Exercise 1

Review of General Chemistry

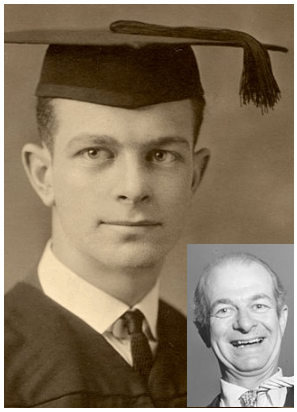


Fig. X1-1

Linus Pauling (1901 - 1994)
The only person to be awarded two unshared Nobel prizes in different fields: chemistry (1954), peace (1962)
http://nobelprize.org/chemistry/laureates/1954/
http://nobelprize.org/peace/laureates/1962/
http://osulibrary.orst.edu/specialcollections/coll/pauling/

This Exercise has been designed to help you review many of the concepts learned in general chemistry that will be essential for continuing your learning in this organic chemistry course. If you make a mistake on a problem or are unable to answer one, make sure you find out how to do the problem. It is very important to learn from mistakes. The concepts needed to solve these problems are part of the foundation you will need to succeed in organic chemistry. Answers to the problems with an * are in Appendix A.

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

1. Express the following numbers in scientific notation: a.* 0.0820 b. 5280 c. 0.0040

2. Is there a difference between accuracy and precision and if so, what is the difference?

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

a.* $(6.00\times10^{23})(2.5\times10^{-4})$ =
b. $(1.5\times10^{-8})(8.0\times10^{-2})$ =
c.* $7.2\times10^{-4}/8.0\times10^{-2}$ =
d. $5.6\times10^{-3}/7.0\times10^{1}$ =
e. * $3.2 + 14.19$ =
f. $325.3 + 4.721$ =
g.* $7.7\times10^{-1}/1.1\times10^{3}$ =
h. $2.5\times10^{5}/5.0\times10^{2}$ =
i.* $3.41\times10^{4} + 6.27\times10^{3}$ =
j. $1.23\times10^{1} + 2.34\times10^{2}$ =
k. $\dfrac{(5.4\times10^{2})(8.0\times10^{-3})}{(4.0\times10^{1})(9.0\times10^{-5})}$ =

4.* 23.9 grams of water at 100ºC occupy a volume of 25.0 mL. What is the density of water at 100ºC?

5. Ether is added to a graduated cylinder (mass = 95.76 g) to the 25.0 mL mark. The cylinder and contents now weigh 113.58 g. What is the density of ether?

6.* If the density of gasoline is 0.70 g/mL, what is the mass in grams of 5.0×10^{1} L of gasoline?

7. The density of acetic acid is 1.05 g/mL. What volume do you need to provide 125 grams of acetic acid?

8.* In 1897, J. J. Thompson, using a Crooke's tube, determined a value for the charge to mass ratio (e/m) of the electron close to the currently accepted value of 1.76×10^{8} coulombs/g. In 1909, R. A. Millikan, using his famous oil drop experiment, determined the value of e to be close to the currently accepted value of 1.6022×10^{-19} coulombs. Using a unit conversion, calculate the mass of an electron.

9. The e/m value for a proton is 9.577×10^{4} coulombs/g. Calculate the mass of a proton.

10. Calculate the ratio of the mass of the proton to the mass of the electron.

11. The density of liquid water at several temperatures is given below. Very few substances exhibit the anomalous density behavior exhibited by water. Explain the previous sentence. Would there be any significant consequences if water behaved "normally" (consider lakes freezing in the winter)?

temp. (°C)	30	25	20	15	10	5	3.98	0 (liq.)	0 (ice)
density (g/mL)	0.99567	0.99707	0.99823	0.99913	0.99973	0.99999	1.00000	0.99987	0.9168

12. The story of Air Canada Flight 143 (made into a movie as *Flight 171*) from Montreal to Edmonton on July 23,1983, affords an interesting and relevant example of the importance of unit conversions (Banks, P. *Chem. Matters*, Oct. 1996, 12-15). A ground crew determined that the flight would require 22,300 kg of fuel and the tanks contained 7,682 liters. To calculate how many liters of fuel needed to be added, they used a conversion factor of 1.77 and assumed the units were kg/L. Unfortunately the conversion factor 1.77 has units of lbs/L. From 1.77 lbs/L, calculate the conversion factor in kg/L.

13. **Every time a problem is solved you should ask if the conversion factors used and the answer make sense.** The ground crew assumed the density of the fuel to be 1.77 kg/L. Consider the density of water and of fuel (Are fuels such as gasoline more or less dense than water?). Does the conversion factor 1.77 kg/L make sense? Explain your answer.

14. Calculate the volumes in liters needed respectively using the incorrect 1.77 kg/L and the correct value.

15. Calculate the shortage in liters of fuel that resulted from the use of 1.77 kg/L instead of the correct value.

Incidentally, thanks to the heroic work of the flight crew and the air controllers, the flight made a safe emergency landing on an abandoned air strip near Winnipeg considerably short of its destination. In this case a tragedy was averted by both a careful response to the problem and luck. However, proper use of conversion factors with appropriate units coupled with some thinking would have avoided the need for the heroics and a chance for tragedy. You should be able to find more on this incident by typing in Flight 143 in to a search engine such as Google.

16. Webercise: The information needed to answer the questions below can be found at the sites:
    http://web.lemoyne.edu/~giunta/rayleigh0.html
    http://web.lemoyne.edu/~giunta/rayleigh.html

    a. What was puzzling Rayleigh in the first paper?
    b. The stereotyped scientist is usually pictured as a white male with no hair or wild hair, glasses, a lab coat and he is always alone. While chemists often wear lab coats and should wear eye protection, the rest of these images do not apply to scientists anymore than to any other group of people. Rayleigh's presentation, in fact, directly and very correctly contradicts one of the stereotypes. Explain this contradiction.

    It is generally possible to analyze most scientific advances in terms of the steps associated with an approach commonly called the scientific method: observation (complete and unbiased with questions noted of any not understood phenomena), hypothesis or explanation, testing or experimenting (the primary distinguishing feature of the scientific method), theory (an explanation consistent with further experimentation) and application. The thinking and procedures of Rayleigh are an excellent example of aspects of the scientific method. In question *16a* above, Rayleigh puzzled over the apparent discrepancy in his measurements on the density of nitrogen. Scroll down in his second paper (#2) about one page to his results on the mass of nitrogen obtained from two sources: separation and purification from air and synthesis by chemical means.

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)	_____	_____	_____	_____
chemical nitrogen (g)	_____	_____	_____	_____

d. According to the commonly accepted convention for the use of significant figures, the last digit to the right always has some uncertainty associated with it. If Rayleigh had measured the mass to two or even three significant figures, could any differences in the nitrogen from the two sources have been considered meaningful? Explain your answer.

e. Fortunately, Rayleigh measured the masses to five significant figures and very alertly noted a difference between the two sets of results. Many people would not have paid any attention to the differences in the data but Rayleigh searched for an explanation. What great discovery did Rayleigh make as a result of his search?

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 b. Al c. Mn d. Au

2. How many protons, neutrons and electrons are in a.* Cl b. Cu

3. How many protons, neutrons and electrons are in a.* H b. C c. N d. O e. Br

4. How many protons, neutrons and electrons are in a.* Cu^{2+} b. Cl^{-}

5. Except for small but very important differences in rates of chemical reactions, isotopes (of the same element) behave identically in chemical reactions. The very significant exception to this observation is that replacement of hydrogen-1 by hydrogen-2 (deuterium) can result in rate changes of as much as a factor of seven in chemical reactions. Why is it that hydrogen isotopes have such a large rate difference when intimately involved in a chemical reaction?

6. In contrast to chemical reactivity, nuclear stability is very dependent on the neutron to proton ratio. For even numbered elements, the number of stable isotopes varies from two to eight whereas for odd numbered elements the number of stable isotopes is in the range 0 (Tc and Pm) to 2. Unstable isotopes undergo radioactive decay often by emitting an α particle (helium nucleus), a β particle or a positron (an electron with a positive charge). All isotopes of elements above bismuth (atomic number 83) are unstable and therefore radioactive to some extent. As you have observed in problems 1 - 3 above, the periodic table enables you to determine the average number of neutrons in stable nuclei found on earth. To determine which isotopes are stable, you need to refer to a table of isotopes. However, it is possible to make predictions by comparing the calculated value from the periodic table to the number in an isotope of interest. For example, we would predict that $^{23}_{12}Na$ should be stable as the average determined from the periodic table is the same as the number in this isotope. On the other hand, we would predict that $^{26}_{12}Na$ is probably radioactive. On the basis of this discussion, make predictions about the stability of:

   a.* $^{3}_{1}H$ b. $^{4}_{2}He$ c. $^{13}_{6}C$ d. $^{14}_{6}C$

7. Confirming your prediction from 6-d above, $^{14}_{6}C$ does undergo β particle emission with a half life of 5730 years.
   a. Write a nuclear reaction for the decay of $^{14}_{6}C$.
   b. What happens in the nucleus to enable the nucleus to emit a β particle?
   c. A piece of pottery is found to contain 1/8 the amount of $^{14}_{6}C$ that would be expected. How old is the piece of pottery?

8. In problems 1 - 4 above, you subtracted the atomic number from the atomic mass to determine the average number of neutrons in the nucleus. The atomic masses that are in the periodic table can be determined by two general methods. Since an experimental measurement of atomic mass is made on samples that contain the mixture of isotopes that naturally occur on earth, the result is an average atomic mass.

   Mass spectrometers can be used to determine the abundances and masses of individual isotopes. This information can be used to calculate the average atomic mass. For example, copper has two stable isotopes, $^{63}_{29}Cu$ and $^{65}_{29}Cu$. The atomic masses of each are 62.9296 and 64.9278 amu respectively and their abundances are 69.17% and 30.83% respectively. The average atomic mass is calculated from:

$$\frac{(69.17)(62.9296) + (30.83)(64.9278)}{100} = 63.55 \text{ amu}$$

   Calculate the atomic mass that should appear for the elements below from the isotopic mass and abundance data below:

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

9. The inside front cover contains a modern traditional (horizontal) periodic table. The original Mendeleev table was actually a vertical model. (e.g., see:
   http://www.aip.org/history/curie/periodic.htm
   http://en.wikipedia.org/wiki/History_of_the_periodic_table
   http://web.lemoyne.edu/~giunta/ea/mendeleevann.html
   The inside back cover contains a modern version of a vertical table (For examples of extended vertical periodic tables, see:
   http://en.wikipedia.org/wiki/Periodic_table_(vertical)
   http://english.turkcebilgi.com/Periodic+table+(vertical)
   Suggest reasons for the predominance of the horizontal model over the vertical model but also suggest some advantages of the vertical model.

10. (Webercise)Later in the course, you will study how mass spectra can be used to facilitate structure determinations of organic compounds. As discussed above, mass spectra can also be used to determine atomic masses and abundances of isotopes. In simplified form, particles introduced into a mass spectrometer are ionized to positively charged particles by a high energy beam of electrons. The positively charged particles are then separated by mass and a printout of isotopic abundance vs mass can be obtained.

Fortunately, there are two excellent compilations of mass spectra on the Internet. One of those sites will be used to determine the naturally (on earth) occurring isotopic abundances of Cl, Br and C. These instructions will walk you through the procedure for the difficult example of uranium. First, go to the site:

http://webbook.nist.gov/chemistry/

For this procedure to work, your computer must have an up-to-date version of Java. Now click on *formula*. In the next window, put a check on *mass spectrum* and type in the UF6. Now click on *mass spectrum*. As the molecular mass of UF_6 is 352 g/mole, we expect a peak at 352 as a result of the peak from UF_6^+. If you put tiny windows around the 352 peak, you will be able to detect a peak of about 0.38 in magnitude. However, for this case apparently, most of the UF_6^+ fragments to UF_5^+ before entering the mass separation part of the instrument. This is all right for our intentions as we are going to try to determine the percentage of isotopes that are $^{235}_{92}U$. Remember that fluorine has only 1 isotope so the ratio of the peak at 330 to the sum of the peaks at 330 and 333 represents the percentage. Notice that the relative peak height of the $^{238}_{92}U$ peak can be determined with your mouse pointer and is 100. The peak at 330 is not observable and cannot be measured as it appears. Using your mouse make a small partial window around the 330 peak and release your mouse. A new spectrum should appear with the 330 peak amplified. While it can now be measured, it is better to put another window around the 330 peak and it will be amplified again. It can now be measured using your mouse as a pointer and should result in a value of about 0.73. Thus the percentage of $^{235}_{92}U$ isotopes is (0.73/0.73 + 100)(100%) = 0.73%. This value is close to the literature value of 0.711%. Now determine the percentages of the $^{37}_{17}Cl$, $^{79}_{31}Br$ and $^{13}_{6}C$ isotopes using the mass spectra of hydrogen chloride, hydrogen bromide and carbon tetrafluoride. For HCl and HBr, you do not have to worry about fragmentation so you will be looking at the ratio of the peaks of the isotopes of masses 38/(38 +36) and 82/(82 + 80) You will need to figure out how to make the mass 38 peak observable. Also, the very small amounts of the presence of hydrogen isotopes has an insignificant effect on the results and can be disregarded. For CF_4, fragmentation occurs just like UF_6 thus the mass ratio of 70/(70 +69) for the CF_3 peaks gives the $^{13}_{6}C$ percentage.

isotope percentages a. $^{37}_{17}Cl$ b. $^{79}_{31}Br$ c. $^{13}_{6}C$

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
http://ie.lbl.gov/education/isotopes.htm

e. The mass of the $^{13}_{6}C$ isotope is 13.0033 g/mol). Use the isotopic abundance of $^{13}_{6}C$ that you determined in 9-b above to calculate the atomic mass that should appear for carbon on a periodic table on earth (Hint: There are only two stable carbon isotopes and the mass of $^{12}_{6}C$ should be known to you.)

C. Inorganic Nomenclature, Formulas and Balancing Equations

1. Give the names of: a. NO_2 b. $Mg(NO_3)_2$ c. $KHCO_3$ d. $CuSO_4 \cdot 5H_2O$ e. $AgC_2H_3O_2$
2. Give the formulas of: a. calcium chloride b. nitric acid c. iron(III) sulfate d. sodium carbonate
3. Write balanced equations and net ionic equations for each of the following:
   a.* The single replacement reaction of magnesium with sulfuric acid
   b. The double replacement reaction of calcium nitrate with potassium phosphate
4. Write balanced equations for each of the following:
   a. The decomposition of hydrogen peroxide to water and oxygen
   b. The combustion of ethanol (C_2H_6O)

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 b. C c. Mn d. Sr e. Ca^{2+} f. Cl^-

2. Give possible values for the quantum numbers n, ℓ, m, s for: a.* a 2s electron b. a 3d electron

3.* The quantum numbers 4, 2, 1, ↿ represent what kind of electron?

4. The quantum numbers 5, 1, 1, ↿ represent what kind of electron?

5. The number of unpaired electrons for each of the following is: a.* Ca b. Ni c. P d. Al^3+

6. An element must have at least one unpaired electron to be paramagnetic (attracted to a magnet). Otherwise it is diamagnetic. Which of the following elements is paramagnetic: Zn, Fe, Hg, Ar, Sr

7. The order of filling of the sublevels is sometimes unexpected. For instance, the 3d orbital fills after the 4s. Different techniques have been developed to help students remember the order of filling but the easiest and handiest method uses the ever present periodic table. Explain how the periodic table demonstrates that the 3d orbital fills after the 4s orbital.

8. Most textbooks contain a diagram that shows the relative energy levels of the orbitals. The energy levels are represented by lines or boxes but are in fixed positions. As electrons are added to orbitals, energy levels do slightly shift. For instance, based on the fixed energy level diagram, the configurations $1s^2 2s^2 2p_x^2$ and $1s^2 2s^2 2p_x^1 2p_y^1$ should have the same energy. Explain why the latter configuration is the the lower energy level (thereby explaining Hund's Rule).

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

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

   b. Explain why the melting points work for distinguishing ionic from covalent bonds for the compounds given (Hint: consider the bonding in crystalline ionic compounds). Recognize that some covalent compounds also have high melting points with diamond (m.p. > 3550 °C) being an extreme example.

   c. Name, if possible, an ionic compound that is not solid at room temperature.

10. Study the data in the two tables below.

Table 1-1

compound	formula	boiling point (°C)
methane	CH_4	-161.7
pentane	C_5H_{12}	36.1
decane	$C_{10}H_{22}$	174.0
pentadecane	$C_{15}H_{32}$	270.6
eicosane	$C_{20}H_{42}$	343
fluorine	F_2	-188
chlorine	Cl_2	-34.6
bromine	Br_2	58.8
iodine	I_2	184.3

Table 1-2

CH_4	NH_3	H_2O	HF
-161.7	-33.4	100	-19.5
SiH_4	PH_3	H_2S	HCl
-111.8	-87.4	-60.7	-85.0
GeH_4	AsH_3	H_2Se	HBr
-88.5	-55	-41.5	-67.0
SnH_4	SbH_3	H_2Te	HI
-52	-17.1	-2.2	-35.4

The numbers are the boiling points in °C.

a. In Table 1-1 and the first column of Table 1-2, all of the compounds can be considered to be non-polar. Why do the boiling points increase for the three series of compounds?

b. In Table 1-2, the boiling points going down from the 2nd row to the bottom, consistent with the previous observation, increase. However, ammonia, water and hydrogen fluoride are substantially higher than expected. The reason for this is an extremely important kind of intermolecular force that is responsible for regional shapes in proteins and the double helix in DNA. What is the name of this force and when can it occur?

c. Does it appear that this force exists in hydrogen chloride? Explain your answer.

d. It is very important to notice apparent inconsistencies such as those for ammonia, water and hydrogen fluoride. Often inconsistencies lead to very important discoveries. There is another inconsistency going across each row. What is this inconsistency and try to explain it for the first row. Explaining the inconsistency for the remaining rows is more difficult but give it a try if you choose.

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
b. CH_2=CH_2 ethylene or ethene
c. HC≡CH acetylene or ethyne
d. CH_2O formaldehyde or methanal
e. CO_2 carbon dioxide
f. HCN hydrogen cyanide
g. CH_3Cl methyl chloride or chloromethane
h. HCOOH formic acid or methanoic acid

i. What is the hybridization of oxygen in water?
j. What is the hybridization of nitrogen in ammonia?

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

1.* A typical glass of water contains about 230 grams of water. How many moles and molecules of water does it contain?

2.* The mass in grams of 1 atom of argon is (be sure to first ask yourself what the approximate power of ten should be for the answer to this problem):

3.* For an unknown element, 3.45×10^{-3} moles weigh 0.331 g. The element is probably:

4.* The limit of the most sensitive balance that can currently be built is about 1×10^{-6} g. For the element iron, what is the smallest number of atoms that could be detected by a balance?

5.* It is common practice to send newly synthesized compounds to microanalytical laboratories to determine the mass percentages of the elements present. The percentages are then used to calculate empirical formulas. It is very doubtful that you will do this in your organic course work but it is still important that you remember how to do these calculations.

   a. Determine the empirical formula and the molecular formula of a compound that consists of 87.41% nitrogen and 12.58% hydrogen and has a molecular mass of 32 g/mol.

   b. Ask yourself if the answer above is possible. For example, if you arrive at a formula of NH_5, what should you do next?

6.* Theoretical and percent yield calculations are very important in organic chemistry. For every synthesis you perform in the laboratory, it is necessary to determine the masses of the starting materials and products so that the percent yield (on a mole basis of course) can be calculated. For commercial syntheses especially, the percent yield is used for determining the cost of producing the product. 2.3 grams of sodium reacts violently with excess water and 0.080 grams of hydrogen gas are collected. What are the theoretical and percent yields of hydrogen gas?

7.* From the ignition of 5.0 grams of hydrogen with 80.0 grams of oxygen, 25 grams of water are collected. What was the percent yield of water?

8. Explain how you would prepare 250 mL of a NaCl solution that is: a.* 0.10 M b. 1.000×10^{-1} M

9.* Explain how you would prepare 500 mL of a 0.050 M HCl solution from a 6.0 M HCl solution.

10. The mass of the earth is about 6.0×10^{27} g. Assuming that it is made of iron, how many atoms are in the earth?

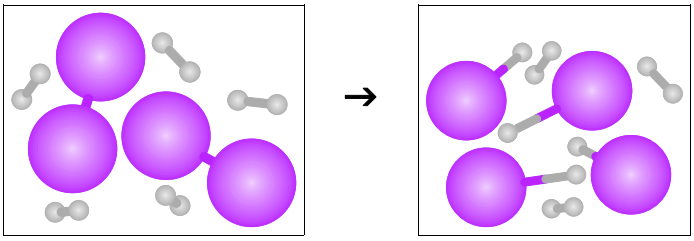
11. The mass in grams of 1 molecule of carbon dioxide is:

12. By titration it is found that 1.50 g of an organic acid contains 2.50×10^{-2} moles. Before you calculate the answer to this problem, you should ask yourself what the range of possible answers should be. If your answer falls out of that range, it is good cause to go over your calculations.

   a. What is the expected range of answers?

   b. What is the molecular mass of the acid?

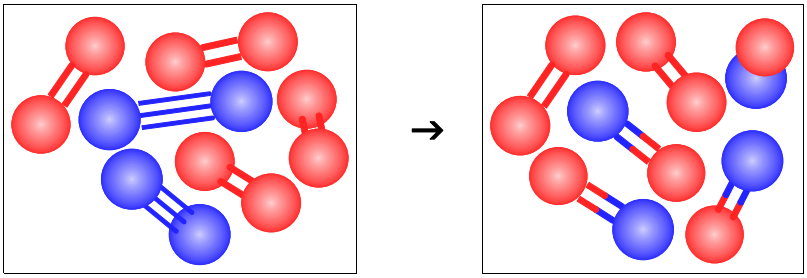
13.* The chemical equation for the reaction to the right is:



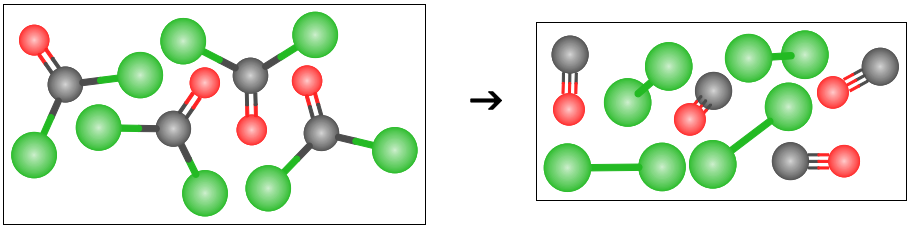
a. $5\ H_2 + 2\ I_2 = 4\ HI + 3\ H_2$
b. $H_2 + I_2 = 2\ HI$
c. $5\ H_2 + 2\ O_2 = 4\ H_2O + 3\ H_2$
d. $N_2 + O_2 = 2\ NO$
e. none of the above

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

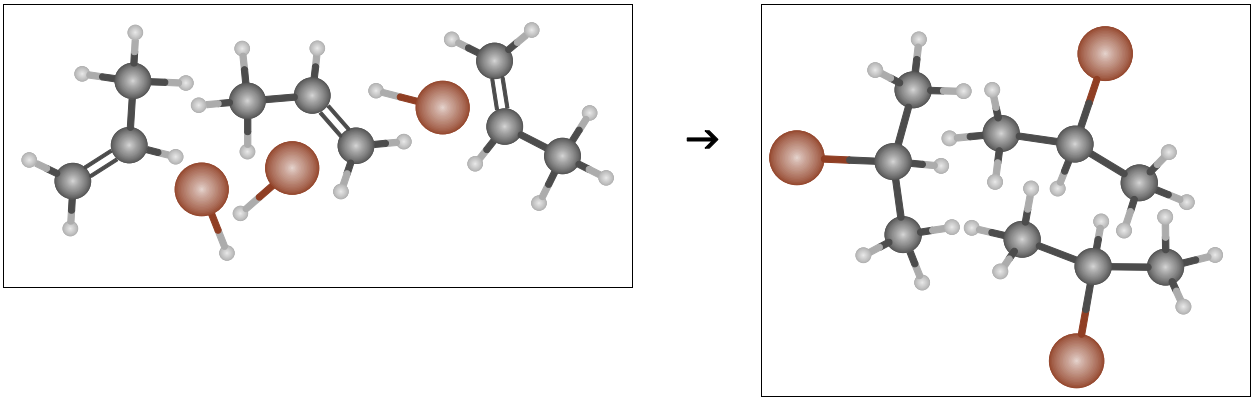
15. Assuming the reactants in figure to the right are nitorgen and oxygen, write a balanced equation for the reaction. Which reactant is used in excess?



16. The reaction to the right depicts the decomposition of phosgene. Write a balanced equation for the reaction.

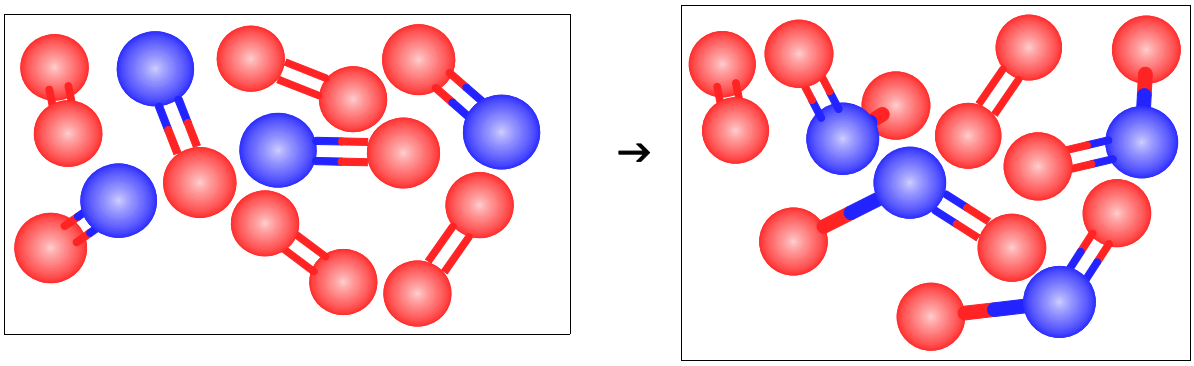


17. 1-Propene reacts with hydrogen bromide to yield 2-bromopropane. Write the equation for the reaction. The reaction shown below gives the predominate product but if peroxide is added to the reaction mixture, an isomer is the predominant product. Draw the structure of the isomer.



The reactions below illustrate the reaction of hydrazine with oxygen, oxygen with nitrogen monoxide and methanol with oxygen in scrambled order. Write balanced chemical equations for each system.

18.



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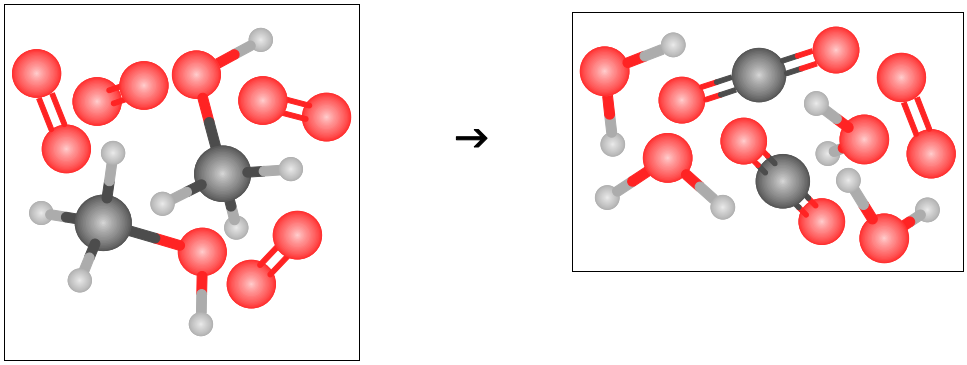
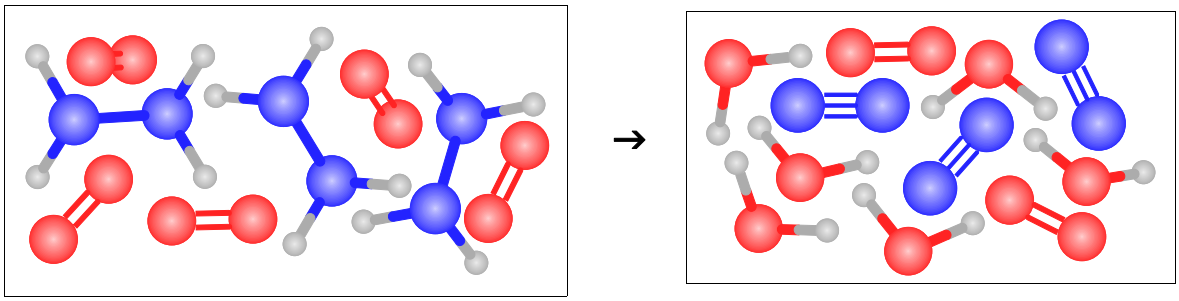
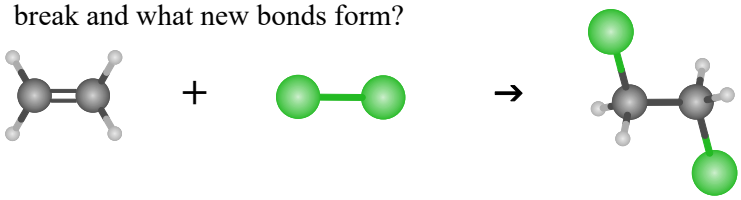


20.



21. Determine the empirical formula and the molecular formula of a compound (Freon 11) that consists of 8.74% carbon, 77.43% chlorine and 13.83% fluorine and has a molecular mass of 137 g/mol.

22. a. For the combination reaction illustrated below between ethylene and chlorine, what bonds must break and what new bonds form?



b. Write a balanced equation for the combination reaction of hydrogen with chlorine. What bonds must break and what new bonds form?

c. 28 grams of ethylene are reacted with 85 grams of chlorine and 75 grams of product are obtained. What are the theoretical and percent yields for the reaction?

23. The balanced equation for the reaction of acetylene with chlorine is:

$$C_2H_2 + 2\ Cl_2 = C_2H_2Cl_4$$

13 grams of acetylene are reacted with 35 grams of chlorine and 25 grams of product are obtained. What are the theoretical and percent yields for the reaction?

24. Explain how you would prepare 250 mL of a NaOH solution that is (Hint: be careful with this one. There are some considerations here not present in #8 above): a. 0.10 M b. 1.000×10^{-1} M

25. Explain how you would prepare 500 mL of a 0.050 M HCl solution from a 6.0 M HCl solution.

26. What are the concentrations of calcium ion and nitrate ion in a solution that is 0.10 M $CaCl_2$?

F. Equilibrium

Write the correct equilibrium expression for the following reactions:

1.* $2NO_{2(g)} = N_2O_{4(g)}$

2. $N_{2(g)} + O_{2(g)} = 2\ NO_{(g)}$

3. $HF_{(aq)} = H^+ + F^-$

4. $CN^- + H_2O_{(l)} = HCN_{(aq)} + OH^-$

5. $HC_2H_3O_{2(aq)} + C_2H_5OH_{(l)} = C_4H_8O_{2(l)} + H_2O_{(l)}$
   acetic acid ethanol ethyl acetate

6. $CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}$

The answers for the questions below are: a. left b. right c. no change

Assume an aqueous HF solution (#3 above) is at equilibrium. In which direction will the system shift to reachieve equilibrium if:

7.* HCl is added to the system?

8. NaF is added to the system?

9. NaOH is added to the system?

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?

11. ethanol is added to the system?

12. ethyl acetate is removed from the system?

13. water is removed from the system?

G. Acids, Bases and pH

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

1.* $HNO_{3(aq)} + H_2O_{(l)} = H_3O^+ + NO_3^-$

2. $NH_{3(aq)} + H_2O_{(l)} = NH_4^+ + OH^-$

3. $CO_3^{2-} + H_2O_{(l)} = HCO_3^- + OH^-$

4. $H_2PO_4^- + H_2O_{(l)} = H_3O^+ + HPO_4^{2-}$

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. $H^+ + OH^+ = H_2O\ H$

6. $CH_3CH_2\text{-}OH + Zn^{2+} = [CH_3CH_2–O(H)–Zn]^{2+}$

7. $CH_3Cl + AlCl_3 = CH_3–Cl^+–AlCl_3^-$

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

9. Fill in the blanks in the following table:

	pH	$[H^+]_{(mol/L)}$	$[OH^-]_{(mol/L)}$	pOH
a.*	4.7	_____	_____	_____
b.	_____	$7.7x10^{-3}$	_____	_____
c.	_____	_____	$2.3x10^{-8}$	_____
d.	_____	_____	_____	3.6

10. a. Using a periodic table as the only resource, calculate the approximate molarity of pure water at room temperature.

    b. Does the concentration of water change significantly (from the value in 10-a) when enough acetic acid is added to make the solution 0.1 M acetic acid?

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:

$$HA_{(aq)} + H_2O_{(l)} = H_3O^+ + A^- \qquad K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

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. Is it a valid procedure to incorporate the water concentration into the acid dissociation constant? Base your answer on the results of parts *a* and *b* of this problem.

d. The expression for the dissociation of water, K_w, has also been simplified by incorporating the concentration of water into K_w. What is the value of K for the dissociation of water?

11. Acid and base strength are very important concepts in organic chemistry that often considerably help with the understanding of mechanisms of reactions. While acid dissociation constants (K_a) or base dissociation constants (K_b), are sometimes used to discuss relative acid or base strength, it is more common practice to use pK_a values when comparing acid strength. Even for base strength, the pK_a values of the conjugate acid of the base is usually used for comparison and discussion purposes.

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

$pK_b = 14 - pK_a$

b. Rank the following acids from strongest to weakest:
pK_a (acid 1) = -2 pK_a (acid 2) = 5 pK_a (acid 3) = 10

c. Rank the following bases from strongest to weakest:
pK_a (base 1) = 12 pK_a (base 2) = 9 pK_a (base 3) = 4

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

a. If the water is kept in an open container, shortly after distillation, the pH will noticeably drop. Why?

b. What will the pH be if you add 1 drop (0.050 mL) of 0.10 M HCl to the water (at pH = 7)?

c. If the water had been buffered to a pH = 7, what would have happened to the pH with the addition of the drop of 0.10 M HCl?

13.* 0.6530 grams of a primary standard acid (potassium hydrogen phthalate, molecular mass = 204.23 g/mole) require 23.32 mL of a NaOH solution of unknown concentration to reach the endpoint. What is the concentration of NaOH?

14.* If 16.0 mL of a 0.120 M NaOH solution are required to neutralize 25.0 mL of an HCl solution, what is the concentration of the HCl solution?

15.* If 21.3 mL of a 0.120 M NaOH solution are required to neutralize 0.400 grams of an unknown monoprotic acid, what is the molecular mass of the acid?

16. If 14.0 mL of a 0.160 M NaOH solution are required to neutralize 11.0 mL of a sulfuric acid solution, what is the concentration of the H_2SO_4 solution?

17. 0.3000 g of a diprotic acid requires 32.86 mL of 0.1100 M NaOH to reach the second end point. What is the molecular mass of the acid?

H. Thermodynamics

1. What is the relationship between free energy and enthalpy and entropy?

2. What is the relationship between free energy and the equilibrium constant for a reaction?

solution	concentration (mol/L)	heat of formation (kJ/mol)
hydrochloric acid	1.00	-164.4
sodium hydroxide	1.00	-469.6
sodium chloride	1.00	-407.1
water		-285.9
nitric acid	1.00	-206.6
sodium nitrate	1.00	-446.2

3.* From the data in the table above, calculate the molar heat of neutralization for the reaction between equal volumes of 2.00 M hydrochloric acid and 2.00 M sodium hydroxide.

4. From the data in the table above, calculate the molar heat of neutralization for the reaction between equal volumes of 2.00 M nitric acid and 2.00 M sodium hydroxide.

5. Why do the answers to #3 and #4 come out similar to each other?

Webercise: Hess's law calculations using data available on the Internet. The *NIST* (National Institute of Standards and Technology) site on the Internet

http://webbook.nist.gov/chemistry/

can be used to obtain data for Hess's Law calculations. In this exercise, you will find the heats of formation of water (liquid and gas) and carbon dioxide as well as the heats of formation and combustion for methane (g), ethane (g), propane (g), and 2,2,4-trimethylpentane (l). [Note: Commercially 2,2,4-trimethylpentane is called isooctane. The commercial name is not consistent with the naming system used by organic chemists but unfortunately finds common usage. Isooctane is one of the standards for determining the octane rating of gasoline. Its octane rating has arbitrarily been assigned a value of 100.] The heats of formation will be used to calculate the heats of combustion (using Hess's Law) for hydrogen, methane, ethane, propane, and 2,2,4-trimethylpentane (l). The calculated values for the hydrocarbons will be compared to the heats of combustion given at the *NIST* site.

At the NIST site, click on "Name" and then enter the name of the compound of interest in the box. For carbon dioxide, water, methane, ethane and propane, click on "gas phase thermochemistry" data and scroll down and find the standard heats of formation data [$\Delta_f H^\circ_{gas}$]. and fill in the data in the table below. For water and 2,2,4-trimethylpentane, select "Condensed phase thermochemistry" and record the standard heats of formation [$\Delta H_f{}^\circ_{liquid}$]. For methane, ethane, propane and 2,2,4-trimethylpentane, you should also select "Reaction thermochemistry data" and record the top value [$\Delta H_c{}^\circ$]. To make sure you are in the right place, the value for methane is -890.7 kJ/mol.

6. Write the reactions for the combustion of hydrogen, methane, ethane, propane and 2,2,4-trimethylpentane. Assume the water is formed in the condensed phase.

   a. $H_2(g) + O_2(g) =$

   b. $CH_4(g) + O_2(g) =$

   c. $C_2H_6(g) + O_2(g) =$

   d. $C_3H_8(g) + O_2(g) =$

   e. $C_8H_{18}(l) + O_2(g) =$

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

substance	ΔH_f° gas (kJ/mol)	ΔH_f° liquid (kJ/mol)	ΔH_c° (calculated) (kJ/mol)	ΔH_c° (from *NIST*) (kJ/mol)	ΔH_c° (from *NIST*) (kJ/g)
carbon dioxide		na	na	na	
water			na	na	
methane		na			
ethane		na			
propane		na			
2,2,4-trimethylpentane			(from liquid)	(from liquid)	

8. Which of the potential fuels, methane, ethane, propane, 2,2,4-trimethylpentane is the most efficient? Explain your answer.

J. Oxidation-Reduction

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

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

2. For the reactions below that are redox reactions, label the reactant that is undergoing oxidation with a capital O and the reactant that is undergoing reduction with a capital R. Label the oxidizing agent with OA and the reducing agent with RA. **When appropriate, first write the reaction in net ionic form.**

a.* $Mg_{(s)} + ZnCl_{2(aq)} = MgCl_{2(aq)} + Zn_{(s)}$

b.* $2\ AgNO_{3(aq)} + CaCl_{2(aq)} = 2\ AgCl_{(s)} + Ca(NO_3)_{2(aq)}$

c. $2\ C_2H_{6(g)} + 7\ O_{2(g)} = 4\ CO_{2(g)} + 6\ H_2O_{(g)}$

d. $Na_2O_{(s)} + H_2O_{(l)} = 2\ NaOH_{(aq)}$

e. $2\ KClO_{3(s)} = 2\ KCl_{(s)} + 3\ O_{2(g)}$

f. $4\ Fe_{(s)} + 3\ O_{2(g)} = 2\ Fe_2O_{3(s)}$

g. $Cl_{2(aq)} + 2\ KBr_{(aq)} = Br_{2(aq)} + 2\ KCl_{(aq)}$

h. $Ca(HCO_3)_{2(aq)} = CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$

K. Spectroscopy

1. The energy of electromagnetic radiation is related to the frequency of the radiation by $E = h\nu$ and the speed of light is the product of the wavelength and the frequency, $c = \lambda\nu$. Derive the equation for the relationship between energy and wavelength.

2. The microwave oven in your house uses electromagnetic radiation that has a wavelength about 0.01 cm. The wavelength range of visible light is 400 - 700 nm. Which is more energetic, microwave or visible light and is it appropriate to say that a microwave "nukes" the food? Explain your answer.

3 According to Beer's Law, the absorption of light at a given wavelength is proportional to the product of the path length and the concentration, $A = \varepsilon bc$ where ε is the proportionality constant, b the pathlength and c the concentration. At a wavelength of 270 nm, a 0.040 M solution of acetone in water has an absorption of 0.64 in a 1.00 cm cell. The absorption of a solution of unknown concentration of acetone in water was 0.48 at the same wavelength and in the same cell. What is the concentration of acetone in the unknown? (Assume that there is zero absorption of light by water at 270 nm.)