Name:_____**SOLUTIONS**_____   Section (circle): 1   2   3   4   5

Chemistry 11, Fall 2006
Final Exam
December 18, 2006
9:00 AM – 12:00 PM

As always, full credit will not be given unless you have written down the reasoning or calculations you used to obtain the correct answer. **Work on the back of pages will not be graded!** Pay attention to significant figures. Please check now that your exam has twelve pages (including this one). A periodic table and a list of formulas are attached at the back of the exam. If you finish early, just leave your completed exam on the front desk. If you have a question, we will be up on the fifth floor. You have two hours to complete this exam.

It is against the honor code at Amherst College to either give or receive help on this exam.
*The work you turn in must be yours and yours alone.*

Xtra credit: What is your favorite element and why (write in the space below?)

Question	Points	Score
XC	02	
I	25	
II	25	
III	21	
IV	25	
V	09	
VI	25	
VII	20	
Total	152	

I. Hybridization: Insecticides (Parathion) and Chemical Warfare Agents (Sarin) (25 points)

Both of the chemicals in this question act to inhibit an enzyme responsible for the breakdown of the neurotransmitter, acetylcholine. In the case of **SARIN (structure below)** , the inhibition is so severe, even minute exposure causes death. **SARIN** was used in the terrorist attacks in Tokyo, Japan in 1995 that killed 12 commuters and injured nearly one thousand. In the case of **PARATHION (see next page for structure)**, this inhibition is mild and the compound can be used as an insecticide. This question explores some of the similarities and differences between these two compounds.

A. The chemical warfare agent, **SARIN** (15 points)
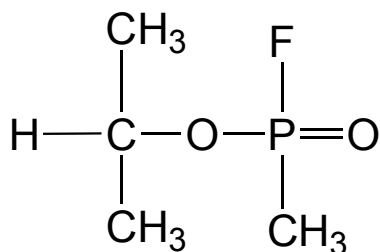
1. Draw in all lone pairs on the structure of **SARIN** and indicate formal charges if non-zero.

2. What is the steric number ____4____ of the O atom between the P and C atoms and resultant geometry ___bent_____ and P-O-C bond angles ___104.5°_____? (note resonance is NOT a factor in determining the geometry of this structure)

   a. What hybrid orbitals does this O atom (the one between the C and the P) use to construct its sigma bonds in this molecule? _____sp^3_____

   b. The P atom is tetrahedral, but it has a double bond. Normally, the atoms we have considered use a left over p orbital to make a double bond. Why is using a leftover p orbital a problem for this P atom? If P is tetrahedral with sp^3 hybridization, then all the p orbitals are already used up____

   c. Report the n and ℓ quantum numbers of the valence atomic orbital on P **most likely** to contribute to the π bond to the oxygen? _n = 3____, _ ℓ = _2____

   d. Identify the longest _____P-C____ and shortest _all C-H_____ bonds in the molecule.

B. Now consider **PARATHION** (10 points):

a. This nitrogen atom contains single bonds to O and C and one double bond to O. Draw in all implicit hydrogens and lone pair electrons. Don't forget formal charge.

b. Indicate the shortest __C-H in ring) and longest__P-S____ bonds in the molecule. (in your answer to this question, consider P-S bond to be a single bond)

O_2N—

S
||
P—O—C—CH$_3$
|
O
|
H—C—H
|
CH$_3$

H
|
C—CH$_3$
|
H

c. Focusing on the P as a central atom. The geometry here is once again tetrahedral.
    I. Predict the bond dipoles P-O bonds have greatest en difference

    See arrow bisecting the O-P-O bond of the tetrahedral P

d. Is any part of this molecule planar or aromatic? Y or N (circle one). Why?
    6 membered ring is like benzene, planar and aromatic (4n+2 = 6 electrons when n = 1)

e. Is it possible to draw reasonable resonance structures for this compound? If yes, draw one such structure below.
   Resonance structures exist for the double bonds in the six membered ring of the parathion
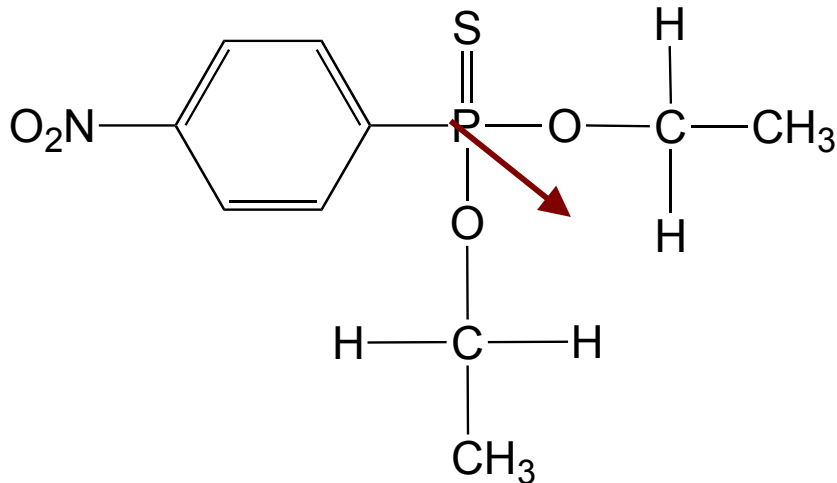
C. Both SARIN and PARATHION bind covalently to the enzyme. This event starts when an O atom on the enzyme (slightly negative) "attacks" the P atom in SARIN or PARATHION. The O atom's lone pair seeks out the P atom because the P is a bit electropositive. Use your knowledge of electronegativity, bond and molecular dipoles, and whatever else you can to determine which molecule, SARIN or PARATHION reacts more completely with the enzyme and why. The phosphorous atom on SARIN is more electropositive because of its bond to fluorine, which is the most electronegative element. This makes it react more completely with the enzyme and is why it is lethal while PARATHION is relatively safe.

3

II. Molecular Orbital Model (25 points)

NO is a stable molecule that is found both as a neurotransmitter and as a component of smog in cities such as Los Angeles. It was voted « Molecule of the Year » by *Science* Magazine in 1993.

1. Draw the Lewis structure for nitric oxide (including formal charge) and use it to answer the following questions. (6 pts)

$: \overset{\cdot}{N} = \overset{\cdot\cdot}{O} :$

the formal charge on N and O is zero
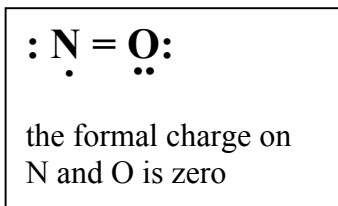
   a. What is the predicted NO bond order (i.e. single, double, triple)? __double__

   b. On which atom is the unpaired electron located? _N_

   c. Does adding an electron to form NO⁻ *strengthen, weaken or have no effect* on the bond (underline the correct choice)?

   d. Does removing an electron to form NO⁺ *strengthen, weaken, or have no effect* on the bond (underline the correct choice)?

2. Below, draw the molecular orbital diagram for NO assuming that there is no sp mixing. Include the atomic orbital levels of the N and O atoms, being sure to make clear their relative energies. Label the orbitals and distribute the electrons among the orbitals. (10 points)
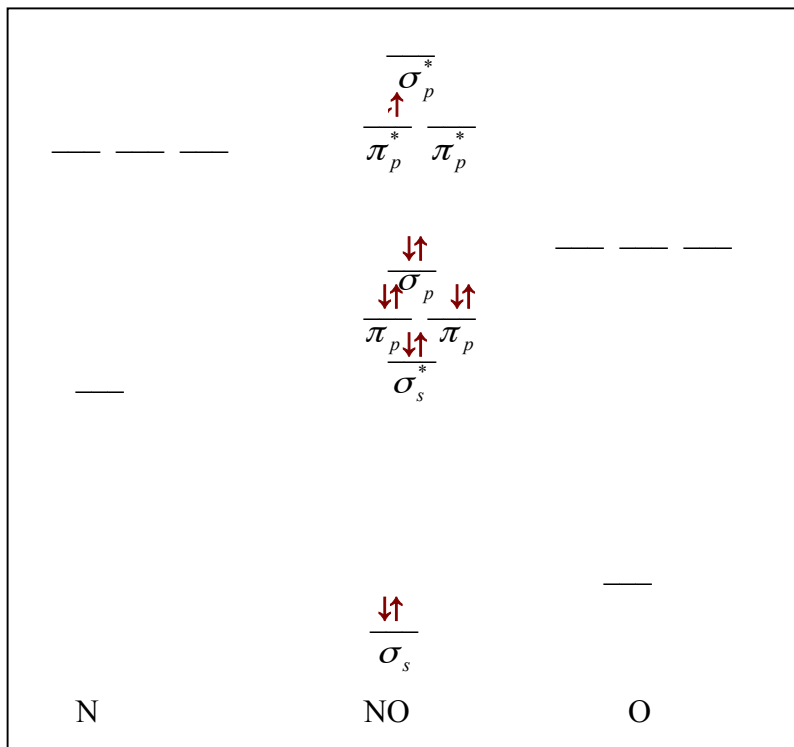
   a. What is the predicted NO bond order? __BO = 2.5__

   b. On which atom is the unpaired electron localized? _antibonding, N_

   c. Does adding an electron to form NO⁻ *strengthen, weaken or have no effect* on the bond (underline the correct choice)?

   d. Does removing an electron to form NO⁺ *strengthen, weaken, or have no effect* on the bond (underline the correct choice)?

The idealized molecular diagram you have sketched on the previous page is a bit wrong in the following way (please don't take this personally, even the textbooks would get this one wrong). The unpaired electron makes the electron density asymmetric. This splits the degeneracy of the π and π* orbitals and mixes things up a little bit. Here is the resultant MO diagram for NO, that takes that into account. (9 points)
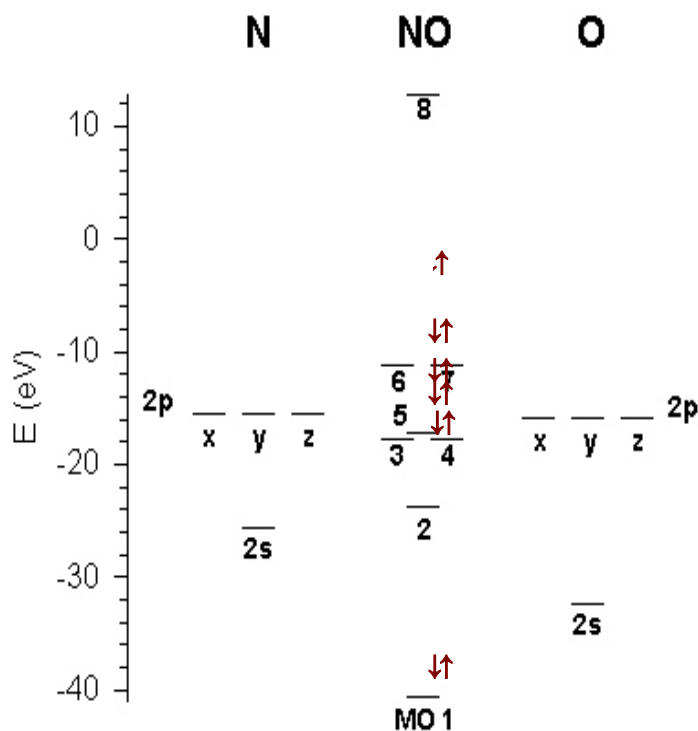
⇆In answering the questions below, use the terms MO8, MO7, etc, as used in the diagram at left, to designate a particular molecular orbitals, or MO.

a. Identify the four bonding MOs
    __MO1, MO3, MO4, MO5

b. Identify the four antibonding MOs
    MO2, MO6, MO7, MO8

c. Identify the two MOs that come about from combining the 2s atomic orbitals on N and O _MO1, MO2

d. Identify the three bonding MOs that come about from combining the 2p orbitals on N and O MO3, MO4, MO5

e. Identify the three antibonding MOs that come about from combining the 2p on N and O. MO6, MO7, MO8

f. Put the valence electrons into these orbitals, following the regular rules. See the 11 electrons distributed in the MOs above in red

g. Normally, the lowest energy transition in a molecule is from the HOMO (highest occupied molecular orbital) to the LUMO (Lowest unoccupied molecular orbital. That is not the case in NO. What IS the lowest energy transition? MO5 → MO6 because the 11 electrons for NO leave the highest occupied MO unfilled, and with the right energy photon, an electron can just pop up from the bonding MO5 to the antibonding MO6.

III. Transition Metal Chemistry (21 points, 3.5 pts each)

1. What empty metal hybrid orbitals are used by the ligands in cis-$[Pt(II)Cl_2(NH_3)_2]$?

    Hybrid orbitals sp^2d

2. What empty metal hybrid orbitals are used by the ligands in $[Pt(II)(NH_3)_6]Cl_2$?

    Hybrid orbitals sp^3d^2

3. How do the energies of the metal's d orbitals split in the the octahedral complex above and why?

    Fivefold degenerate orbitals split into lower energy t_{2g} set from d_{xy}, d_{yz}, and d_{xz} and a higher energy e_g set from dz^2 and $dx^2\text{-}y^2$. They split this way because the incoming ligands electrons are along the x, y, and z axis.

4. Sometimes, a molecule's paramagetism depends upon the strength of the crystal field splitting of the ligands. Why does it not matter for this molecule whether or not the NH_3 is a strong or weak field ligand?

    Regardless of whether or not you have strong or weak field splitting, you will have 2 unpaired electrons in a d8 system.

5. How do you experimentally determine whether or not a complex IS paramagnetic?

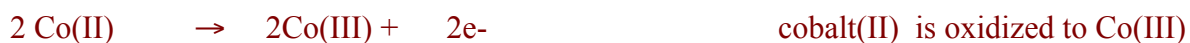   **Measure the mass in an out of a magnetic field**

6. List all the possible linkage isomers for a transition metal complex that contains 1 Co(III) ion, 6 NH_3 molecules and 3 Cl^- ions.

    There are no linkage isomers because NH_3 and Cl^- can only bond one way.

Lab Based Question (25 points)

A student in Chemistry 11 synthesized *trans*-[Co(en)$_2$Cl$_2$]Cl in Lab Experiment VII by dissolving 7.234 g of cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) in approximately 20 mL of distilled water. To the solution, he added 29.95 mL of 10.0 wt % aqueous ethylenediamine solution (density = 0.990 g/mL) with vigorous stirring. After an additional 10 minutes of stirring, he added 10.0 mL of 7.50 wt % aqueous hydrogen peroxide (H$_2$O$_2$) solution (density = 1.03 g/mL).   Finally, he added 24.00 mL of concentrated aqueous hydrochloric acid (36.5 wt % HCl; density 1.18 g/mL), and heated the solution until it changed color and reduced in volume. He then cooled the sample down, washed it twice, and filtered it. **6.144** g of product material was collected.

1. Write down the two balanced half reactions for this synthesis, indicating what is oxidized and what is reduced. Since the reaction takes place in an acidic solution, you may add protons and water as necessary. If a neutral molecule is involved, your redox equation should contain the entire molecule. If an ion is oxidized or reduced, consider ONLY the individual ion. (6 pts)

$$2\ Co(II) \quad \rightarrow \quad 2Co(III) + \quad 2e- \qquad\qquad\qquad \text{cobalt(II) is oxidized to Co(III)}$$

$$H_2O_2 \quad + \quad 2H^+ \quad + 2e- \quad \rightarrow \quad 2H_2O \qquad\qquad \text{peroxide } O^{-1} \text{ is reduced to } O^{-2}.$$

2. Identify the limiting reagent and calculate the percent yield of *trans*-[Co(en)$_2$Cl$_2$]Cl based on the starting amount of CoCl$_2$·6H$_2$O. (10 points)

First you need the balanced reactions.

$$\textbf{2CoCl}_2\textbf{·6H}_2\textbf{O} \quad + \quad \textbf{4 en} \quad + \quad \textbf{H}_2\textbf{O}_2 \quad + \quad \textbf{2HCl} \quad \rightarrow \quad \textbf{2}\ \textit{trans}\textbf{-[Co(en)}_2\textbf{Cl}_2\textbf{]Cl} \quad +$$
$$\textbf{2H}_2\textbf{O}$$

Determine the limiting reagent from the moles of starting material:

$$\text{Moles cobalt chloride hexahydrate:} \qquad \frac{7.234g}{237.93 \text{ g/mol}} = 0.03040 moles$$

$$\text{Moles ethylenediamine} \quad \frac{(29.95 \text{ mL} \times 0.990g\,/\,mL) \times 0.100}{60.10 \text{ g/mol}} = 0.0493 moles$$

$$\text{Moles hydrogen peroxide:} \quad \frac{(10.0 \text{ mL} \times 1.03 \text{ g/mL) x } 0.0750}{34.0147 \text{ g/mol.}} = 0.0227 moles$$

$$\text{Moles HCl:} \quad \frac{(24.0 \times 1.18g\,/\,mL) \times .365}{36.4606 \text{ g/mol}} = 0.3000 moles$$

By inspection, if peroxide is limiting at 0.0227 moles, (it is the smallest number of moles, so it makes sense to start here) it would require 4x moles en or 0.0908 moles of en, but en < 4 x peroxide, so peroxide can't be limiting, so try en. If en is limiting, it would require half as many moles of cobalt (OK at 0.02465 moles) and one quarter peroxide (OK at 0.0123 moles) Thus 0.02465 moles of cobalt chloride will react, and 0.02465 mole of product can be produced. This calculates to 7.037 grams of product. The person in part 2 collected 6.144 g. This would give a yield of 87.31% or 87.3% with sig figures.

3. Lab protocol: (9 points)

Our chem. 11 student was very careful to make sure he had on his ____goggles____ (piece of safety equipment worn on the eyes) before starting this experiment. He first added the starting material to the beaker, added water, and he noticed that the solution was _____purple-blue_ (color). Before adding peroxide and acid, he moved the beaker from his benchtop to the _____hood_____ (place in the lab) because he wanted to make sure that fumes from the ____HCl_____ (chemical name) would not be inhaled by anyone and cause harm.   After adding all the chemicals and stirring the solution for a long time, the solution turned to a green__ color, and he was happy he was almost finished. After the solution cooled a bit, he filtered the crystals on a _____buchner___ funnel, and did a rinse first with _____weak HCl__and then with _____ethanol_____ to dry the crystals. Just to make sure he had the right compound, he placed 100 mg of dry crystal into a volumetric flask, added water to exactly 25 mL, and then took a spectrum. This is what he saw:
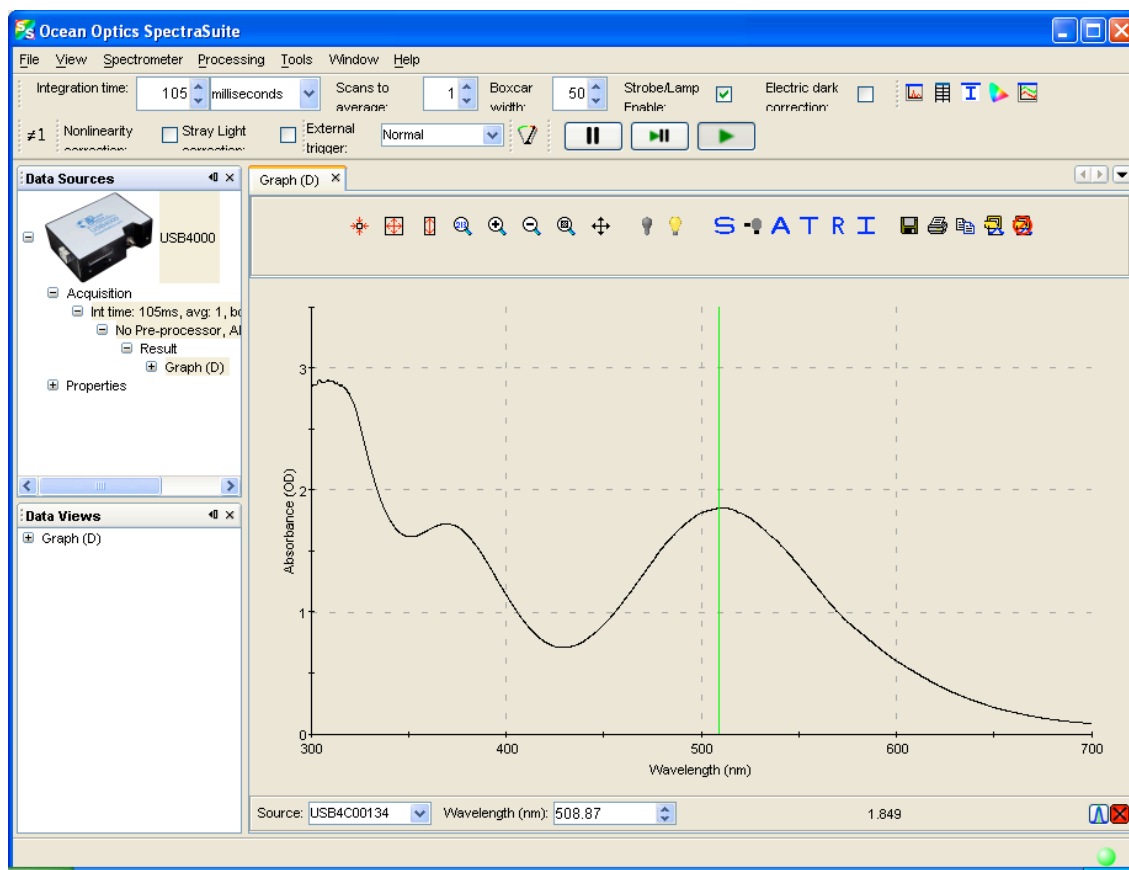
From this spectrum, he was able to calculate that: _Wavelength of the d to d transition is 508.87 nm, so the energy of the d to d splitting is $\Delta = \dfrac{hc}{\lambda} = \dfrac{6.626\times10^{-34}\,Js \times 3.00\times10^{8}\,m/s}{508.87\times10^{-9}\,m}$ = 3.9 x 10^{-19} J
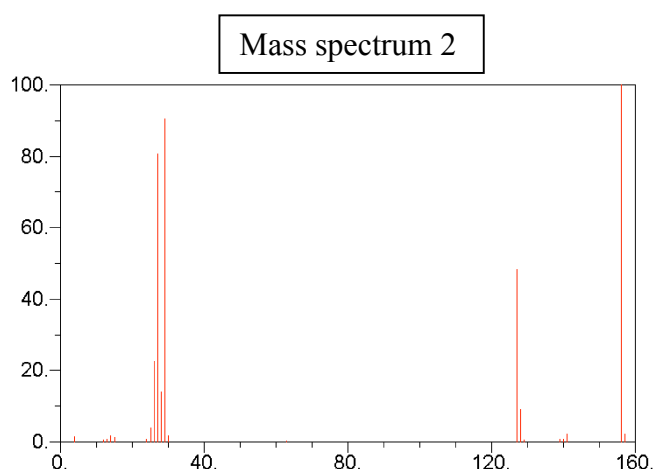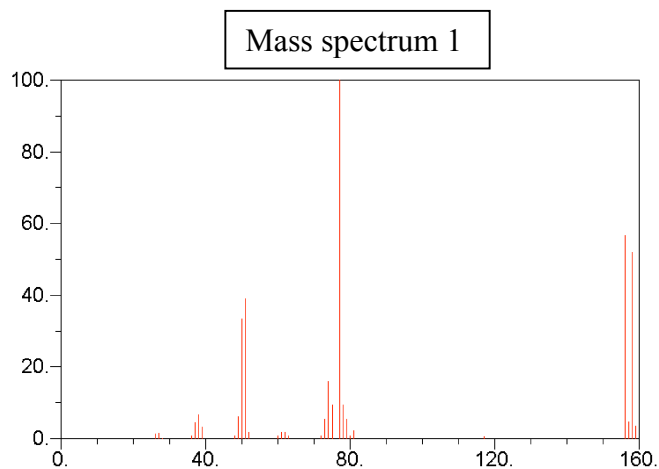
V. Mass Spectroscopy (09 pts)

1.   The mass spectra for three compounds: iodoethane (C_2H_5I), bromobenzene (C_6H_5Br), and dichlorobenzene ($C_6H_4Cl_2$) are shown below. On the NEXT page, assign each mass spectrum to the correct compound, and explain what information you used to make this determination. (12 points)
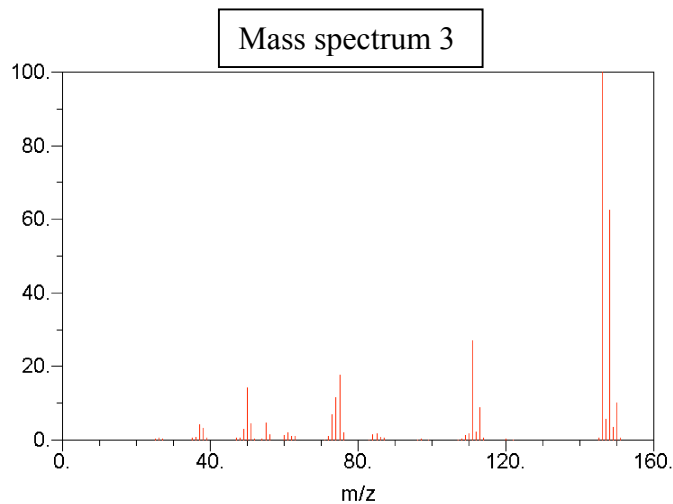
Things to know: The peak observed at the highest molar mass is the parent mass in all cases and only z=+1 ions are created. The natural abundances and masses of Br, Cl, and I are:

		Natural Abundance (%)	Mass (a.m.u.)
Br isotopes:	^{79}Br	50.69	78.92
	^{81}Br	49.31	80.92
Cl isotopes:	^{35}Cl	75.77	34.97
	^{37}Cl	24.23	36.97
I isotopes:	^{127}I	100.00	126.90

Mass spectrum 1

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Mass spectrum 2

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Mass spectrum 3

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Mass spectrum 1: bromobenzene (C_6H_5Br), Why? Because there is a doublet in the parent peak representative of the two isotopes of Br at approximately 50% abundance each

Mass spectrum 2: iodoethane (C_2H_5I), Why? Because there is NO isotopic signature from the halide, consistent with iodines 100% abundance for ^{127}I

Mass spectrum 3: dichlorobenzene ($C_6H_4Cl_2$) Why? Because there is a 9:6:1 ration consistent with having two chlorine atoms each of which has a 3/1 ratio of light to heavy isotopes of $^{35}Cl/^{37}Cl$

VI.   **Gas Laws: (25 points, 5 points each)**

The sun is composed almost exclusively of hydrogen (H_2) and helium gases, which, at the very center of the sun exist in a "plasma" state at temperatures of approximately 10^7 Kelvin and a pressure of 2.501 x 10^{11} atm. The central core of the sun is 36.00 % hydrogen (H_2) and 64.00 % helium (He) by mass.   Some scientists believe, that this plasma can be described using the ideal gas law. The following questions allow us to test that assumption.

1. Determine the **mole fractions** and **partial pressures** of hydrogen (H_2) and helium in the solar plasma.

2.   What is the apparent molar mass of the solar plasma.

3. The density of the plasma has been determined to be 158.2 g/cm^3. Given a solar pressure of 2.501 x 10^{11} atm calculate the central solar temperature assuming ideal gas behavior. ($1 \ cm^3 = 1 \ mL$)

4. The density quoted above, 158.2 g/cm^3, seems quite large (more that 10x density of mercury!) and you might be justifiably skeptical that we should use anything like a "gas" law to describe it.

    a. Assume that the plasma contains only helium (this simplifies the calculation). If this is the case, how many particles are there in 158.2 g?

    b. If the helium atoms were behaving normally, each atom could be roughly approximated by a cube 1.000 Å x 1.000 Å x 1.000 Å, where 1 Å = 10^{-8} cm. With these dimensions, and the number of particles calculated above, determine the volume occupied by the helium atoms.

    c. Compare this density (mass/volume) with that of pure helium behaving ideally at STP.

    d. Do you think use of the ideal gas law is appropriate under these circumstances?

5. The a and b coefficients for H_2 and He are shown (He a factor 0.0341, b factor 0.0237; H_2 a factor 0.244, b factor 0.0266).

    a. Explain what each of these corrections is and how it is used in the real gas equation to correct the ideal gas law.

    b. Comment also on whether the relative sizes of these numbers makes sense to you.

    c. What are the units for each of these constants?

VI. Classical and Quantum Mechanics(20 points)

1.   When a sample of metallic lithium (work function 279.7 kJ/mol) is irradiated by blue light
       (423.0 nm), an electron is ejected.

a.)   Determine the velocity of the electron ejected from the metal.

b.)   Find the de Broglie wavelength of this electron.

2. Use the Bohr equation to determine the energy of the 1s orbital in Lithium^{+2}. Which ionization
       energy of Lithium would this be equivalent to?

Li 3rd ionization energy is 11810 kJ/mole

3. Ionization energy measures the energy required to remove an electron from a gaseous sample of a substance. Lithium's first is 520.0 kJ/mole. Use this information to determine the energy of the valence orbital in Lithium.

4. Lithium's second ionization energy is 7297 kJ/mole and measures the amount of energy required to remove an electron from a 1s orbital in Li^{+1}. Why is this energy NOT equal to the energy determined in 2 above.

5. What wavelength of light is necessary to excite an electron from the 1s orbital to the 2s orbital of Lithium?

Assorted Equations, Constants, and Conversion Factors

[M] = moles/liter

pH = -log[H^+]

pH + pOH = 14

$M_1V_1 = M_2V_2$ = # moles

PV = nRT

$P_a = \chi_a P_{total}$

$\chi_a = n_a/n_{tota}$

$[P_{obs} + a(n/V)^2](V-nb) = nRT$

$N_A = 6.022137 \times 10^{23}$

$a_0 = 0.52917725 \times 10^{-10}$ m

$\pi = 3.14159$

$c = 2.9979 \times 10^8$ m/s

$h = 6.626 \times 10^{-34}$ J·s

$m_e = 9.10939 \times 10^{-31}$ kg

$m_p = 1.673 \times 10^{-27}$ kg

$m_n = 1.675 \times 10^{-27}$ kg

Fundamental charge: $e = 1.60218 \times 10^{-19}$ C

1 J = 1 N m = 1 kg m^2 s^{-2}

1 kJ = 10^3 J

E = hν

c = $\lambda\nu$

λ = h/mv

K.E. = $\frac{1}{2}m_e v^2$ = hν – hν_o

E_n = -2.178 x 10^{-18} J (Z^2/n^2)

R = 0.08216 l·atm/(mole·K)

R = 8.3145 J·mol^{-1} K^{-1}

STP≡ 1.000 atm, 273.15 K

1 atm = 760 mmHg = 760 torr

1 nm = 10^{-9} m

1 kg = 10^3 g

$\Delta E = E_f - E_i$ = -2.178 x 10^{-18} J Z^2 ($1/n_f^2$ - $1/n_i^2$)

Heisenberg Uncertainty: $\Delta E(\Delta t) \geq h/4\pi$ $\Delta x(m\Delta v) \geq h/4\pi$

Formal Charge = Group Number – [1/2 $N_{bonding\ electrons}$ + $N_{nonbonding\ electrons}$]

Bond Order = ½ [Bonding Electrons – Antibonding Electrons]

Avogadro's number: $N_A = 6.022 \times 10^{23}$ mol^{-1}

Speed of light: c = 2.9979×10^8 m s^{-1}

Planck's constant: h = 6.626×10^{-34} J s

Neutron mass: m_n = 1.675×10^{-27} kg

Electron mass: m_e = 9.109×10^{-31} kg

WebElements: the periodic table on the world-wide web

http://www.webelements.com/

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																	helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.012											boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305											aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078	scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62	yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [272]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [292]		

Group 3 (continued): lutetium 71 **Lu** 174.97, lawrencium 103 **Lr** [262]

*lanthanoids

lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04

**actinoids

actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]