

**Exercises**  
**Set One**

1. Give the Lewis structure of  $\text{H}_2\text{O}$ ,  $\text{SCl}_2$ ,  $\text{NH}_3$ ,  $\text{ClF}$ , and  $\text{C}_2\text{H}_3\text{O}_2^-$  indicating formal charge where appropriate.
2. What do we mean in chemistry by the word “radical”? Which of the following compounds are “radicals?”  $\text{CH}_3$ ,  $\text{PF}_5$ ,  $\text{HCO}_2$ ,  $\text{NH}_2^-$ .
3. The Lewis structure of  $\text{CO}_2$  is not  $\text{C}=\text{O}=\text{O}$ , where some electrons are missing: you fill them in. What's wrong with this Lewis structure? What is the correct Lewis structure? Why is the one we call “correct” correct?
- 4.1. Draw a Lewis structure for cyclic  $\text{O}_3$ . What, if anything, does this Lewis structure suggest about the stability of cyclic  $\text{O}_3$ ? HINT: Answer this for a Lewis structure model only: that is, electron pairs, octet rules, formal charges; not hybridization.
- 4.2. Draw the Lewis structure for bent  $\text{O}_3$ . Why is this compound reactive?
- 4.3. How is  $\text{SO}_2$  related to  $\text{O}_3$ ? Why is  $\text{SO}_2$  relatively nonreactive (at least as an oxidant) compared to ozone?
- 5.1.1. Compounds that exist but violate the Lewis “octet rule” on the high side are  $\text{PF}_5$ ,  $\text{SO}_4^{2-}$ ,  $\text{IF}_5$ ,  $\text{ClF}_3$ ,  $\text{SF}_6$ ,  $\text{SiF}_6^{2-}$ ,  $\text{SCl}_4$ . Compounds that violate the Lewis “octet rule” and (therefore?) do not exist are:  $\text{SiI}_4$ ,  $\text{SiH}_6^{2-}$ ,  $\text{S}_5^{2-}$  (tetrahedral form),  $\text{PH}_5$ ,  $\text{F}_3^-$ ,  $\text{NF}_5$ . Formulate a “rule” that allows one to understand which molecules belong in one of these classes and which in the other.
- 5.1.2. If someone asked you if  $\text{SBr}_4$  could be synthesized and characterized, what would you say?
- 5.2. Compounds that exist but violate the Lewis “octet rule” on the low side are stable compounds such as  $\text{BF}_3$ ,  $\text{BeCl}_2$ ,  $\text{AlCl}_3$ . Compounds such as  $(\text{CH}_3)_3\text{C}^+$  exist but are quite unstable. Verify these compounds violate the octet. What seems to be the underlying conditions for which a violation of the Lewis rule on the low side is possible.
- 6.1. Write Lewis structures for  $\text{SO}_2^{2-}$  and  $\text{SO}_3^{2-}$ .
- 6.2. Why would you expect that these materials might be called “bases”?
- 6.3. On the basis of your Lewis structures from 6.1., which should react most readily with  $\text{H}^+$ ?

7. Write Lewis structures for  $\text{NO}_2^-$  and  $\text{NO}_2^+$ . Use VSEPR to determine structure. What would you anticipate for the structure of  $\text{NO}_2$ . Justify your answer.

8.0. What happens in an explosion? Get to the basics.

8.1. Why is  $\text{NH}_4\text{NO}_3$  an explosive compound?

9.1.  $\text{N}_2\text{O}_3$  dissolves in  $\text{NaOH}$  to product a solution of  $\text{NO}_2^-$ . Write a balanced reaction. Be able to give a general statement about how to solve this kind of problem.

9.2. Ammonia,  $\text{NH}_3$ , reacts with dioxygen under high temperature catalysis to produce  $\text{NO}$ . Write a balanced reaction.

9.3. Diphosphonic acid,  $\text{H}_4\text{P}_2\text{O}_5$ , which has the two phosphorous atoms bonded to a central oxygen, and is otherwise symmetric, is formed when  $\text{H}_3\text{PO}_3$  reacts with  $\text{PCl}_3$ . Write a balanced reaction.

10. Which should be the stronger acid,  $\text{HClO}_3$  or  $\text{HClO}$ ? HINT: These are common ways of ordering the elements in the formula; they may not reflect connectivity.

11. Make a rough prediction of the thermal gravimetric analysis curve for  $\text{Cu}(\text{H}_2\text{O})_4 \text{SO}_4 \cdot \text{H}_2\text{O}$ . HINT: Think about any difference in bonding between a copper ion and a water molecule, between a sulfate ion and a water molecule, and between a sulfur atom and an oxygen atom in sulfate. HINT: The ultimate product is  $\text{CuO}$ .

12.0.1. Copper metal is produced by reacting  $\text{Cu}_2\text{S}$  with oxygen to produce the metal and  $\text{SO}_2$ . Write a balanced reaction.

12.0.2. Is copper oxidized or reduced in this reaction? S? O?

12. What would you predict for the thermal stability of  $[\text{NH}_4^+][\text{GaH}_4^-]$ ? How would you compare it to the corresponding borohydride?

13.0.1. Order the following in terms of increasing basicity (without looking in tables); give a reason for your ordering:  $\text{OCl}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ .

13.0.2. Which should be the strongest acid,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  or  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ?

13.0.3. Which would be the strongest acid,  $\text{HC}(\text{O})\text{OH}$  or  $\text{H}_3\text{COH}$ ? Why?

13.1. Ammonium nitrate dissolves in water with strong cooling of the solution. Sketch an approximate DSC plot for this process.

13.2. Does it require energy from the surroundings for  $\text{NH}_4\text{NO}_3$  to dissolve? If so we might say the reaction is energetically uphill, like a stone going from a valley to a mountain top. The latter never happens spontaneously; why should  $\text{NH}_4\text{NO}_3$  dissolve spontaneously, as it does?

13.3. Give a molecular model of the process described in 13.2.

14. A sample of  $\text{MgCO}_3$  is heated to decomposition. Write a balanced reaction for the production of

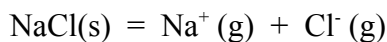
CO<sub>2</sub>. What is the weight percent CO<sub>2</sub>.

15.0.1. How would you compare the size of Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup>? Give a reason for your conclusion.

15.0.2. How would you compare the size of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>? Give a reason for your conclusion.

15.0.3. How would you compare the size of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>? Give a reason for your conclusion.

15.0.4. Imagine destroying an ionic compound by this process:



This process is called the lattice energy, often given the symbol U. Which would you expect to have the largest lattice energy, NaCl(s) or LiF(s)? Give a reason or reasons.

15.0.5. Which would have the largest U, LiF(s) or MgO(s)? Give a reason or reasons. It is getting tiresome to keep typing this last request. It is what we do in this course, so, from now on, **“Always give a reason.”**

15.0.6. What energy factors favor the reaction

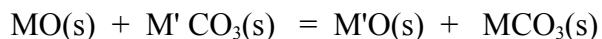


taking place to the right? Which hinder it? HINT: This kind of complicated process should be broken down into simpler steps taking advantage of Hess' law. (What?)

15.0.7. A useful rule is “All cations prefer small anions, but small cations prefer small anions more than large ones do.” Justify this rule assuming that the lattice energy can be approximated by the equation:

$$U = (-1) C_K z_+ z_- / (r_+ + r_-)$$

where the z's are the charges on the cation and anion, and the r's are their radii; C<sub>K</sub> is a constant. HINT: Use the reaction



where M is small and M' is big to carry out your analysis. Write the equations, use mathematics to expand them until you prove the point. Second HINT: Some problems in life take a while to solve, especially if the solution is general and eloquent. This isn't hard, but won't plop down like a dog at your feet either.

15.1. Zinc metal dissolves in dilute acid solution to produce Zn<sup>2+</sup>(aq) and H<sub>2</sub> gas. Write a balanced reaction for this process. What is being oxidized in this process? What elements other than Zn would do this? Which wouldn't?

15.2. Uranium metal dissolves in dilute acid solution to produce UO<sub>2</sub><sup>2+</sup>(aq) and H<sub>2</sub> gas. Write a balanced reaction for this process.

15.3. What is the significance of the (aq) in the last two questions?

16.0. Why do we write U(VI) in problem 15.2. as  $\text{UO}_2^{2+}(\text{aq})$ , but Zn(II) as  $\text{Zn}^{2+}(\text{aq})$ ?

16. Compare  $\text{Na}(\text{H}_2\text{O})_6^+$ , which has no tendency to become  $\text{Na}(\text{H}_2\text{O})_5(\text{OH})$  with  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ , which except in very strong acid solution exists as  $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  (or less positive species such as  $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ), with  $\text{ClO}_4^-$ , which is difficult to protonate. What simple factors might you use to account for this behavior, which is very common among other elements in the periodic table? HINT: An excellent example where “shifting words” doesn't do much to answer the question; i.e., “metal versus non-metal” doesn't tell me much; I simply ask what is a metal and why does it have the properties that it does?

17. What is the oxidation number (oxidation state) of Cl in each of the following:  $\text{HClO}_4$ ;  $\text{ClO}_3^-$ ;  $\text{ClF}_2^+$ ;  $\text{HOCl}$ ;  $\text{AsCl}_3$ .

18.0.1. What might “oxidation number” roughly measure?

18.0.2. What is electronegativity?

18.0.3. Which is more electronegative, F or  $\text{F}^-$ ?

18.0.4. Which is more electronegative, Cl(I), Cl(III), or Cl(V)?

18.0.5. Which is more electronegative, F or  $\text{S}^{2+}$ ? HINT: I care less about your ability to know the answer than I do about your ability to think straight about the issue.

18. Which is most basic,  $\text{PO}_4^{3-}$ , or  $\text{P}_2\text{O}_7^{4-}$ ? Is there more than one factor to consider? What did you think about?

19.0.1. What species are present in pure water?

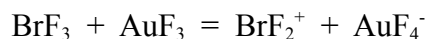
19.0.2. Why is  $[\text{O}^{2-}(\text{aq})]$  very very low in pure water?

19.0.3. What species are present in liquid  $\text{NH}_3$ ?

19.0.4. What is  $[\text{N}^{3-}(\text{NH}_3)]$ , that is, the concentration of nitride ion in liquid ammonia?

19.0.5. Ionic species are present in liquid  $\text{BrF}_3$ . What are they?

19.0.6. How does the reaction, all in liquid  $\text{BrF}_3$ ,



compare to a process in water. Write an example of the latter.

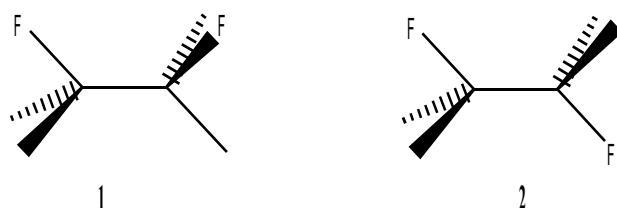
19. Show in detail how a (chain, O-P-O-P-O-P-O, with things hanging off) molecule of  $\text{P}_3\text{O}_{10}^{5-}$  is converted into cyclic  $\text{P}_3\text{O}_9^{3-}$  in water solution. What conditions do you think are necessary in the medium to facilitate the process?

20.0.1. A sample of  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  weighing 3.4750 g is heated in a TGA apparatus to  $165^\circ\text{C}$ . Over the range of  $160$ - $165^\circ\text{C}$  the sample has a decrease in weight of 0.221g. Give a reasonable hypothesis to explain what happens to the chemical.

20. When 0.15g of  $\text{BCl}_3$  is reacted with 0.08g of  $\text{BO}$  to form  $\text{B}_2\text{Cl}_4$ , which reagent is limiting? What is the theoretical yield of  $\text{B}_2\text{Cl}_4$ ?

21.1. In electron diffraction heavy atoms have a greater effect on the electrons than do a hydrogen atom does. Why?

21.2. Assuming that a hydrogen atom has no effect, guess how the radial distribution plots for gauche  $\text{C}_2\text{H}_4\text{F}_2$ , **1**, and anti- $\text{C}_2\text{H}_4\text{F}_2$ , **2**, would differ, if at all. Give a cogent discussion.



21.3. What would you expect for the radial distribution curve for gas phase electron diffraction of difluoroethane if it rotated about the central C-C bond freely? Explain your reasoning.

22.0.1. In the world of small objects, such as electrons and molecules, the energies of all bounded systems are quantized. This is true of the rotation of a molecule about its center of mass. The spacing between the energy levels in rotational motion depends on the moment of inertia of the molecule about each of three cartesian axes. The moment of inertia is defined:

$$I_x = \sum m_i r_i^2$$

where  $m_i$  is the mass of atom  $i$  and  $r_i$  is the distance from the  $x$  axes. Similar equations hold for  $I_y$  and  $I_z$ . Consider the water molecule and let the  $z$  axis be through the oxygen atom and bisect the H-O-H angle. If the O-H bond is  $0.957\text{\AA}$  and the H-O-H angle is  $104.5^\circ$ , find the moment of inertia about the  $z$  axis. HINT: Your answer can be in units of  $\text{kg \AA}^2$ , but should NOT be in units of “per mole.”

22.0.2. What is the Lewis structure of HCN? What does VSEPR predict for the geometry of this molecule?

22.0.2. There is another isomer of HCN that has the form HNC. Draw the Lewis structure. Which isomer do you predict is most stable?

22.0.3. In contrast to HCN (see 22.0.2.) there is evidence from rotational spectra that the analogue with C replaced with Si and N with P has the form HPSi with an H-P-Si angle of  $60^\circ$ . This is presumably because P and Si are much more reluctant to form double or triple bonds than are C and N. This structure was assigned on the basis of fitting experimental  $I$  values (see 22.0.1.) derived from the spectra with those calculated based on structure. In the table are the  $x$ ,  $y$ , and  $z$  coordinates of the three atoms in HPSi for the observed structure. Calculate the three  $I$  values and compare them

with the experimental values of 61.5539, 1.662, and 63.221 g Å<sup>2</sup>/mole about the x, y, and z axes, respectively.

Atom	x	y	z
H	-1.2733	-0.2340	0.0000
P	0.0218	-0.9667	0.0000
Si	0.0218	1.0787	0.0000

22.0.4. To show how sensitive this method can be, here are the coordinates for a HPSi molecule with the same bond distances, but with the H-P-Si angle increased by 10° to 70.5°. Calculate the three I values for this structure and compare with the observed values.

Atom	x	y	z
H	-1.37907	-0.46604	0.0000
P	0.02358	-0.96274	0.0000
Si	0.02358	1.08266	0.0000

22.0.5. Look at the difference between the two structures in 22.0.3. and 22.0.4. and be sure you see why their I values differ. HINT: It is the ratio of I<sub>x</sub> for one structure versus that for another that is critical.

22.0.6. A molecule with formula N<sub>2</sub>O has two possible arrangements of atoms, NNO and NON. Give the Lewis structure of each.

22.0.7. Which of the two from exercise 22.0.6. is most stable?

22.0.8. N<sub>2</sub>O is a reasonably reactive compound at elevated temperatures and supports combustion of wood as well as O<sub>2</sub> does when hot. What in your Lewis structure might suggest this?

22.1. Demonstrate that ethylene has a C<sub>2</sub> symmetry operation; does it have more than one?

22.2. Does B<sub>2</sub>H<sub>6</sub> have a plane of symmetry? Does it have a C<sub>2</sub> axis of rotation? Is anything wrong with the Lewis structure of this molecule? HINT: You may have to look up the structure of this compound.

23.1. Write a Lewis structure for B<sub>2</sub>Cl<sub>4</sub>.

23.2. What does your structure of 23.1. say about the question: "Is B<sub>2</sub>Cl<sub>4</sub> of D<sub>2d</sub> or D<sub>2h</sub> symmetry?"

23.3. In view of your answer to 23.2., comment on what a Lewis structure is trying to tell you and what it has no ability to tell you.

24.1. What symmetry operations are present in **1**?

24.2. What symmetry operations are present in  $\mathbf{2}$ ?

24.3. Find the symmetry operations in  $\text{H}_3\text{PO}$ .

25.1. What proper symmetry operations are present in (a)  $\text{SO}_3$ , (b) planar  $\text{C}_2\text{O}_4^{2-}$ , and (c)  $\text{trans-PtCl}_2(\text{NH}_3)\text{Br}^-$ . HINT: In the last case, ignore the hydrogen atoms on the nitrogen.

25.2. Find the improper symmetry operations in the molecules of 24.1.

26.0.1. Find the symmetry operations in a water molecule. Number the two (identical) hydrogen atoms 1 and 2. Now for each symmetry operation for  $\text{H}_2\text{O}$  determine how many of these hydrogen atoms retain their number after the symmetry operation.

26.0.2. Again, for a water molecule: Put a vector through the two hydrogen atoms starting at hydrogen atom 1 and pointing to hydrogen atom 2. For each symmetry operation for  $\text{H}_2\text{O}$  determine a number that logically tells you what happens to the vector. HINT: Remember that vectors have direction, that you can multiply a vector by 1 and get it back again, or by -1 and reverse its sign, its direction.

26.0.3. Still for a water molecule: Imagine one hydrogen atom moving toward the oxygen atom along its O-H bond. Put in a little vector to denote this velocity of this motion. Imagine the other hydrogen atom moving toward the oxygen atom along its O-H bond with the same velocity. Put in a vector for that. Now determine what happens to the pair of vectors (taken together) under each of the symmetry operations of the water molecule. HINT: Consider the pair of vectors as one object: Either the pair goes to themselves, or the pair disappears, or the pair goes to minus themselves.

26.0.4. Ugh, more water molecule: Imagine one hydrogen atom moving toward the oxygen atom along the O-H bond. Put in a little vector to denote this velocity of this motion. Imagine the other hydrogen atom moving away from the oxygen atom along its O-H bond with the same speed, and, therefore, reversed velocity. Put in a vector for that velocity. Now determine what happens to the pair of vectors (taken together) under each of the symmetry operations of the water molecule. HINT: See the hint for exercise 26.0.3.

26.0.5. Consider the  $\text{SO}_3$  molecule. Number the three (identical) oxygens 1, 2, and 3. Now for each symmetry operation for  $\text{SO}_3$  determine how many of these oxygen atoms retain their number after the symmetry operation. For instance, for a  $180^\circ$  rotation about the S-O(1) bond, O atoms 2 and 3 are not where they were, but O(1) is. So the number associated with that rotation is "1".

26.0.6. Consider  $\text{C}_2\text{O}_4^{2-}$ . Put a little vector on each oxygen atom reflecting the velocity of its motion. Assume all are moving toward the carbon atom to which the oxygen atom is bonded at the same velocity. Now find how many of these vectors go into themselves for each symmetry operation and make a list of those numbers.

26.0.7. Find the various sets of characteristic numbers that add up to your answer to 26.0.6. Here is the list developed in class:

**D<sub>2h</sub>**

	E	C <sub>2</sub> (z)	C <sub>2</sub> (y)	C <sub>2</sub> (x)	i	σ (xy)	σ (xz)	σ (yz)
<b>A<sub>g</sub></b>	1	1	1	1	1	1	1	1
<b>B<sub>1g</sub></b>	1	1	-1	-1	1	1	-1	-1
<b>B<sub>2g</sub></b>	1	-1	1	-1	1	-1	1	-1
<b>B<sub>3g</sub></b>	1	-1	-1	1	1	-1	-1	1
<b>A<sub>u</sub></b>	1	1	1	1	-1	-1	-1	-1
<b>B<sub>1u</sub></b>	1	1	-1	-1	-1	-1	1	1
<b>B<sub>2u</sub></b>	1	-1	1	-1	-1	1	-1	1
<b>B<sub>3u</sub></b>	1	-1	-1	1	-1	1	1	-1

26.1. See Exercise 26.0.7. How many C-O stretches would you expect in the IR for planar C<sub>2</sub>O<sub>4</sub><sup>2-</sup>?

26.2. How many Pt-Cl stretches would you expect in the IR for trans-PtCl<sub>2</sub>(NH<sub>3</sub>)Br?

27. Use resonance to determine the charge on each atom of acetate anion; nitrate anion; the allyl (C<sub>3</sub>H<sub>6</sub><sup>+</sup>) cation.

28. Find the VSEPR structure of ClO<sub>4</sub><sup>-</sup>, NCS<sup>-</sup>, O<sub>3</sub>, CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, C<sub>2</sub>H<sub>2</sub>, Cl<sub>2</sub>CCCCl<sub>2</sub>.

29.0.1. Find the value of

$$-\hbar^2/(2m) d^2/dx^2 \psi$$

where

$$\psi = A e^{-ax}$$

where A and a are constants of some magnitude or another.

29.0.2. Is the answer some constant times  $\psi$  back again? If so, congratulations, you have solved the Schrodinger equation!

29.0.3. What is wrong with the wave function

$$\psi = A e^{-ax}$$

for a parve on a pole that extends from  $x = 0$  to  $x = 1$ ?

29.1. A parve is trapped on a pole with zero potential energy. What happens to the lowest allowed energy of the parve if the length of the pole is doubled?

29.2. Sketch the lowest ( $n = 1$ ) wave function for a parve on a pole.