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

Chemistry 11, Fall 2006
Cumulative 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 seventeen pages (including this one). A periodic table and a list of formulas and electronegativities 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, someone will be checking in once every 30 minutes or so. You have three hours to complete this exam. While you are waiting to start, you may answer the extra credit question below:

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.

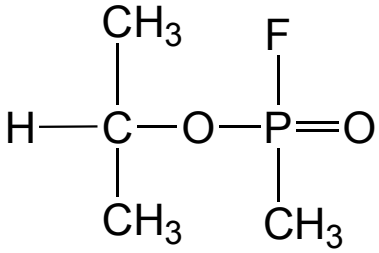
Xtra credit: What is your favorite element and why (write in the space below)?

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

I. Hybridization: (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** (10 points)



1. Draw in all lone pairs on the structure of **SARIN**. Add formal charge if necessary, though the net molecule is neutral.

2. What is the steric number _____ of the O atom between the P and C atoms and resultant geometry _____ and P-O-C bond angles _____? (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? _____

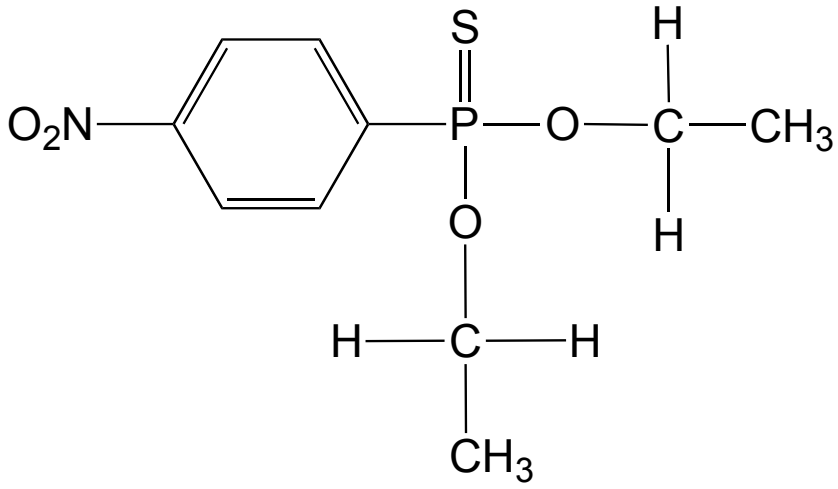
   b. The P atom is tetrahedral, but it has a double bond. Normally, the atoms we have considered use a left over p orbital to make a double bond. Why is using a leftover p orbital a problem for this phosphorous atom?
   _____

   c. Report the n and l quantum numbers of the extra valence atomic orbital that needs to be recruited to make the five bonds on the phosphorous atom _____, _____

   d. Identify the longest _____ and shortest _____ bonds in the molecule.

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

a. First, note that the N atom has single bonds to C and one of the O atoms, and one double bond to the other O atom. Draw in all implicit hydrogen atoms and lone pair electrons, and add formal charge as necessary. Note that the molecule is net neutral.



b. Indicate the shortest _____ and longest _____ bonds in the molecule. (in your answer to this question, consider P-S bond to be a single bond)

c. Focusing on the P as a central atom. The geometry here is once again tetrahedral, predict the bond dipoles.

d. Is any part of this molecule planar or aromatic? Y or N (circle one). Why?

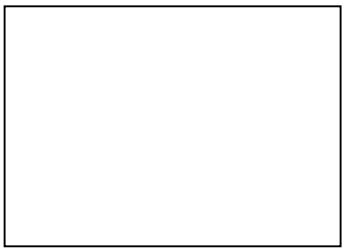
e. Is it possible to draw reasonable resonance structures for this compound? If yes, draw one such structure below.

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.

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)



   a. What is the predicted NO bond order (i.e. single, double, triple)? _____

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

   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)

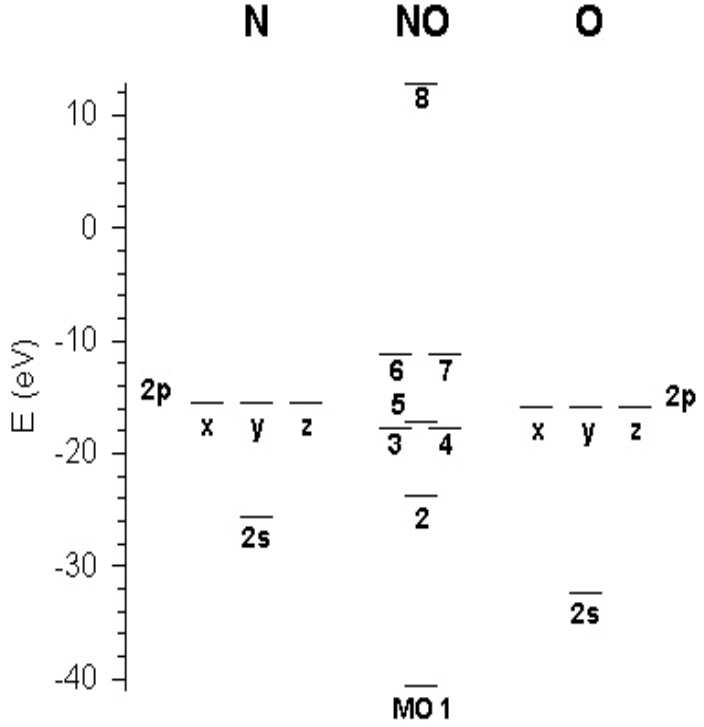
   a. What is the predicted NO bond order?_____

   b. On which atom is the unpaired electron localized? _____

   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)?

3. 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 this 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 _____, _____, _____, _____

b. Identify the four antibonding MOs _____, _____, _____, _____

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

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

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

f. Put the valence electrons into these orbitals, following the regular rules.

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?

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

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

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

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

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?

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

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.

IV. Lab Based Question (25 points)

A student in Chemistry 11 synthesized *trans*-$[Co(en)_2Cl_2]Cl$ in Lab Experiment VII by dissolving 7.234 g of cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) 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_2O_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.

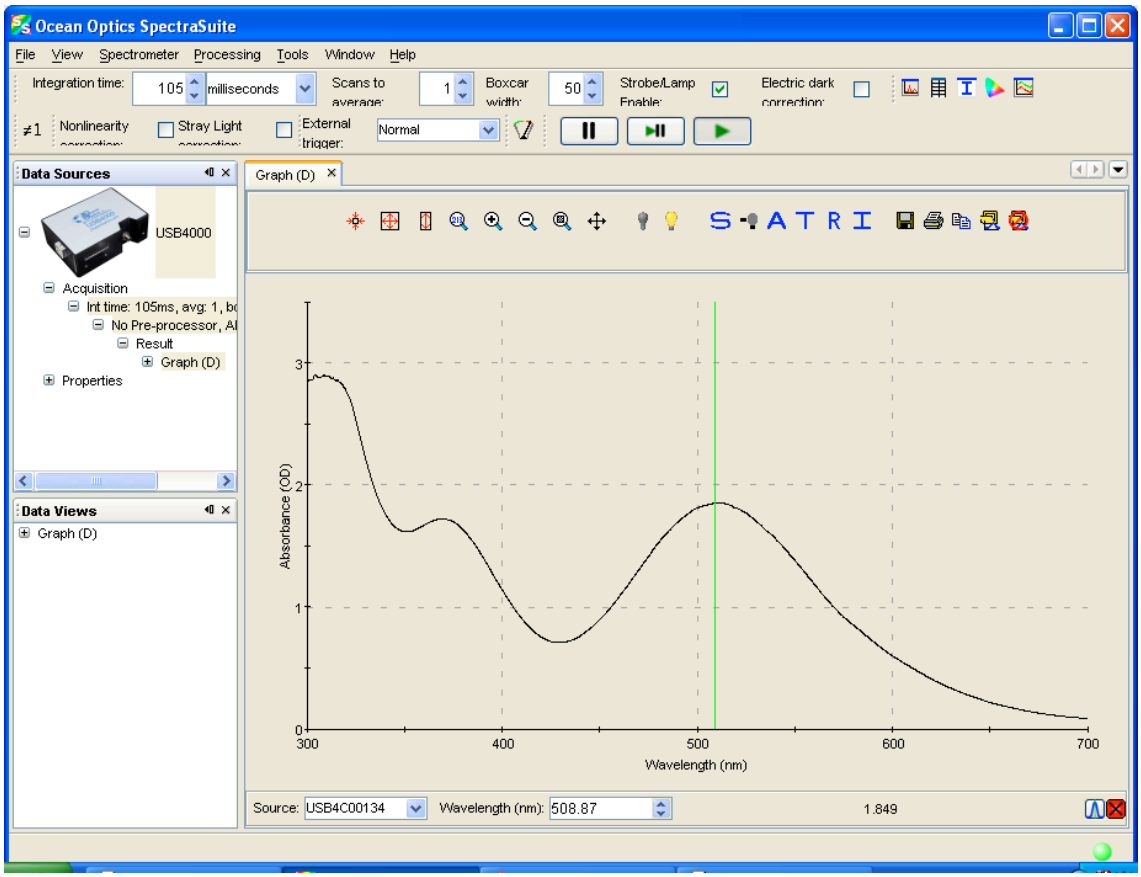
1. Write down the two balanced half reactions for this synthesis, indicating what is oxidized and what is reduced. Since the reaction takes place in an acidic solution, you may add protons and water as necessary. If a neutral molecule is involved, your redox equation should contain the entire molecule. If an ion is oxidized or reduced, consider ONLY the individual ion. (4 pts)

2. Write down the complete chemical reaction for this synthesis and make sure it is mass and charge balanced. (4 pts)

3. Identify the limiting reagent and calculate the percent yield of *trans*-$[Co(en)_2Cl_2]Cl$ (molar mass 285.549 g/mole) based on the amounts of starting materials used: 7.234 g $CoCl_2 \cdot 6H_2O$ (molar mass 237.945 g/mole), 29.95 mL of 10.0 wt% aqueous ethylenediamine solution (density 0.990 g/mL, molar mass 60.098 g/mole), 10.0 mL of 7.5 wt % hydrogen peroxide (density 1.03 g/mL; molar mass 34.016 g/mole), and 24.00 mL of 36.5 wt % solution of hydrogen chloride (density 1.18 g/mL, molar mass 36. 461 g/mole). 6.144 g of product material was collected. Don't forget those significant figures! (8 pts)

4. Lab protocol: (9 points total)

Our chem. 11 student was very careful to make sure he had on his _____ (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 _____ (color). Before adding peroxide and acid, he moved the beaker from his benchtop to the _____ (place in the lab) because he wanted to make sure that fumes from the _____ (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 _____ color, and he was happy he was almost finished. After the solution cooled a bit, he filtered the crystals on a _____ funnel, and did a rinse first with _____ and then with _____ 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:

_____

_____

_____

_____

_____

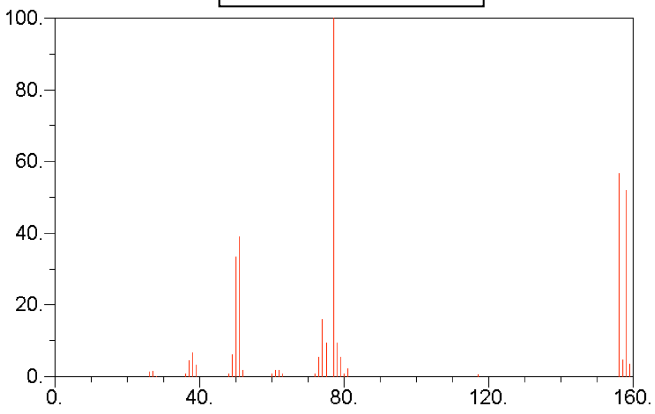
V. Mass Spectroscopy (9 pts, 3 pts each)

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:

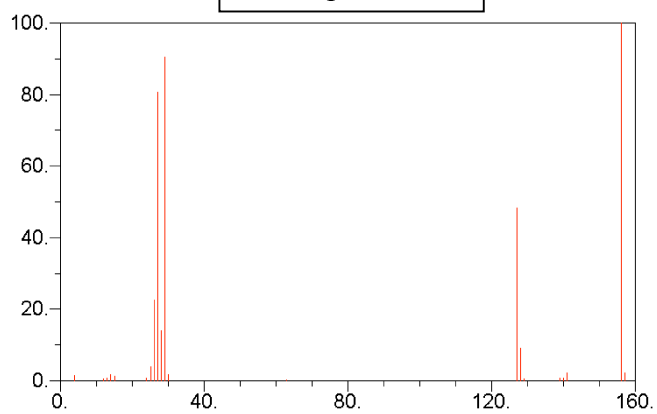
		Natural Abundance (%)	Mass (a.m.u.)
Br isotopes:	^{79}Br	50.69	78.92
	^{81}Br	49.31	80.92
Cl isotopes:	^{35}Cl	75.77	34.97
	^{37}Cl	24.23	36.97
I isotopes:	^{127}I	100.00	126.90

Mass spectrum 1



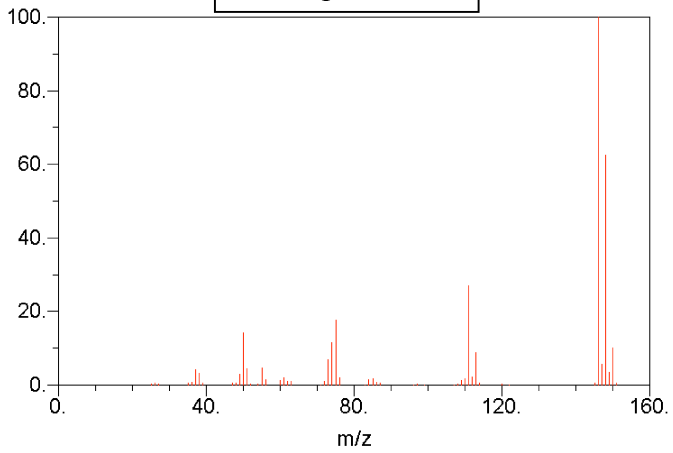
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

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: _____How do you know this based in the parent peak alone?

Mass spectrum 2: _____How do you know this based in the parent peak alone?

Mass spectrum 3: _____How do you know this based in the parent peak alone?

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 2.501×10^{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. Use the relationship between the mole fraction and the individual molar masses to determine the apparent molar mass of the mixture of hydrogen (H_2) and helium in the solar plasma.

3. The density of the plasma has been determined to be 158.2 g/cm^3. Given a solar pressure of 2.501×10^{11} atm calculate the central solar temperature assuming ideal gas behavior. Remember, it is a good approximation that 1 cm^3 = 1ml.

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. This question tries to determine how close the atoms are in this plasma

a. Simplify the plasma to contain only helium, how many particles are there in 158.2 g?

b. If the helium atoms were behaving normally, they 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. If the He atoms were touching each other, and there were no spaces between the atoms, the volume in b. above would be the volume of the system. Calculate this density under these circumstances.

d. Determine the density of pure helium behaving ideally at STP.

e. Compare these densities to determine if you think use of the ideal gas law is appropriate under these circumstances?

5. The a and b coefficients are H_2: 0.244, 0.0266; He: 0.0341, 0.0237 respectively.

   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. A comparison of the relative sizes of these coefficients gives you information about the similarities and differences between these two compounds. Explain.

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

VII Classical and Quantum Mechanics(20 points 4 pts each)

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 $Lithium^{+2}$.

3. Ionization energy measures the energy required to remove an electron from a gaseous sample of a substance. Lithium's first ionization energy 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}. The third ionization energy can be determined from the data in question 2 on the previous page and also measure the energy to remove an electron from the 1s orbital. What are the factors that go into making those two numbers so very different.

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
$P_a = \chi_a P_{total}$
$\chi_a = n_a/n_{total}$
$[P_{obs} + a(n/V)^2](V\text{-}nb) = nRT$

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

$E = h\nu$

$c = \lambda\nu$

deBroglie: $\lambda = h/mv$
K.E. = $\frac{1}{2}(m_e v^2) = h\nu - h\nu_o$
Bohr: $E_n = -2.178 \times 10^{-18}$ J (Z^2/n^2)

$\Delta E = E_f - E_i = -2.178 \times 10^{-18}$ 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]

$N_A = 6.022137 \times 10^{23}$
$a_0 = 0.52917725 \times 10^{-10}$ 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

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$c = 2.9979 \times 10^8$ m s^{-1}
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

1 cm^3 = 0.001 L

H 2.20						
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Ga 1.81		As 2.18		Br 2.96
Rb 0.82	Sr 0.95	In 1.78		Sb 2.05		I 2.66
Cs 0.79	Ba 0.89					

Table I. Electronegativies of selected elements

WebElements: the periodic table on the world-wide web

http://www.webelements.com/

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 9.0122												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 *	lutetium 71 Lu 174.97	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 **	lawrencium 103 Lr [262]	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]		

*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]

Key: element name, **atomic number**, **symbol**, atomic weight (mean relative mass)

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements 111–112 and 114 so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the common spelling is **sulphur.**
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2001 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope.