1)\left(n+\frac{1}{2}\right)\alpha_e - J^2(J+1)^2 D_c$$

For this particular transition, the energy difference between these two states gives

$$\begin{aligned}\frac{\Delta E_{n,J}}{hc} &= 2\varpi_e - 6\varpi_e x_e + 4B_e - 14\alpha_e - 32D_c \\ &= 768.36\ cm^{-1} - 8.79\ cm^{-1} + 0.456648\ cm^{-1} - 7.504\times10^{-3}\ cm^{-1} - 1.2902\times10^{-6}\ cm^{-1} \\ &= 760/019\, cm^{-1}\end{aligned}$$

Score for Page

13. (10 points, extra credit) A particle of mass *m* in a one-dimensional box is subject to the potential shown in the figure. Calculate the approximate energy of the state with quantum number *n*, using perturbation theory.



This is a perturbation problem. Without the ramping figure, the wave function is: $\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$. The unperturbed energy of this state is: $E_n^{(0)} = \frac{h^2 n^2}{8ma^2}$

The first order correction to this energy is:

$$E_n^{(1)} = \int_0^a \psi^*(x)\hat{H}_{pert}\psi(x)dx = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\hat{H}_{pert}\sin\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{2V_0}{a}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\left[\frac{x}{a}\right]dx = \frac{2V_0}{a^2}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{2V_0}{a^2}\left\{\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{a}\right)}{\frac{4n\pi}{a}} - \frac{\cos\left(\frac{2n\pi x}{a}\right)}{8\frac{n^2\pi^2}{a^2}}\right\}_0^a$$

$$= \frac{2V_0}{a^2}\left\{\frac{a^2}{4} - 0 - 0 + 0 - \frac{1}{8\frac{n^2\pi^2}{a^2}} + \frac{1}{8\frac{n^2\pi^2}{a^2}}\right\}$$

$$= \frac{V_0}{2}$$

So, the energy of this state through first order is

$$E_n = E_n^{(0)} + E_n^{(1)} = \frac{h^2n^2}{8ma^2} + \frac{V_0}{2}$$

Score for Page