Exercise 1 - Review of General Chemistry

Answers with an * are also in ***Appendix A*** of the student manual.

A. Scientific Notation, Significant Figures, Accuracy and Precision, Unit Conversions

1. Express the following numbers in scientific notation: *a.** $8.20x10^{-2}$ *b.* $5.28x10^{3}$ *c.* $4.0x10^{-3}$

2. Is there a difference between accuracy and precision and if so, what is the difference? Accuracy is a measure of how close a measurement is to the actual value. *Precision represents the agreement between different measurements of the value (precision can often be determined from the number of significant figures in a measurement). A measurement can be accurate and lack precision and vice versa but usually the two correlate with each other.*

3. Determine the answers to the following calculations without using a calculator:

*a.** $(6.00x10^{23})(2.5x10^{-4}) = 1.5x10^{20}$

b. $(1.5x10^{-8})(8.0x10^{-2}) = 1.2x10^{-9}$

*c.** $7.2x10^{-4}/8.0x10^{-2} = 9.0x10^{-3}$

d. $5.6x10^{-3}/7.0x10^{1} = 8.0x10^{-5}$

*e. ** $3.2 + 14.19 = 17.4 = 1.74x10^{1}$

f. $325.3 + 4.721 = 330.0 = 3.300x10^{2}$

*g.** $7.7x10^{-1}/1.1x10^{3} = 7.0x10^{-4}$

h. $2.5x10^{5}/5.0x10^{2} = 5.0x10^{2}$

*i.** $3.41x10^{4} + 6.27x10^{3} = 4.04x10^{4}$

j. $1.23x10^{1} + 2.34x10^{2} = 2.46x10^{2}$

k. $\frac{(5.4x10^{2})(8.0x10^{-3})}{(4.0x10^{1})(9.0x10^{-5})} = 1.2x10^{3}$

4.* $9.56x10^{-1}$ *g/mL*

5. $7.13x10^{1}$ *g/mL*

6.* $3.5x10^{4}$ *g*

7. *119 mL*

8.* $9.10x10^{-28}$ *g*

9. $1.77x10^{-24}$ *g*

10. $1.84x10^{3}$

11. *With very few exceptions, as substances cool, their densities increase and increase again when freezing occurs. If water behaved typically, lakes would freeze at the surface because that is where it is coldest but the ice would sink and the process would continue until the lake becomes solid. This would severely limit the type of life that could survive in the lake in cold winters.*

12. $8.03x10^{-1}$ *kg/L*

13. *Hydrocarbons float on water and have densities less than the density of water. Since 1.77 kg/L is significantly higher that the density of water, the value does not make sense.*

14. $4.92x10^{3}$ *L*, $2.01x10^{4}$ *L*

15. $1.52x10^{4\ L}$

16. a. *The "nitrogen" in the two cases had slightly but significantly different masses.*

    b. *Rayleigh asks for help from other scientists and mentions that he works with Professor Ramsay and takes his advice. Scientists would make very little progress working alone.*

c. Give the average of the two sets of numbers to 2, 3, 4 and 5 significant figures:

nitrogen source	2 sig. fig.	3 sig. fig.	4 sig. fig.	5 sig. fig.
atmospheric nitrogen (g)	*2.3*	*2.31*	*2.310*	*2.3102*
chemical nitrogen (g)	*2.3*	*2.30*	*2.299*	*2.2990*

d. *Even to three significant figures, the numbers are within experimental error of each other. Thus to three significant figures the numbers would probably be assumed to the same and the discovery of argon would have had to await another day.*

e. *After considerable research and thought, Rayleigh concluded that in addition to nitrogen and oxygen, there must be a significant amount of another gas in the atmosphere.*

B. Atomic Structure: Protons, Neutrons, Electrons, Isotopes and the Periodic Table

Answer the following using only a periodic table as a source of information. Give as much information as possible using only the atomic number and atomic mass.

1. How many protons, neutrons and electrons are in a.* F *F has 9 protons, an average of 10 neutrons and probably is predominately 1 isotope with 10 neutrons and 9 electrons (only one isotope of fluorine occurs naturally)*

   b. Al *Al has 13 protons, an average of 14 neutrons and probably is predominately 1 isotope with 14 neutrons and 13 electrons (only one isotope of aluminum occurs naturally)*

   c. Mn *Mn has 25 protons, an average of 30 neutrons and probably is predominately 1 isotope with 30 neutrons and 25 electrons (only one isotope of manganese occurs naturally)*

   d. Au *Au has 79 protons, an average of 118 neutrons and probably is predominately 1 isotope with 10 neutrons and 79 electrons (only one isotope of gold occurs naturally)*

2. How many protons, neutrons and electrons are in a.* Cl *Cl has 17 protons, an average of 18.45 neutrons and at least 2 isotopes must occur naturally and 17 electrons. (actually, Cl has 2 naturally occurring isotopes, about 75% have 18 neutrons and 25% have 20 neutrons but this information cannot be determine from the atomic mass alone).*

   b. Cu *Cu has 29 protons, an average of 34.55 neutrons and at least 2 isotopes must occur naturally and 29 electrons. (actually, Cu has 2 naturally occurring isotopes, about 69% have 34 neutrons and 31% have 36 neutrons but this information cannot be determine from the atomic mass alone).*

3. How many protons, neutrons and electrons are in a.* H *H has 1 proton, an average of 0 neutrons (and probably is predominately 1 isotope with 0 neutrons) and 1 electron (actually there are 2 naturally occurring stable isotopes of H, 99.98% have 0 neutrons and 0.02% have 1 neutron but this information cannot be determined from the atomic mass alone).*

   b. C *C has 6 protons, an average of 6 neutrons (and probably is predominately 1 isotope with 6 neutrons) and 6 electrons (actually there are 2 naturally occurring stable isotopes of C, 98.9% have 6 neutrons and 1.1% have 7 neutrons but this information cannot be determined from the atomic mass alone).*

   c. N *N has 7 protons, an average of 7 neutrons (and probably is predominately 1 isotope with 7 neutrons) and 7 electrons (actually there are 2 naturally occurring stable isotopes of N, 99.6% have 7 neutrons and 0.4% have 7 neutrons but this information cannot be determined from the atomic mass alone).*

   d. O *O has 8 protons, an average of 16 neutrons (and probably is predominately 1 isotope with 8 neutrons) and 8 electrons (actually there are 3 naturally occurring stable isotopes of O, 99.76% have 8 neutrons, 0.038% have 9 neutrons and 0.20% have 10 neutrons but this information cannot be determined from the atomic mass alone).*

e. Br *Br has 35 protons, an average of 45 neutrons (and probably is predominately 1 isotope with 45 neutrons) and 35 electrons (actually there are 2 naturally occurring stable isotopes of Br and by coincidence, the average comes out close to a whole number, 50.7% have 44 neutrons, 49.3% have 46 neutrons but this information cannot be determined from the atomic mass alone).*

4. How many protons, neutrons and electrons are in a.* Cu^{2+} *Cu^{2+} has 29 protons, an average of 34.55 neutrons and at least 2 isotopes must occur naturally and 27 electrons.*

b. Cl^- *Cl^- has 17 protons, an average of 18.45 neutrons and at least 2 isotopes must occur naturally and 18 electrons.*

5. *For most elements, isotopes differ in mass by small percentage amounts but for hydrogen, deuterium is double the atomic mass of light hydrogen.*

6. a.* *${}^{3}_{1}H$ or tritium deviates by 2 neutrons from the average number calculated from the atomic mass and number (0). Early in the chart a deviation of 2 indicates that the nucleus is probably (and is) unstable.*

b. *${}^{4}_{2}He$ has 2 neutrons in agreement with the average calculated from the atomic mass and is expected to be stable.*

c. *${}^{13}_{6}C$ has 7 neutrons which deviates by 1 from the average calculated from the atomic mass. While this isotope is stable, this information cannot be deduced from the periodic table alone.*

d. *${}^{14}_{6}C$ has 8 neutrons which deviates by 2 from the average calculated from the atomic mass. This early in the chart, this deviation leads to a suspicion but not strong evidence that the isotope would be radioactive (as it is).*

7. Confirming your prediction from 6-d above, ${}^{14}_{6}C$ does undergo β particle emission with a half life of 5730 years.
   a. $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e^-$
   b. *A neutron splits into a proton and an electron.*
   c. *$1.73x10^4$ years*

8.

	element	mass (g/mol)	abundance (%)	Answer
a.*	Li	6.015	7.42	*6.94*
		7.016	92.58	
b.	Mg	23.985	78.70	*24.31*
		24.986	10.13	
		25.982	11.17	

9. *We read left to right and the predominant form (horizontal) of the periodic table is arranged according to increasing atomic number from left to right. Since we read this way, this arrangement puts our focus on periods. The vertical arrangement is more in line with the original table developed by Mendeleev and left to right puts our focus on groups (families). Both presentations in the shortened form fit conveniently on 8.5 by 11 inch paper but the horizontal table must be rotated 90^o whereas the vertical form does not need rotating.*

10.

isotope percentages *a. ${}^{37}_{17}Cl$ [32.7/(32.7 +100)]100% = 24.6% b. ${}^{79}_{31}Br$ [100/(100 + 98)]100% = 50.5%*
c. ${}^{13}_{6}C$ [1.09/(1.09 +100)]100% = 1.08%

d. Find and compare the literature values for the above isomers using sites such as:
http://www.webelements.com/
http://www.sisweb.com/mstools.htm *${}^{37}_{17}Cl$ 24.23% ${}^{79}_{31}Br$ 50.69% ${}^{13}_{6}C$ 1.10%*
http://ie.lbl.gov/education/isotopes.htm

e. *12.01*

C. Inorganic Nomenclature, Formulas and Balancing Equations

1. Give the names of: a. NO_2 nitrogen dioxide b. $Mg(NO_3)_2$ *magnesium nitrate* c. $KHCO_3$ *potassium hydrogen carbonate (potassium bicarbonate)* d. CuSO4 • $5H_2O$ *copper(II) sulfate pentahydrate* e. $AgC_2H_3O_2$ *silver acetate*

2. Give the formulas of: a. calcium chloride $CaCl_2$ b. nitric acid HNO_3 c. iron(III) sulfate $Fe_2(SO_4)_3$ d. sodium carbonate Na_2CO_3

3. Write balanced equations and net ionic equations for each of the following:
   a.* The single replacement reaction of magnesium with sulfuric acid
   $Mg(s) + H_2SO_4(aq) = MgSO_4(aq) + H_2(g)$
   $Mg + 2 H^+ = Mg^{2+} + H_2$
   b. The double replacement reaction of calcium nitrate with potassium phosphate
   $3 Ca(NO_3)_2(aq) + 2 K_3PO_4(aq) = 6 KNO_3(aq) + 2 Ca_3(PO_4)_2(s)$
   $3Ca^{2+} + 2 PO_4^{3-} = Ca_3(PO_4)_2(s)$

4. Write balanced equations for each of the following:
   a. The decomposition of hydrogen peroxide to water and oxygen
   $2 H_2O_2(l) \rightarrow 2 H_2O(l) + O_2(g)$
   b. The combustion of ethanol (C_2H_6O)
   $C_2H_6O(l) + 3 O_2(g) \rightarrow 2CO_2(g) + 3 H_2O(g)$

D. Electronic Structure, Bonding and Intermolecular Attractions (For Lewis structures and polarities of molecules, see ***Exercise 2***)

1. Give the electronic structures of : a.* Li $1s^22s^1$ b. C $1s^22s^22p^2$ c. Mn $1s^22s^22p^63s^23p^64s^23d^5$
   d. Sr $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$ e. Ca^{2+} $1s^22s^22p^63s^23p^6$ f. Cl^- $1s^22s^22p^63s^23p^6$

2. Give possible values for the quantum numbers n, l, m, s for: *a.* a 2s electron n = 2, l = 0, m = 0, s can be* $\frac{1}{2}$, $-\frac{1}{2}$ *b. a 3d electron n = 3, l = 2, m can be -2, -1 0, 1, 2, s can be* $\frac{1}{2}$, $-\frac{1}{2}$

3.* *4d*

4. *5p*

5. *a.* Ca 0 b. Ni 2 c. P 3 d.* Al^{3+} *0*

6. Which of the following elements is paramagnetic: Zn, Fe, Hg, Ar, Sr *Fe*

7. *The elements scandium through zinc follow calcium which has 4s electrons.*

8. *In the former configuration both outer elecrons are in the same orbital whereas the electrons are in orthogonal p orbitals in the second configuration. Since electrons have the same charge and repel each other, the lower energy level will have the electrons in orbitals that minimize their interaction.*

9. a. On the basis of melting points, classify each of the compounds as having ionic or covalent bonds.

Compound	M.P. (°C)	bond	Compound	M.P. (°C)	bond
LiH	680	*ionic*	$CaCl_2$	772	*ionic*
CH_4	-182	*covalent*	$SiCl_4$	-70	*covalent*
H_2O	0.00	*covalent*	$CuBr_2$	492	*ionic*
LiF	842	*ionic*	C_8H_{18} (octane)	-57	*covalent*
CF_4	-150	*covalent*	AgCl	455	*ionic*
NaCl	801	*ionic*	C_6H_6O (phenol)	43	*covalent*
CCl_4	-23	*covalent*	ZnO	1975	*ionic*

b. *High melting points are characteristic of lattice bonding such as the bonding in ionic crystals. Diamond is also a lattice and hence its high melting point. Covalent compounds are attracted to each other by much weaker forces such as hydrogen bonding and London forces and melting points are generally much lower than for compounds with lattice bonding.*

c. Name, if possible, an ionic compound that is not solid at room temperature. *There are many but most have organic cations. http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix*

10. a. *The boiling points increase due to increasing London forces. London forces depend on many variables including shape but generally increase as the number of electrons increase.*

b. *The name of this attractive force is hydrogen bonding and is considered to be of significance only when hydrogen is bonded to fluorine, oxygen or nitrogen. If it is bonded to one of the three, it can hydrogen bond only to one of the same three elements.*

c. *The boiling point of HCl is lower than the boiling points of H_2S and HBr indicating that hydrogen bonding is not important for HCl.*

d. *The strength of hydrogen bonding should increase going across the 2nd period. However, the boiling points indicate that water has stronger forces than HF. This is usually explained by saying that due to the two hydrogens on water, water has more hydrogen bonding than HF. This raises a question about NH_3 but geometry needs to be considered also. Why the other hydrogen halides do not fit the trends for the period is probably related to the number of hydrogens but the explanation is not clear to this author.*

11. While you probably covered hybridization in your general chemistry course, it will be assumed that you will basically start from scratch on this topic in your organic chemistry class. Even so, a few problems are included below. If you have any difficulty drawing the structures of these compounds, do ***Exercise 2*** and then return to this problem.

What is the hybridization of carbon in:

a. CH_3-CH_3 ethane *sp^3*

b. CH_2=CH_2 ethylene or ethene *sp^2*

c. HC≡CH acetylene or ethyne *sp*

d. CH_2O formaldehyde or methanal *sp^2*

e. CO_2 carbon dioxide *sp*

f. HCN hydrogen cyanide *sp*

g. CH_3Cl methyl chloride *sp^3*

h. HCOOH formic acid or methanoic acid *sp^2*

i. What is the hybridization of oxygen in water? sp^3 (however, water can also be explained by assuming the oxygen is not hybridized and the H-O-H bond angle is greater than 90^o because of repulsion between the hydrogens.

j. What is the hybridization of nitrogen in ammonia? sp^3

E. Chemical Calculations: the Mole, Molarity, Formulas and Stoichiometry

1.* *(230 g)(1mole/18.0g) = 13 moles (13 moles)(6.022x10^{23}molecules/1mole) = 7.7x10^{24} molecules*

2.**(1 atom)(1 mole/6.022x10^{23} atoms)(39.95 g/1 mol) = 6.634x10^{-23} g*

3.* *0.331g/3.45x10^{-3} moles = 95.9 g/mole. The element is probably Mo*

4.* *(1x10^{-6} g)(1mole/55.8g)(6.022x10^{23} atoms/1 mol) = 1x10^{16} atoms*

5.* a. *Assume 100.0 g of compound.*

$87.41\ g\ N \times \frac{1\ mol\ N}{14.007\ g\ N} = 6.240\ mol\ N \qquad 6.240/6.240 = 1$

$12.58\ g\ H \times \frac{1\ mol\ H}{1.0079\ g\ H} = 12.48\ mol\ H \quad 12.48/6.240 = 2 \qquad NH_2$

$32/16 \times NH_2 \rightarrow N_2H_4$

b. *A Lewis structure can be drawn for N_2H_4 that satisfies all the guidelines for Lewis structures.*

6.* $2\ Na(s) + 2\ H_2O(\ell) = 2\ NaOH(aq) + H_2(g)$

$(2.3\ g\ Na)(1\ mol\ Na/23.0\ g\ Na)(1\ mol\ H_2/2\ moles\ Na)(2.02\ g\ H_2/1\ mol\ H_2) = 0.10\ g\ H_2$ *(theoretical yield)*

$(0.080\ g/0.10\ g)100\% = 8.0\times10^{1}\%$

7.* $2\ H_2(g) + O_2(g) = 2\ H_2O(g)$

$(5.0\ g\ H_2)(1\ mol\ H_2/2.02\ g\ H_2)(2\ moles\ H_2O/2\ moles\ H_2)(18.0\ g\ H_2O/1\ mol\ H_2O) = 45\ g\ H_2O$

$(8.00\times10^{1}\ g\ O_2)(1\ mol\ H_2/32.0\ g\ O_2)(2\ moles\ H_2O/1\ mole\ O_2)(18.0\ g\ H_2O/1\ mol\ H_2O) = 90\ g\ H_2O$

Theoretical yield = 45 g H_2O since hydrogen was limiting reagent.

$(25\ g/45\ g)100\% = 56\%$ *yield*

8. Explain how you would prepare 250 mL of a NaCl solution that is: a.* 0.10 M
(0.25 L)(0.10 mole/L)(58.5 g NaCl/mole NaCl) = 1.5 g NaCl
Dilute 1.5 g NaCl to 250 mL with water.

b. 1.000×10^{-1} M *The problem here is that most chemicals are not available in pure enough form to be used as primary standards. In other words, because they are only 99% or less in purity, weighing the compound only results in 2 significant figures. Sodium chloride can be obtained in very pure form but at a very high price. If the highly pure form is used, it must be weighed to 4 significant figures and diluted to a volume with 4 significant figures (e.g., 250.0 mL as in a volumetric flask). An alternative that is necessary for most chemicals since they are not available in pure enough form is to make the solution the approximate molarity as in 8a and then determine the concentration using an analytical method such as titration.*

9.* $M_1V_1 = M_2V_2 \qquad (0.050)(500)/(6.0) = 4.2\ mL$
Dilute 4.2 mL of 6.0 M HCl to 500 mL with water.

10. $6.0\times10^{27}\ g \times \frac{1\ mole}{55.847\ g} \times \frac{6.022\times10^{23}\ molecules}{1\ mole} = 6.5\times10^{49}$ *molecules Fe*

11. $1\ molecule \times \frac{1\ mole}{6.022\times10^{23}\ molecules} \times \frac{44.0\ g}{1\ mole} = 7.31\times10^{-23}\ g$

12. a. What is the expected range of answers? *about 30 to 500 g/mol*

b. What is the molecular mass of the acid? $1.50g/2.50\times10^{-2}\ moles = 60\ g/mol$

13.* *b.* $H_2 + I_2 = 2\ HI$

14. For the reaction above (#13), what was the limiting reagent? I_2

15. $N_2(g) + O_2(g) = 2\ NO(g)$ O_2

16. $COCl_2(g) = CO(g) + Cl_2(g)$

17. $C_3H_6(g) + HBr(g) = C_3H_7Br(l)$ $CH_3CH_2CH_2Br$

18. $N_2(g) + NO(g) = NO_2(g)$

19. $2\ CH_3OH(l) + 3\ O_2(g) = 2\ CO_2(g) + 4\ H_2O(g)$

20. $N_2H_4(g) + O_2(g) = N_2(g) + 2\ H_2O(g)$

21. CCl_3F

22. a. *A π bond in ethylene and the Cl-Cl bond break and 2 C-Cl bonds form.*

b. $H_2 + Cl_2 = 2\ HCl$ *H-H and Cl-Cl bonds break and 2 H-Cl bonds form.*

c. *99 grams, 76%*

23. *41 g* $6.0x10^1$%

24. a. 0.10 M *Dilute 1.0 g NaOH to 250 mL with water.*
b. $1.000x10^{-1}$ M *NaOH is hygroscopic and cannot be weighed accurately. Therefore it is necessary for this case to make a solution that is approximately 0.10 molar and then titrate a primary standard such as KHP to determine the concentration of the NaOH solution.*

25. *Dilute 4.2 mL of 6 M HCl to 500 mL with water.*

26. Ca^{2+} *0.10 M* Cl^- *0.20 M*

F. Equilibrium

Write the correct equilibrium expression for the following reactions:

1.* $2NO_2(g) = N_2O_4(g)$ $K_{eq} = [N_2O_4]/[NO_2]^2$

2. $N_2(g) + O_2(g) = 2\ NO(g)$ $K_{eq} = [NO]^2/[N_2][O_2]$

3. $HF(aq) = H^+ + F^-$ $K_a = [H^+][F^-]/[HF]$

4. $CN^- + H_2O(l) = HCN(aq) + OH^-$ $K_{eq} = [HCN][OH^+]/[CN^-][H_2O]$

5. $HC_2H_3O_2(aq) + C_2H_5OH(l) = C_4H_8O_2(l) + H_2O(l)$ $K_{eq} = [C_4H_8O_2][H_2O]/[HC_2H_3O_2][C_2H_5OH]$
acetic acid ethanol ethyl acetate

6. $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

7.* HCl is added to the system? *left*

8. NaF is added to the system? *left*

9. NaOH is added to the system? *right*

Assume the acetic acid, ethanol, ethyl acetate, water system (#5) is at equilibrium. In which direction will the system shift to reachieve equilibrium if:

10. acetic acid is added to the system? *right*

11. ethanol is added to the system? *right*

12. ethyl acetate is removed from the system? *left*

13. water is removed from the system? *right*

G. Acids, Bases and pH

For each reaction, label each reactant and product as: Brönsted acid, Brönsted base, conjugate acid, conjugate base.

1.*	$HNO_{3(aq)}$	+	$H_2O_{(l)}$	=	H_3O^+	+	NO_3^-
	BA		*BB*		*CA*		*CB*
2.	$NH_{3(aq)}$	+	$H_2O_{(l)}$	=	NH_4^+	+	OH^-
	BB		*BA*		*CA*		*CB*
3.	CO_3^{2-}	+	$H_2O_{(l)}$	=	HCO_3^-	+	OH^-
	BB		*BA*		*CA*		*CB*
4.	$H_2PO_4^-$	+	$H_2O_{(l)}$	=	H_3O^+	+	HPO_4^{2-}
	BA		*BB*		*CA*		*CB*

In organic chemistry, the Lewis definitions of acids and bases are also commonly used. A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. In the following reactions label the reactants as Lewis acids or bases.

5.	H^+	+	OH^+	=	H_2O
	LA		*LB*		H
					|
6.	CH_3CH_2-OH	+	Zn^{2+}	=	$[CH_3CH_2–O–Zn]^{2+}$
	LB		*LA*		
7.	CH_3Cl	+	$AlCl_3$	=	$CH_3–\underset{+}{Cl}–\underset{-}{Al}Cl_3$
	LB		LA		

8. Given that $K_w = [H^+][OH^-] = 1x10^{-14}$, derive the equation $pH + pOH = 14$
   $\log [H^+][OH^-] = \log[H^+] + \log[OH^-] = -14$, $-\log[H^+] - \log[OH^-] = 14$, $pH + pOH = 14$

9. Fill in the blanks in the following table:

	pH	$[H^+]_{(mol/L)}$	$[OH^-]_{(mol/L)}$	pOH
a.*	4.7	*$2x10^{-5}$*	*$5.0x10^{-10}$*	*9.3*
b.	*2.1*	$7.7x10^{-3}$	*$1.3x10^{-12}$*	*11.9*
c.	*6.4*	*$4.3x10^{-7}$*	$2.3x10^{-8}$	*7.6*
d.	*10.4*	*$4.0x10^{-11}$*	*$2.5x10^{-4}$*	3.6

10. a. *$[1.0x10^3$ g/L$]/18$ g/mL = 55.6 M*

    b. *The slight decrease in the concentration of the water is very small compared to errors of equilibrium constants.*

    Although the dissociation of an acid is commonly written as indicated below:

$$HA_{(aq)} = H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

better representations of the process and the resulting equilibrium expression are:

$HA(aq) + H_2O(l) = H_3O^+ + A^-$ $\quad\quad K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$

The equilibrium expression is usually simplified by multiplying both sides of the equation by the concentration of water and defining a new constant, the acid dissociation constant, K_a as $[K][H_2O]$.

c. *It is a very good approximation as the water concentration is essentially constant unless huge amounts of solute are added.*

d. *$1.8x10^{-16}$*

11. a. Show that the relationship of the pK_a for the conjugate acid of a base to the pK_b is given by:

$pK_b = 14 - pK_a$ $\quad\quad K_b = K_w/K_a \quad logK_b = logK_w - logK_a$

b. Rank the following acids from strongest to weakest:

pK_a (acid 1) = -2	pK_a (acid 2) = 5	pK_a (acid 3) = 10
strongest		*weakest*

c. Rank the following bases from strongest to weakest:

pK_a (base 1) = 12	pK_a (base 2) = 9	pK_a (base 3) = 4
strongest		*weakest*

12. Assume that you have 1.00 L of water that has very recently been distilled and has pH = 7.

a. *0.04% of the air is carbon dioxide. As the CO_2 is absorbed, the pH will drop.*
b. *5.3*
c. *The pH would remain very close to 7.*

13.* *0.1371 M*

14.* *0.0768 M*

15.* *156 g/mol*

16. *0.102 M*

17. *166 g/mol*

H. Thermodynamics

1. *$\Delta G = \Delta H - T\Delta S$*

2. *$\Delta G = -RTlnK$*

3.* *-407.1 - 285.9 - (-164.4 - 469.6) = -59.0 kJ/mol*

4. *-446.2 - 285.9 - (-206.6 - 469.6) = -55.9 kJ/mol*

5. *The net ionic equation for both is the same.*

6. a. $H_2(g) + 1/2\ O_2(g) = H_2O(l)$

b. $CH_4(g) + 2\ O_2(g) = CO_2(g) + 2\ H_2O(l)$

c. $C_2H_6(g)$ + $7/2\ O_2(g)$ = *$2\ CO_2(g)$ + $3\ H_2O(l)$*

d. $C_3H_8(g)$ + $5\ O_2(g)$ = *$3\ CO_2(g)$ + $4\ H_2O(l)$*

e. $C_8H_{18}(l)$ + $25/2\ O_2(g)$ = *$8\ CO_2(g)$ + $9\ H_2O(l)$*

7. Table of data and Hess's law calculation results

substance	$\Delta H_f°{}_{gas}$ (kJ/mol)	$\Delta H_f°{}_{liquid}$ (kJ/mol)	$\Delta H_c°$ (calculated) (kJ/mol)	$\Delta H_c°$ (from *NIST*) (kJ/mol)	$\Delta H_c°$ (from *NIST*) (kJ/g)
carbon dioxide	*-393.52*	na	na	na	na
water	*-241.83*	*-285.83*	na	na	na
methane	*-74.87*	na	*-890.3*	*-890.7*	-55.5
ethane	*-83.8*	na	*-1560.7*	*-1560.7*	-51.9
propane	*-104.7*	na	*-2219.2*	*-2219.2*	-50.3
2,2,4-trimethylpentane	*-224.1*	*-259.3*	*-5461.3 (from liquid)*	*-5461.3 (from liquid)*	-47.8

8. Which of the potential fuels, methane, ethane, propane, 2,2,4-trimethylpentane is the most efficient? Explain your answer. *If the fuel is purchased on a per gram basis and the cost per gram is the same, methane should be the choice as the heat of combustion drops as the number of carbons increases. However, if the price per gram differs, the price should be taken into account.*

J. Oxidation-Reduction

1. What is the oxidation number of the element indicated in the problems below?

a.* iron in Fe_2O_3 *3*
b. copper in $Cu(OH)_2$ *2*
c. cerium in $CeCl_3$ *3*
d. tin in SnO *2*
e. sulfur in SO_4^{2-} *6*
f. phosphorous in Na_3PO_4 5
g. oxygen in H_2O_2 *-1*
h. nitrogen in nitrate *5*
i. nitrogen in nitrogen dioxide *4*
j. nitrogen in nitrite *3*
k. nitrogen in nitrogen monoxide *2*
l. nitrogen in dinitrogen monoxide *1*
m. nitrogen in N_2 *0*
n. nitrogen in ammonia -3

2.

a.* $Mg(s)$ + $ZnCl_2(aq)$ = $MgCl_2(aq)$ + $Zn(s)$
Mg + Zn^{2+} = Mg^{2+} + $Zn(s)$
O, RA R, OA

b.* $2\ AgNO_3(aq)$ + $CaCl_2(aq)$ = $2\ AgCl(s)$ + $Ca(NO_3)_2(aq)$
Ag^+ + Cl^- = $AgCl(s)$
not a redox reaction

c. $2\ C_2H_6(g)$ + $7\ O_2(g)$ = $4\ CO_2(g)$ + $6\ H_2O(g)$
O, RA R, OA

d. $Na_2O(s)$ + $H_2O(l)$ = $2\ NaOH(aq)$
$Na_2O(s)$ + $H_2O(l)$ = $2\ Na^+$ + OH^-
not a redox reaction

e. $2\ KClO_3(s) = 2\ KCl(s) + 3\ O_2(g)$
In this reaction, the chlorine is reduced and the oxygen oxidized.

f. $4\ Fe(s) + 3\ O_2(g) = 2\ Fe_2O_3(s)$
O, RA R, OA

g. $Cl_2(aq) + 2\ KBr(aq) = Br_2(aq) + 2\ KCl(aq)$
$Cl_{2(aq)} + 2\ Br^- = Br_{2(aq)} + 2\ Cl^-$
R, OA O, RA

h. $Ca(HCO_3)_2(aq) = CaCO_3(s) + H_2O(l) + CO_2(g)$
$Ca^{2+} + 2\ HCO_3)_2^- = CaCO_{3(s)} + H_2O(l) + CO_{2(g)}$
not a redox reaction

K. Spectroscopy

1. $E = h\nu = hc/\lambda$

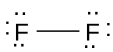
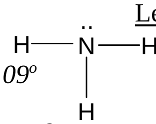
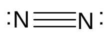
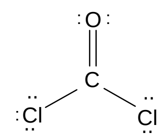
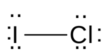
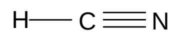
2. *Visible light is much more energetic than microwave light per photon. Gamma rays are much higher in energy than visible light so it is very inappropriate to say that microwaves nuke food.*

3 *0.030 M*

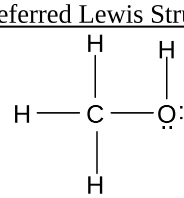
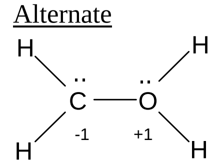
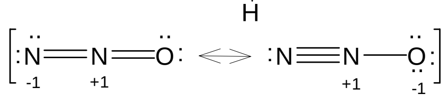
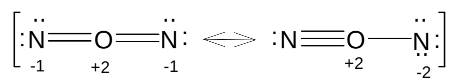
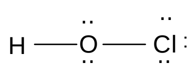
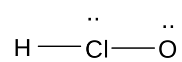
Exercise 2 - Lewis Structures, Isomers, Bond Polarity, Molecular Models and Geometry

A. Review of General Chemistry

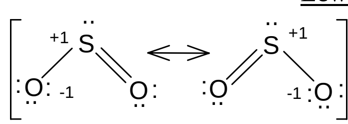
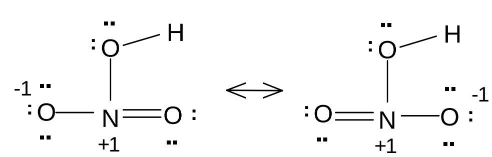
1.

	Molecule	Lewis Structure		Molecule	Lewis Structure
a.	F_2		d.	NH_3 *sp^3 polar 109º*	
b.	N_2		e.	$COCl_2$ (phosgene) *sp^2 polar 120º*	
c.	ICl	 *polar*	f.	HCN *sp polar 180º*	

2. For the molecules below, draw the two reasonable possible Lewis structures. As above, determine the bond angle(s), molecular polarity and the hybridization of the central atoms. Calculate and indicate values of non-zero formal charges. Based on formal charges, circle the preferred structure and construct a model of it

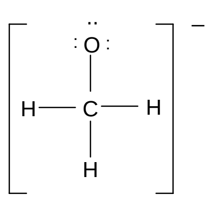
	Molecule	Preferred Lewis Structures	Alternate
a.	CH_4O *sp^3 polar 109º*		
b.	N_2O *sp polar 180º*		
c.	HClO *sp^3 polar 109º*		

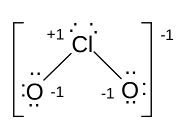
3. For each of the molecules below, draw the two reasonable resonance structures and indicate the nonzero formal charges that are present (if any) in each of the structures. For each, construct a model of one of the resonance structures. (Hint: sulfur and nitrogen are the central atoms respectively and the hydrogen in nitric acid is bonded to an oxygen.)

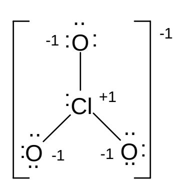
	Molecule	Lewis Structures
a.	SO_2	
b.	HNO_3	

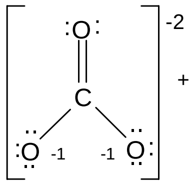
4. For each polyatomic ion in the chart below, draw all the reasonable resonance structures, indicate nonzero formal charges and construct a model of one of the resonance structures of each ion. Determine the indicated bond angle(s).

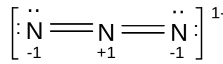
Lewis Structures

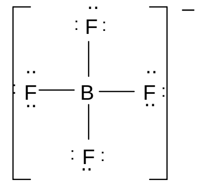
a. CH_3O^- 

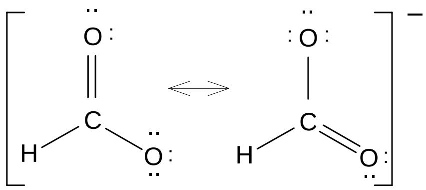
b. ClO_2^- 

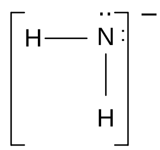
c. ClO_3^- 

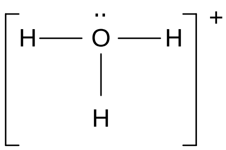
d. CO_3^{2-}  + 2 more resonance structures

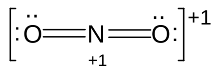
e. N_3^- 

f. BF_4^- 

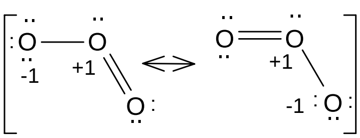
g. HCO_2^- 

h. NH_2^- 

i. H_3O^+ 

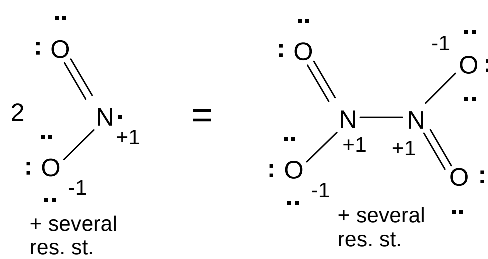
j. NO_2^+ 

5. *The bond angle is predicted to be 120°. As oxygen is the second most electronegative element, the positive formal charge on the central oxygen undoubtedly causes ozone to be at a relatively high energy level and therefore very reactive.*

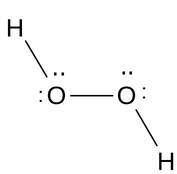


6. $2\ NO_2(g) \leftrightarrows N_2O_4(g)$

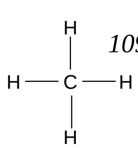
NO_2 is a free radical and therefore highly energtic and reactive. The dimer has its own problems with adjacent like formal charges on the nitrogens and negative formal charges on oxygens that can repel each other in another conformational postion..

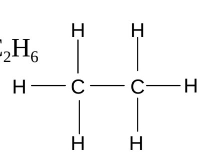


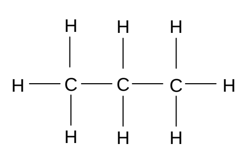
7. *The oxidation state of oxygen in hydrogen peroxide is -1 as contrasted with its usual oxidation states of -2 or 0. This unusual oxidation number undoubtedly raises the energy level and makes it more reactive.*



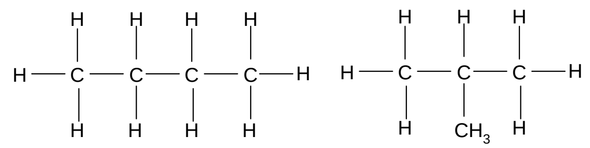
B. Organic Chemistry

1. CH_4  *109°*

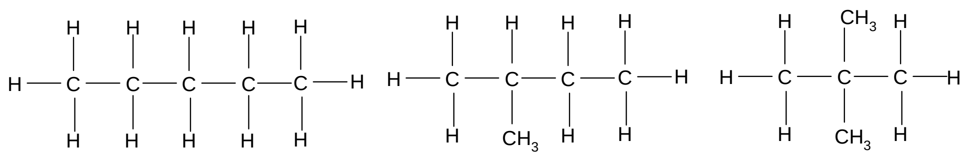
2. C_2H_6 

3. C_3H_8. 

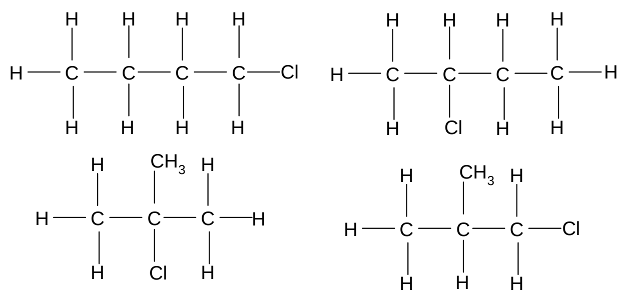
4.



5.

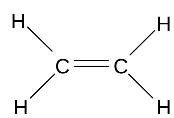


6.



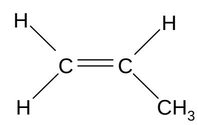
7, 8, 9, 10 require models.

11.

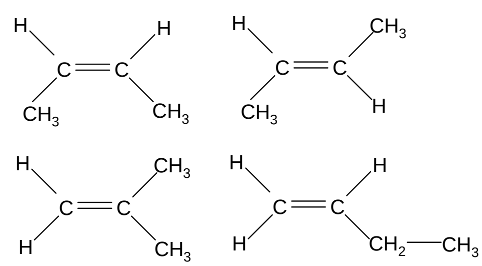


120°

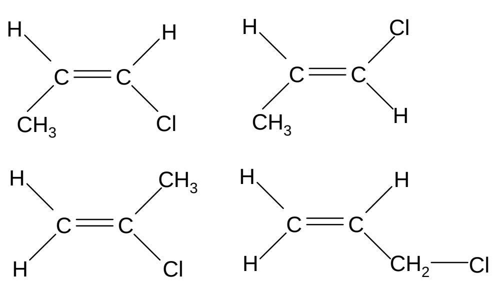
12.



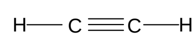
13.



14.

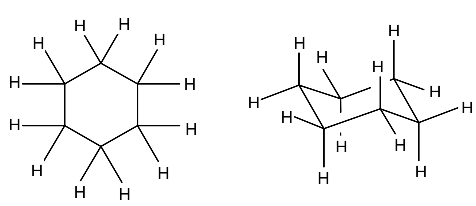


15.



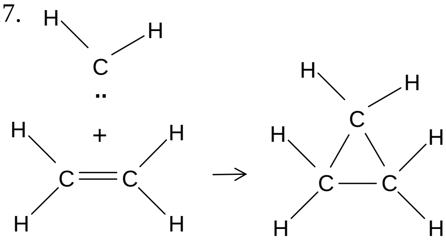
180°

16.

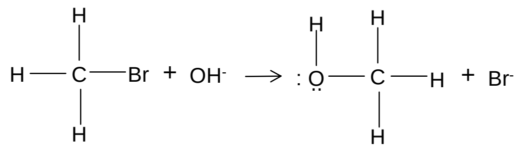


109°

17.

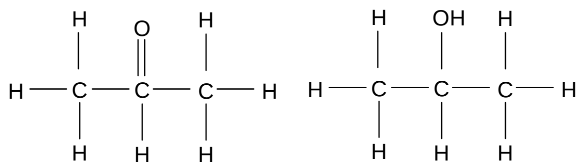


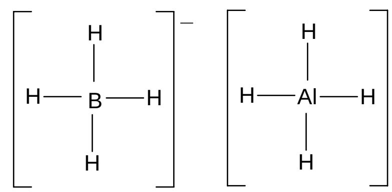
Methylene is complicated by the fact that the 2 electrons can have opposite spins resulting in a singlet state. But the lowest energy state is probably a triplet with the 2 electrons having the same spin. Either way, because of the two nonbonded electrons, methylene is expected to be even more reactive than a radical and it is.

18. 

The carbon of the bromomethane has a partial positive charge as a result of its polar bond with bromine. As a result, the nucleophile, OH^-, attacks the site of positive charge on the carbon from the backside to avoid the partial negative charge and the bulk of the Br resulting in the displacement of the Br^-.

19. a. Draw the Lewis structures of acetone and isopropyl alcohol.
    b. Draw the Lewis structures of the borohydride and aluminum hydride ions.





oxid. numbers B +3, Al +3, H -1

20. a. Do the numbers above suggest a reason for the existence of the field of organic chemistry?
    There are many more organic compounds that have been characterized than compounds of all of the other elements put together.

    b. Does the rapid increase in the number of isomers after 10 carbons seem intuitively correct? Briefly explain your answer. *Because carbon has 4 bonds and bonds in a tetrahedral fashion, the number of isomers is expected to increase dramatically as the number of carbons increases.*