PROFESSIONAL DEVELOPMENT

AP® Chemistry

Alternative Approaches to Teaching Traditional Topics

Curriculum Module

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Introduction

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As we look forward to teaching chemistry in the 21st century, we also anticipate some of the changes that will be occurring. Much of what we have done in the past has been good, but some aspects of our science educational system have been seriously flawed. As we move into this new century, we realize that "lecture" as a sole tool of imparting scientific knowledge is less than satisfactory. And students who only recall facts do not become the critical thinkers that we need to solve the societal problems we are facing. New times call for new methods and serious rethinking of how we go about imparting scientific knowledge to our students.

While this curriculum module seems to be very divergent in theme, it is really unified by using new approaches to guide students into deeper and more thorough understanding of the concepts. The kinetics section guides students using simulations and graphing to understand some of the underlying concepts occurring during chemical reactions. The electron density lessons provide a new way of approaching more difficult concepts of intermolecular forces, ionization energies and sizes of ions.

While some of this material might seem different or even strange at first, I invite you to try these modules with your students. I think that you will find that the guided inquiry units deepen student understanding and help clarify misconceptions.

Kinetics

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Chemical Kinetics in a Different "Order"

Chemical kinetics is the study of the speed of chemical reactions. Most students have some intuition about speeds of chemical reactions. Low temperatures slow down the speed of chemical reactions, and high temperatures increase the speed of chemical reactions. However, students do not have experience with concentration effects. Most students have heard the word *catalyst* and are likely to associate the word with an increase in the speed of a reaction. Students, however, do not have a clear understanding of exactly what catalyst means, other than that it makes reactions go faster.

Before starting, determine students' prior knowledge on the subject of chemical kinetics.

When most teachers begin a discussion of chemical kinetics, it generally takes the form we most often see in textbooks. Introduce the definition of the rate (velocity) of a chemical reaction, followed by a discussion of factors that affect rates of reactions, etc.

What follows is an alternative introduction to chemical kinetics that will provide an introduction to chemical kinetics from a particulate level and introduce students to a number of important ideas, including reaction mechanism, elementary steps, bimolecular reactions, intermediates, concerted reactions, orientation, activation energy and effective collision.

Begin this approach by looking at two chemical equations:

$$4\ HBr_{(g)} + O_{2(g)} \rightarrow 2\ Br_{2(g)} + 2\ H_2O_{(g)}$$

$$NO_{(g)} + CO_{2(g)} \rightarrow NO_{2(g)} + CO_{(g)}$$

When looking at the equations, discuss with students information they already know about the reactions. Discuss the following: stoichiometry, structure of the reactants and the products, enthalpy of the reaction (how it is calculated), and whether the reactions

are exothermic or endothermic (the HBr reaction has a ΔH of -276 kJ mol^{-1} and the NO reaction has a ΔH of +226 kJ mol^{-1}). Next ask students — and this is more than likely the first time students have considered — how the reactants are converted to products. That is (clarify the question), how do four molecules of HBr and one molecule of O_2 produce two molecules of Br_2 and two molecules of H_2O? Most students will not be able to explain this concept. Even though all the species are in the gas phase, most students will not consider how the molecules of the reactants are moving around, colliding with one another and the walls of the container. It is difficult for students to understand this concept after the first reaction. Have the students consider the second reaction and ask the same question: How do the reactants NO and CO_2 get to NO_2 and CO?

Here you may be able to elicit a response. Again all the molecules are in the gas phase. In the second reaction the only thing that is happening is that an oxygen atom is transferred from CO_2 to NO. Can the students explain this concept? If they do not immediately give an explanation, allow them to draw Lewis structures of the reactants and products. What differences do they see in the structures? NO and NO_2 are complex because they both have unpaired electrons. That is not a critical issue at this point; we want them to explain that the oxygen atom has moved from the C to the N. Drawing the structures will allow the students to think about the arrangement of the atoms, an important topic for discussion.

Once you get the students to focus on the fact that an oxygen atom has been transferred, the next question becomes how does this transfer occur? How can an oxygen atom move from CO_2 to NO_2? Here we are trying to get the students to state that a collision has to occur between NO and CO_2. How would a collision occur? Remember, all the reactants are in the gas phase, so how would a gas sample of the two reactants appear? Students should provide descriptions of the molecules in the gas phase as moving around colliding with one another and the walls of the container. Once the students realize that the molecules are moving around and colliding, get them to think about orientation issues. If an NO molecule collides with a CO_2 molecule, how would the oxygen atom transfer? Here some students will recognize that the orientation of the collision is important. They have generated the Lewis structures of all the molecules, so they know the oxygen atom is moving from a C atom to the nitrogen atom. The orientation of the NO when it collides with the CO_2 has to occur when the nitrogen in NO hits a terminal oxygen atom. A collision of a terminal oxygen atom in CO_2 with the oxygen atom in NO is an orientation that could generate a product. Similarly, if the nitrogen atom in NO collides with the carbon atom in CO_2 one would not expect an effective collision.

Ask if anyone else has any thoughts on other factors that might be important for a collision between the two reactant molecules to be effective. If there is no response, ask students what is happening in a gas sample. Are all the molecules in the sample moving at the same speed? Yes? No? If no, then ask for explanations. Get the students to indicate that the molecules are moving at different speeds — some are slow, some are fast, and some are very slow and some are very fast. Ask them to consider the importance of speed for a collision to be effective. What has to happen for an oxygen atom to be transferred (if we were able to take pictures very quickly during an effective collision)? Here we want the

students to indicate that the C=O double bond has to be broken (endothermic) and an N-O bond has to form (exothermic). Hopefully they will indicate that collisions between slow molecules might not be effective even if the orientation were correct. So now we have three criteria for the conversion of reactants to products: there has to be a collision between the two particles; the orientation must be optimum; and the particles must have sufficient energy (be moving fast enough).

To see to what extent the students have picked up on these three important factors that control the speed of a chemical reaction, there are two very nice simulations available online that will reinforce these ideas. The simulations are:

Reaction: R + BG ----> RG + B
http://introchem.chem.okstate.edu/DCICLA/KRGBM.htm

Reaction: 2G + B ----> G_2B
http://introchem.chem.okstate.edu/DCICLA/K2GBM.htm

Reaction video link: http://genchem1.chem.okstate.edu/BDA/MechKinetic.html

These two simulations were written and developed by John Gelder (Oklahoma State University), Michael Abraham (The University of Oklahoma) and Kirk Haines (a student programmer).

These simulations include inquiry activities that are available at the MoLE Project website (http://genchem1.chem.okstate.edu/CCLI/Startup.html). To access the simulations and written activities, teachers must provide a limited amount of information about themselves (name, e-mail address and school). The simulations are Java-based and require (in some cases) that the version of the Web browser being used be accessorized with some software. The page at http://genchem1.chem.okstate.edu/CCLI/Help.html provides the necessary information to run the simulations.

The first simulation that models the reaction is:

R + BG ----> RG + B

This reaction involves an atom transfer, similar to the reaction between carbon dioxide and nitrogen monoxide. The simulation models the gas phase collisions between the reactants, and when the orientation is correct and the total energy of the collision is correct, a reaction occurs. Begin the discussion by allowing the students to watch the reactants (R and BG) move around the container colliding. Ask the students to describe what they observe. They should observe an atom (red) and a molecule (blue/green) moving in the container. After everyone observes the same thing, write the chemical equation and ask the students: What must happen for the reactants to convert to products? Based on the previous discussion students should recognize that the R atom must collide with the BG molecule such that the R atom hits the G part of the BG molecule. When the collision occurs, a minimum amount of energy is needed. Once these factors have been discussed, click on the reaction button and allow the reaction to occur. Describe the chart recorder and what it shows. The chart recorder tracks the

amounts of all four substances over the course of the reaction. Change the drop-down option to Replay, and "rewind" the reaction to watch effective and noneffective collisions between the reactants in slow motion. During the discussion of this reaction, terms such as "bimolecular collision" can be introduced. The second simulation will introduce the concept of a mechanism. It is important to point out that the reaction occurs just as the chemical equation is written.

Now run the second simulation. Explain that this is a new reaction (which the students will immediately recognize). Ask students the formula of each of the two reactants. Explain that they are to watch what happens when you start the reaction, and based on what they observe, write the balanced chemical equation. Once the students have the correct balanced chemical equation, ask whether the reaction occurred in a single step or in more than one step.

Now students are ready to use the word *mechanism*, as a stepwise path that converts reactants to products. The first reaction occurs in a single step and is called a concerted reaction. The second reaction occurs by a two-step mechanism; both steps are bimolecular. Also discuss the intermediate species in the reaction. This is a substance that is produced in an early step of a mechanism and is consumed in a later step. Although it is a little difficult to differentiate in the second reaction, one of the steps is slower than the other. This is called the rate determining step.

Now students are ready to revisit the more complicated reaction,

$$4\ HBr_{(g)} + O2_{(g)} \rightarrow 2\ Br_{2(g)} + 2\ H_2O_{(g)}$$

The students are not likely to be able to come up with a mechanism, but they should recognize that based on the stoichiometry of the reaction, the reaction will not be a concerted reaction.

A proposed mechanism that you can share with the students is:

$$HBr + O_2 \rightarrow HOOBr$$

$$HOOBr + HBr \rightarrow HOBr + HOBr$$

$$HOBr + HBr \rightarrow H_2O + Br_2$$

$$HOBr + HBr \rightarrow H_2O + Br_2$$

Mechanisms consist of a series of elementary steps that when added together yield the overall reaction. When we use the term *elementary* step, we mean that each step of the mechanism occurs exactly as it is written. This is not usually true for the overall reaction, unless the reaction is concerted.

Did you ever wonder why some chemical reactions proceed lightning fast, while others take months, years or even thousands of years? Mixing potassium metal with water results in fast, violent reaction. Yet the decomposition of carbon in the form of diamond

to carbon in the form of graphite takes thousands of years. Did you ever wonder how catalysts work to increase the speed of a chemical reaction? Or why changing the temperature has such a dramatic change in the speed of a reaction?

Chemical kinetics is the study of the rates and mechanisms of chemical reactions. Measuring the rate or speed of a chemical reaction is straightforward. Remember, speed is a change in distance with time. Speed in chemical reactions is simply the change in the amount of a reactant or product with time. The way this information is obtained in the laboratory will depend on the particular reaction that is performed but generally consists of using some technique to measure the concentration of one of the species in a chemical reaction over time. For example, if in a particular reaction one of the reacting chemicals undergoes a color change, it would be possible to measure the intensity of the color every minute. If a gas was produced in a chemical reaction, it would be possible to measure the volume of gas produced over time, with the correct equipment. But what do we do with this experimental information once we have collected it?

Chemical kinetics concerns itself with what happens while a reaction is under way, not just in the final outcome. Chemical kinetics does not change the chemical reaction; it simply provides a clearer picture of what happens during the progress of the chemical reaction. With this knowledge it is possible to control the conditions of a reaction to increase the amount of the desired products. If we were able to travel to the molecular level and watch the progress of the reactants in the course of the reaction and the many changes they undergo in proceeding to the products, we would observe chemical kinetics. If we were able to observe firsthand how the electrons behaved during a chemical reaction we would see chemical kinetics firsthand.

In chemical kinetics we are interested in what happens to reactants during the course of the chemical reaction. The best way to try to understand reactions in this way is to study how fast the reactions occur, i.e., the rate of a chemical reaction. We will find that reactions, even reactions that are unrelated chemically, exhibit behavior associated with the speed that allows a chemist to classify them in a limited number of categories.

In summary, chemical kinetics is the study of:

1. The rate at which reactants are converted to products during the course of a chemical reaction.
2. The factors, which include temperature, pressure, concentration, catalyst and surface area, that affect the rate of a chemical reaction.
3. The sequence of steps, or the mechanism, that we believe occurs when reactants are converted to products.

Teaching Integrated Rate Law via Graphing

The integrated rate law can often be overwhelming to students. However, when application is related to graphing, order can easily be determined.

Present the integrated rate law equations in the form of a straight line. When the equations are written in the form of y = mx + b; it is easy to determine which components should be graphed to yield a straight line. Note that the slope will be equal to "k" — the rate law constant. Performing a linear transformation on data often clarifies data in the science classroom.

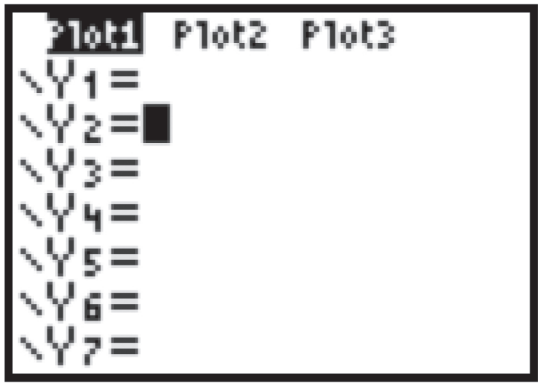
Zero order:	$[A] = -kt + [A]_o$
First order:	$\ln[A] = -kt + \ln[A]_o$
Second order:	$1/[A] = kt + 1/[A]_o$

Graphing Calculator (TI-84+) Instructions

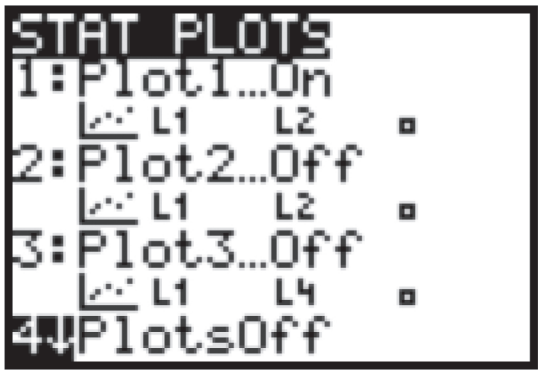
If teaching students to graph as a classroom activity, have the students do a bit of housekeeping on the calculator before beginning this exercise. It is difficult to view mistakes unless everyone is on the "same page."

Housekeeping: These steps may be completed in any order.

1. **Y=** clear any random equations

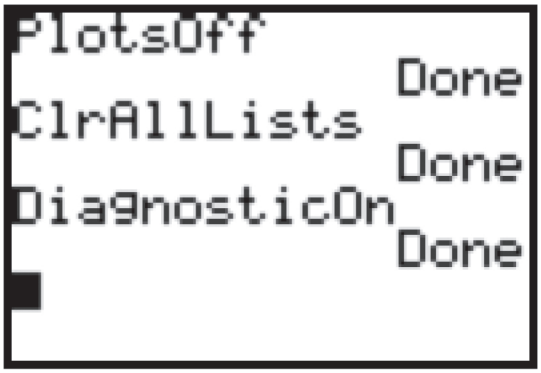


2. **2nd Y=** (turn off all plots)



3. **2nd +** (this takes you to memory — clear all lists)

4. **2nd 0** (takes you to catalog — turn on diagnostics)

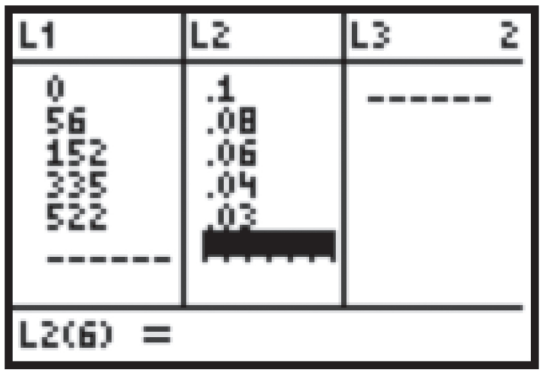


Given a list of data of time and concentrations, enter time in list 1 and concentration in list 2. (STAT: edit to find lists)

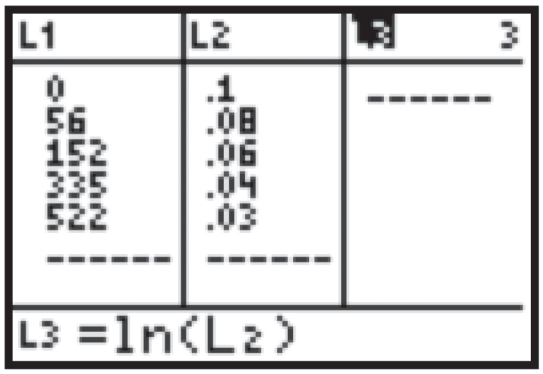
Data was collected in the table below for the following dimerization:

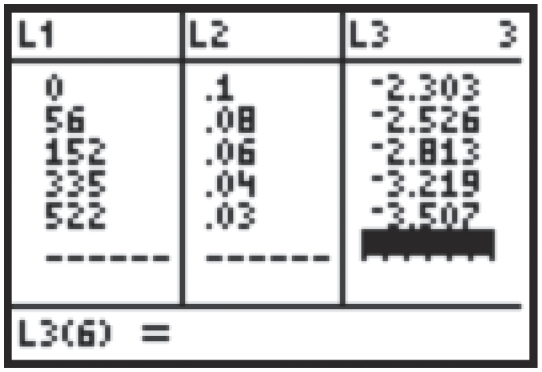
$$2\ C_2F_{4(g)} \rightarrow C_4F_{8(g)}$$

$[C_2F_4]$	Time (s)
0.100	0
0.080	56
0.060	152
0.040	335
0.030	522

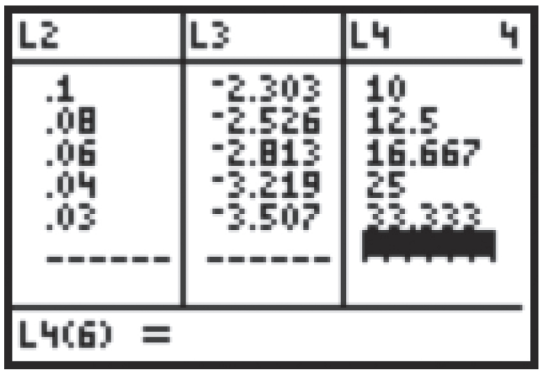


Arrow over to list 3; arrow up to highlight L3; type ln L2 and enter; this transforms all of the concentrations into ln of concentration.



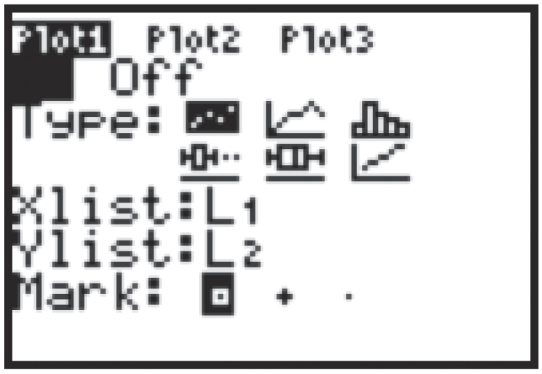


Arrow over to L4 and arrow up to highlight L4; type 1/L2 and enter; this transforms all of the concentrations into the inverse.

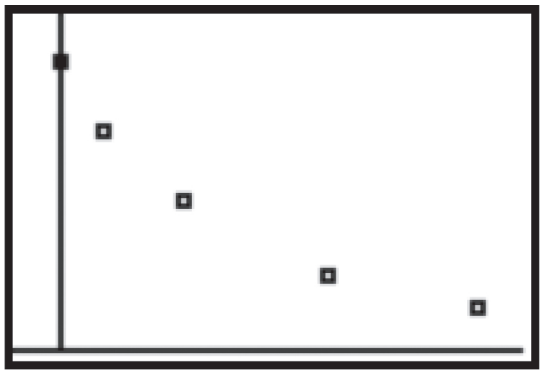


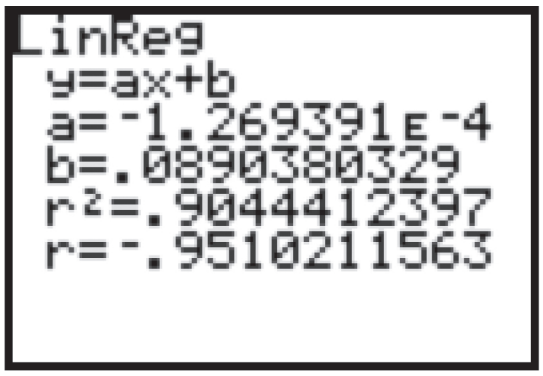
Now you are ready to view the graphs.

2nd Y= takes you to STATPLOT; turn on Plot 1; be sure to choose the first graph (scatter plot) to view your data; be sure that X = L1 and Y = L2; choose any type of mark.

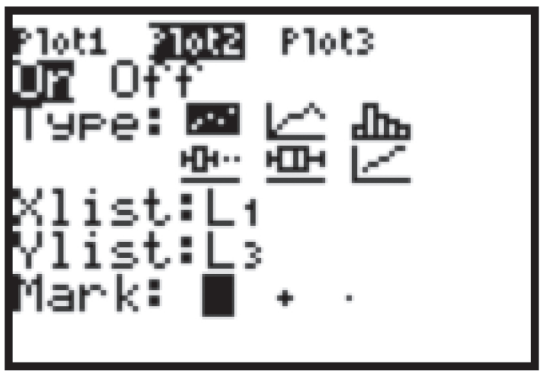


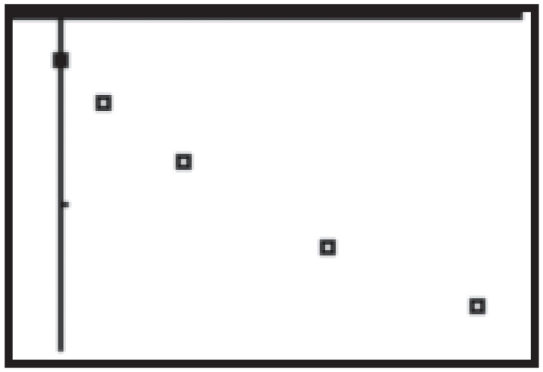
Press the Zoom key and then the number 9; this will automatically fit the data to your window. Look at the graph; if the graph appears to be a straight line, then calculate the equation for a straight line and look at the correlation coefficient. Press STAT→CALC and choose "4" linear regression; be sure to tell the calculator what two sets of data are used for calculation.

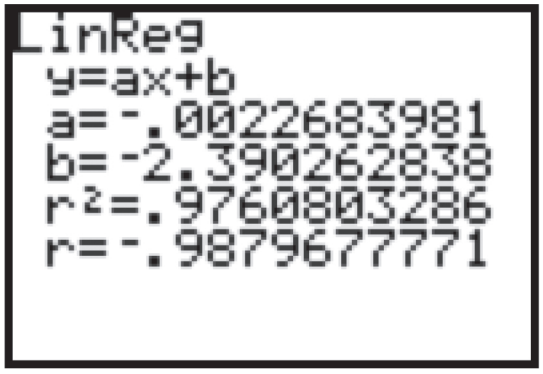




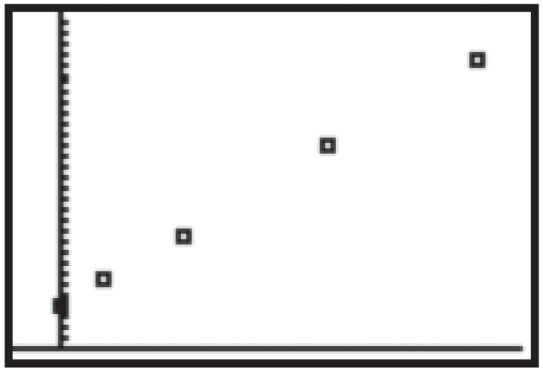
Check next for first order: Turn off Plot 1 and turn on Plot 2. Follow the steps above, changing Y= to L3 instead of L2; view the graph and calculate the equation.

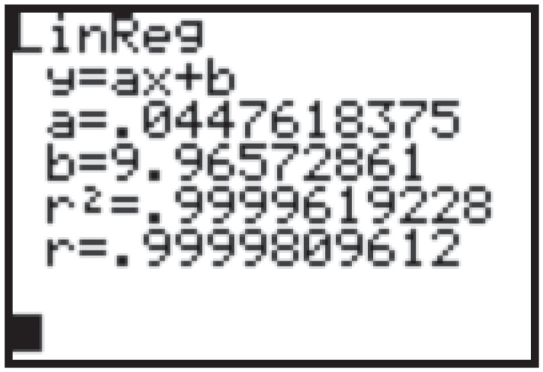






Check next for second order: Turn off Plot 2 and turn on Plot 3. Follow steps above, changing Y= to L4; view the graph and calculate the equation.





To determine if the order is zero, first or second order, choose the plot that gives the best linear fit of the data (the correlation coefficient closest to the number 1).

The last plot (L1 vs. L4) yields the best-fit line. The reaction must be 2nd order with respect to C_2H_4.

Once this is determined, the slope ("a") of the line will give the value of the rate law constant.

Graphing via the calculator is a valuable tool and a great time-saving instrument that allows students to explore and identify order and rate constant quickly and with great success!

Kinetics Sample Plan Guide

Schedule:

50-minute class periods (four days per week); one double lab period (100 minutes) per week

Day 1:

Introduction to kinetics via mechanisms (brainstorming session, animation of reaction mechanisms, writing mechanisms). So … discussion of collision theory; brief introduction into order of reaction. Assignment: Read kinetics chapter; begin homework problems. (Assign a wide range of problems from end of text or favorite source — OWL Cenage Publishing homework system is a great online homework system with immediate feedback to the student.) (50 minutes)

Day 2:

What is rate of a reaction? Exploring the rate law and factors that affect rate (demos). Hand out AP Kinetics worksheet (due day before exam). (50 minutes)

Day 3:

Introduction of methods used to calculate rates of reaction: instantaneous rates, differential rate law, integrated rate law, mechanisms. Calculate instantaneous rate from graph; calculate order from initial rate data. (50 minutes)

Day 4:

Using graphical methods to determine order from laboratory data. Work problem with students using one of the following: graphing calculator (TI-84+), Logger Pro software or Excel. (50 minutes)

Day 5:

Pre-lab Iodine Clock and Crystal Violet (both parts). Perform lab — Iodine Clock reaction. (100 minutes)

Day 6:

Perform Crystal Violet lab with temperature extension. (Advanced Chemistry with Vernier) (50 minutes)

Day 7:

Post-lab experiments. Discussion of how to process data, etc. Introduce the Arrhenius equation and discuss how this can be used to calculate the activation energy for the Crystal Violet experiment. (50 minutes)

Day 8:

Quiz over calculation of rate law. Discussion of catalysis (homogeneous and heterogeneous) and effect on rate (demo Cobalt Catalyst — Flinn); inhibitors and effect on rate. (50 minutes)

Day 9:

Using integrated rate law to calculate half-life problems. Answer questions from homework problems; AP® worksheet is due. (50 minutes)

Day 10:

Exam Kinetics (100 minutes)

Kinetic Worksheet

Name: _____

Problem 1: 1991 B

$$2\ ClO_2(g) + F_2(g) \rightarrow 2\ ClO_2F(g)$$

The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial $[ClO_2]$ (mol L^{-1})	Initial $[F_2]$ (mol L^{-1})	Initial Rate of Increase of $[ClO_2F]$ (mol L^{-1} sec^{-1})
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.20	9.6×10^{-3}

(a) Write the rate law expression for the reaction above.

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of $[F_2]$?

(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a)? Justify your choice.

I.

$ClO_2 + F_2 \leftrightarrow ClO_2F_2$ (fast)

$ClO_2F_2 \rightarrow ClO_2F + F$ (slow)

$ClO_2 + F \rightarrow ClO_2F$ (fast)

II.

$F_2 \rightarrow 2\ F$ (slow)

$2\ (ClO_2 + F \rightarrow ClO_2F)$ (fast)

Problem 2: 1972

$$2\ A + 2\ B \rightarrow C + D$$

The following data about the reaction above were obtained from three experiments.

Experiment	[A]	[B]	Initial Rate of Formation of C (mole·liter^{-1} min^{-1})
1	0.60	0.15	6.3×10^{-3}
2	0.20	0.60	2.8×10^{-3}
3	0.20	0.15	7.0×10^{-4}

(a) What is the rate equation for the reaction?

(b) What is the numerical value of the rate constant *k*? What are its dimensions?

(c) Propose a reaction mechanism for this reaction.

Problem 3: 1974 D

A measure of the rate of a reaction is its half-life. One method of determining the half-life of a first order reaction is to plot certain appropriate data. Sketch a graph that illustrates the application of such a method. Label each axis with its name and appropriate units, and show how the half-life can be obtained from the graph.

Problem 4: 1984 B

For a hypothetical chemical reaction that has the stoichiometry 2 X + Y → Z, the following initial rate data were obtained. All measurements were made at the same temperature.

Initial Rate of Formation of Z (mol L^{-1} sec^{-1})	Initial $[X]_o$ (mol L^{-1})	Initial $[Y]_o$ (mol L^{-1})
7.0×10^{-4}	0.20	0.10
1.4×10^{-3}	0.40	0.20
2.8×10^{-3}	0.40	0.40
4.2×10^{-3}	0.60	0.60

(a) Give the rate law for this reaction from the data above.

(b) Calculate the specific rate constant for this reaction and specify its units.

(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are $[X]_o$ = 0.80 molar, $[Y]_o$ = 0.60 molar and $[Z]_0$ = 0 molar?

(d) From the mechanisms below select the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates.

(1) X + Y → M (slow)
X + M → Z (fast)

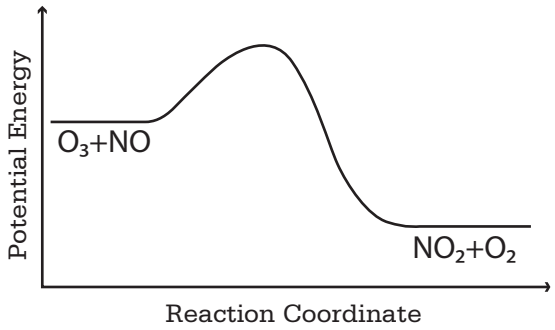
(2) X + X ↔ M (fast)
Y + M → Z (slow)

(3) Y → M (slow)
M + X → N (fast)
N + X → Z (fast)

Problem 5: 1998 D

Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram.

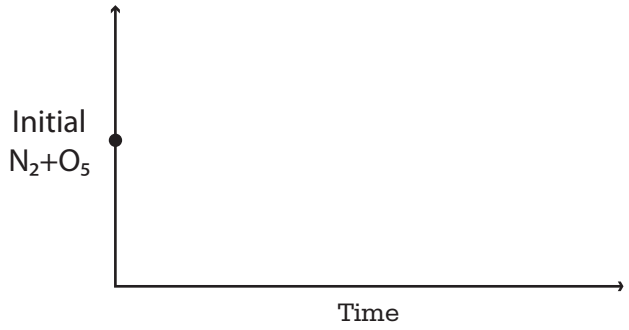


(i) The activation energy (E_a) for the forward reaction

(ii) The enthalpy change (ΔH) for the reaction

(b) The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.

(i) Using the axes, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

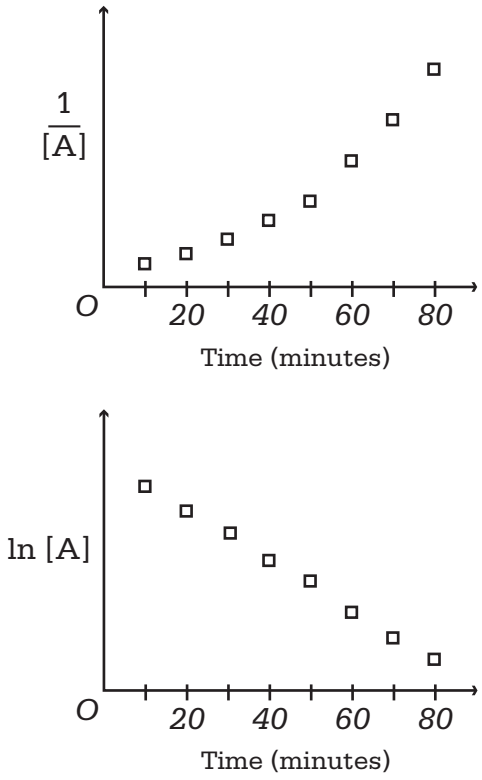


(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, *t*.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, *k*, could be determined.

(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, *k* ? Explain.

(c) Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.



Use the information in the graphs above to answer the following.

(i) Write the rate-law expression for the reaction. Justify your answer.

(ii) Describe how to determine the value of the rate constant for the reaction.

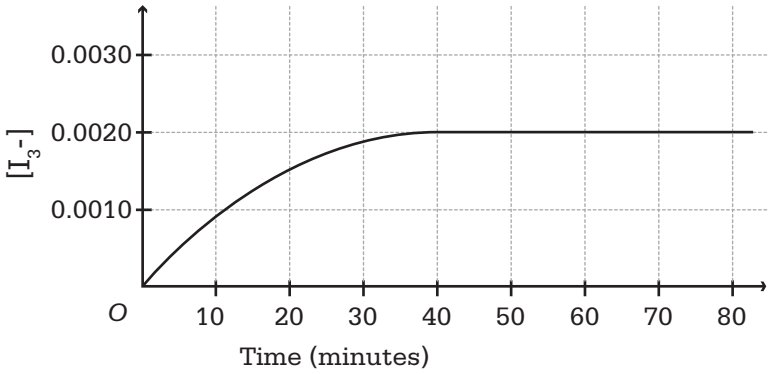
Problem 6: 2001 D

$$3\ I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_3^-(aq) + 2\ SO_4^{2-}(aq)$$

Iodide ion, $I^-(aq)$, reacts with peroxydisulfate ion, $S_2O_8^{2-}(aq)$, according to the equation above. Assume that the reaction goes to completion.

(a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert $I^-(aq)$ to $I_3^-(aq)$.

(b) In an experiment, equal volumes of 0.0120 *M* $I^-(aq)$ and 0.0040 *M* $S_2O_8^{2-}(aq)$ are mixed at 25°C. The concentration of $I_3^-(aq)$ over the following 80 minutes is shown in the graph below.



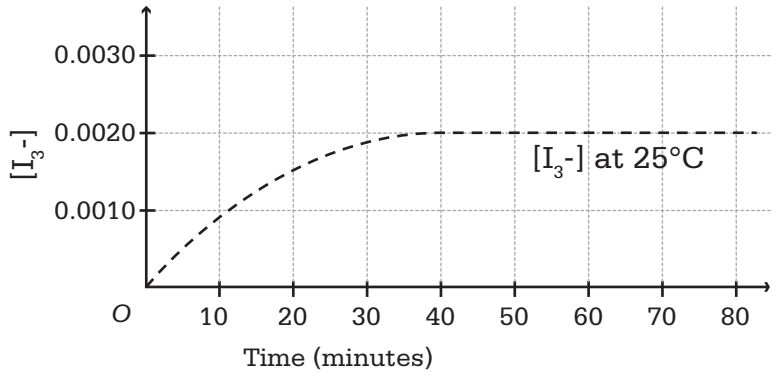
(i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning.

(ii) Explain how to determine the instantaneous rate of formation of $I_3^-(aq)$ at exactly 20 minutes. Draw on the graph above as part of your explanation.

(c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to $I^-(aq)$ and with respect to $S_2O_8^{2-}(aq)$.

(d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant, *k*, for the reaction.

(e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at 35°C rather than at 25°C.



Using Electron Density to Build Molecular Comprehension: Applications to Periodic Properties and Molecular Polarity

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What You Will Find in This Module

This module provides an introduction to using the concept of electron density to reinforce conceptual explanations of atomic size, ionization energy, bonding and polarity. A full description of electron density and how it can be used in Pre-AP® and AP Chemistry classes is given. The accompanying student worksheets could be given as take-home problems or converted to PowerPoint slides that foster class discussion on the use of atomic and molecular electron distributions to explain a wide range of phenomena that might be encountered on the AP Exam. The end of this handout provides additional problems that complement the questions in each student handout. In my classes, I use similar problems in small groups to allow students the opportunity to apply concepts of bonding and to help them explain physical and chemical phenomena in terms of molecular structure. Finally, several references from the *Journal of Chemical Education* and online resources are supplied for teachers to further explore the use of electron density in their classes.

Introduction for Teachers

One of the things that makes chemistry both exciting yet difficult for students is the interconnectiveness of material. From the fundamental ideas of thermodynamics, equilibrium, kinetics and molecular structure, a student can ultimately determine *why* chemistry happens. However, mastering and applying these ideas can be daunting.

Perhaps one of the most applicable concepts of the list is molecular structure. Indeed, I often reinforce the fact to students that if one knows the distribution and energetics of electrons in a molecule, the reactivity of that molecule can be determined. Unfortunately, to quantitatively understand electron dynamics requires an intimate knowledge of quantum mechanics, which teachers cannot supply in a first-year college chemistry course. Consequently, we introduce various visual methods and diagrams such as orbital representations and electron configurations to help students visualize electron distributions in atoms and molecules.

One of the most useful visual representations of "where the electrons are" in a molecule is *electron density*. Formally, the electron density is a mathematical function, $\rho(r)$, that defines the number of electrons that can be found within a small three-dimensional shell at a distance r from the nucleus of the atom. Formally, the electron density is found by multiplying the number of electrons in the atom or molecule by the absolute value of the square of the wavefunction for the atom or molecule. Consequently, the electron density is *not* an approximation and is easily calculated for molecular systems using computational algorithms. Thus, in allowing students to visualize problems utilizing the electron density, we are not approximating the electronic structure of a molecule at all. Instead, we are using a tool that is conceptually easy to understand and mathematically rigorous.

How does the electron density of a simple atom look? If one were to graph the electron density as a function of distance, a plot similar to Figure 1 is obtained:

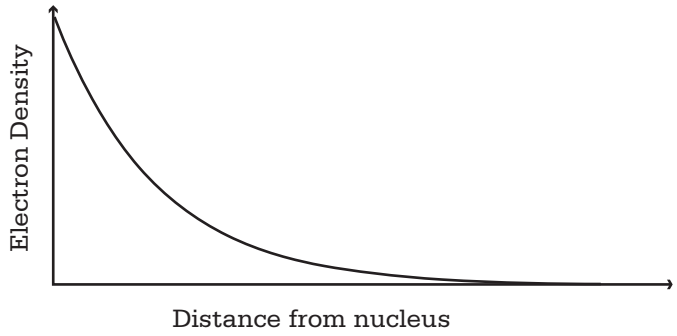


Figure 1: A sample plot of the electron density as a function of nuclear distance.

This plot agrees with what we would expect to see for this molecule. Specifically, the probability is very high that we would find electrons close to the nucleus, as indicated by the large values of electron density for electrons at a small distance from the nucleus. As you move away from the nucleus, the probability of finding electrons drops substantially.

In many cases the most convenient way to view the electron density is by visualizing a density isosurface. Specifically, this is a three-dimensional surface around the atom where the electron density has a constant value. Shown below are two different *isosurfaces* for both the magnesium atom and the water molecule. In both cases, note as the value of the electron density becomes larger, the surface contracts in size.

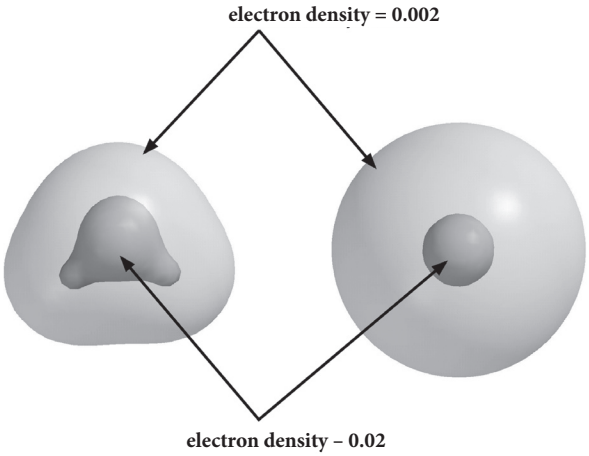


Figure 2: Isodensity surfaces of the electron density for both water (left) and magnesium (right). Note that higher isodensity surfaces capture electrons close to the nucleus.

Quantum mechanical calculations show that an electron density isosurface value of 0.002 gives an excellent description of the overall size of an atom or molecule, while values in the range of 0.080 illustrate the bonding electrons and can be used to verify candidate Lewis Structures for a molecule. Finally, higher values of electron density begin to elucidate the core electrons of atoms in molecules.

Although we can discuss an infinite number of electron density surfaces, the one students will understand most easily is what I will define as the **molecular electron density** (or MED). This is the surface discussed in the literature with an isovalue of 0.002 and is considered to be an excellent description of the size of an atom or molecule. The first handout, "Electron Density and the Sizes of Atoms and Ions," has students explore the electron density of magnesium and its ions. This handout begins with a short discussion of electron density and explains the question of why the electron density isosurfaces get *closer* to the nucleus as the value of the density becomes larger. To help students observe this trend, a short QuickTime movie is provided (http://pricelessscience.com/collegeboard/argon.mov) that shows the electron density of the argon atom at successively larger and larger values, starting with the MED. That students *observe* and *describe* the forces acting on valence electrons and, in addition, how these changes in forces affect size and ionization energy is critical to their understanding of the periodic trends and why they occur. Thus, one could use this first handout to aid both student understanding and communication skills, as they explain why the MEDs change from ion to ion. Shown below is the picture of Mg^{2+} and Mg^{3+} electron densities referenced in the handout for student comparison.

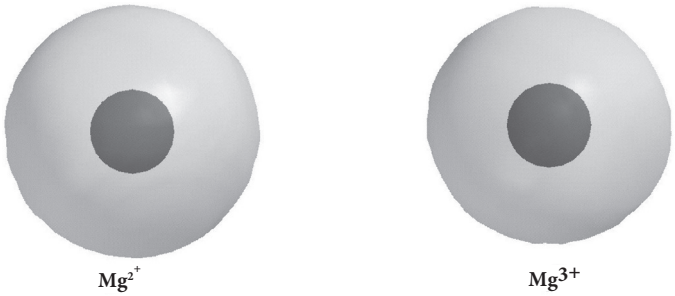


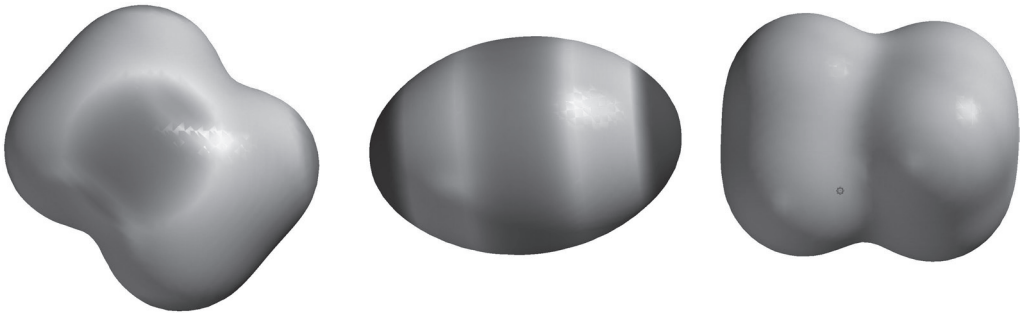
Figure 3: Electron densities of Mg^{2+} and Mg^{3+} for student comparison (see Appendix 1).

The second handout, "Electron Density of Molecules," can be used in conjunction with discussions of bond length, bond strength and polarity. The handout discusses a series of diatomic compounds formed among the halogens as well as compounds between the halogens and hydrogen. Specifically, this handout introduces and thoroughly explains the concept of the **Molecular Electrostatic Potential** (**MEP**). The problems in the handout apply this concept to the ideas of both bond polarity and molecular polarity, using simple diatomic and triatomic examples. In several places students are asked to obtain and discuss data, and from this information create mental pictures of what happens to electron distributions during bonding. The usefulness of MEPs in displaying molecular polarity is readily apparent, as molecules with a permanent dipole moment will have an asymmetry of color in the MEP. Direct correlation can also be made using electronegativity values. The end of this guide contains two summary problems to assess student understanding after the concepts of each handout have been discussed in class. Answers to these problems are included.

Additional Problems for Students

Question 1:

Shown below are the MEPs of ethane, ethene and ethyne, members of three important classes of organic molecules.



(a) Draw the Lewis diagrams for ethane, ethene and ethyne.

(b) Identify which MEP corresponds to each structure. Justify your choice.

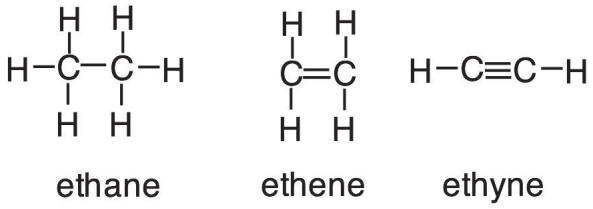
(c) Identify the hybridization of each carbon atom in the three molecules.

(d) Based on the MEPs, are the molecules polar or nonpolar? Explain.

(e) Based on the Lewis diagrams and the MEPs, account for the negative areas of electrostatic potential in the first two structures.

Answers to Question 1:

(a)



(b) The shape of the molecules allows us to see what each structure is. Ethane is comprised of two tetrahedrons and is the structure on the right. Ethene is a flat molecule and is the structure on the left. Finally, ethyne is linear and is the molecule in the middle.

(c) Ethane: sp^3, ethene: sp^2, ethyne: sp

(d) All of the MEPs are symmetric. Therefore, each molecule is nonpolar.

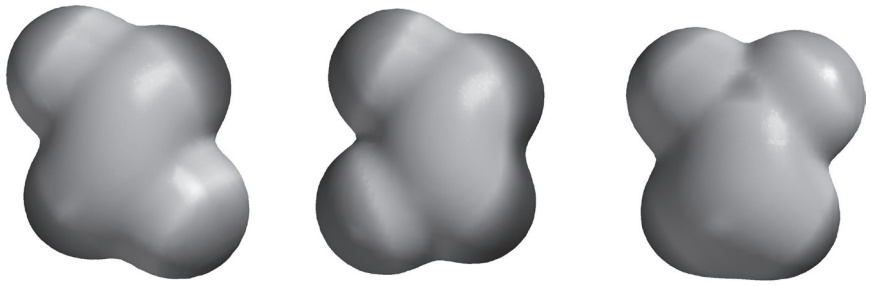
(e) The red areas of the MEPs of ethene and ethyne correspond to areas of multiple bonding. In ethane, we note specifically that the electron-rich area is above (and below if you could see it) the molecule. This corresponds to the pi bonding resulting from the overlap of p orbitals on the carbons of ethene. The triple bond is very visible in the MEP of ethyne. Relative to this triple bond, the hydrogens themselves are electron deficient.

Question 2:

Several isomers exist with the formula $C_2H_2F_2$. These isomers fall into one of two categories: **structural** isomers and **geometric** isomers.

(a) Explain the difference between a structural isomer and a geometric isomer.

(b) Draw Lewis diagrams for all possible isomers (both structural and geometric) for $C_2H_2F_2$ Shown below are the MEPs for all possible isomers of $C_2H_2F_2$.



(c) Identify which MEP belongs to each Lewis diagram. Justify your choice.

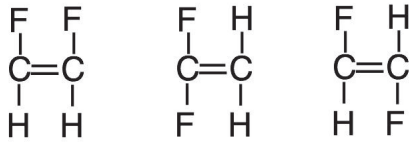
(d) Which of the isomers is polar? Explain.

(e) Based on the MEPs, if more than one isomer is polar, which has the greatest dipole moment? Justify your answer.

(f) Which of the molecules above would have the *lowest* boiling point? Explain.

Answers to Question 2:

(a) A structural isomer occurs when a molecule has the same molecular formula but is bonded differently. For example, HCN and HNC are two structural isomers. In contrast, a geometric isomer occurs when a molecule has different three-dimensional structures with the same atomic connectivity. Typically this occurs when a molecule cannot rotate a bond (as in the case above) or has nonsuperimposable mirror images (enantiomers) that have the same connectivity but cannot be converted into the same spatial structure.

(b) 

(c) Differences in electronegativity and size allow for the identification of each MEP. As F is larger and more electronegative than H, the structure on the left must correspond to the trans isomer of 1,2-difluoroethene. The middle structure is cis-1,2-difluoroethene, and the one on the right is the 1,1-difluoro isomer.

(d) Looking at asymmetry in the MEP, the 1,1-difluoro isomer and the cis-1,2-difluoro isomer are both polar, as the pulls from the fluorines cannot be canceled out on the molecule. In contrast, the trans isomer is symmetric, as each fluorine's pull is exactly canceled by the other.

(e) The cis isomer shows a greater electron asymmetry (as indicated by color). Hence, we would expect it to be more polar. (This can be checked by students using a suitable reference source such as the *Handbook of Chemistry and Physics*.)

(f) The molecule with the weakest intermolecular forces would be expected to have the lowest boiling point. In this case the trans isomer, which is not polar, will only experience London forces. Since there is no permanent polar contribution to the IM forces in this molecule, the energetic requirement needed to overcome these forces should be the smallest. Hence it should have the lowest boiling point.

Electron Density and Sizes of Atoms and Ions — Sample Student Answers

You have just watched a video depicting the **electron density** of the argon atom. Remember, the electron density is a mathematical function that describes the number of electrons of an atom or molecule that can be found within a small volume at a certain distance from the nucleus. To visualize the density, we frequently look at isosurfaces, which are a set of points from the nuclei of atoms or molecules that have a constant value of the electron density.

Consider the forces acting on an electron: If every electron had a "choice," which orbital would it choose? In accordance with the Aufbau principle, each electron would have the lowest energy (and greatest attraction to the nucleus) if it were in the 1s orbital. Only repulsion between electrons and the Pauli Exclusion Principle prevent more than two electrons from occupying an orbital. As electrons continue to fill orbitals, the electrons fill so that they will maintain the lowest total energy possible. Consequently, the **density** of electrons should be higher at closer distances to the nucleus. This is depicted in the video, as each successive picture illustrates larger and larger values of electron density.

Electron density can assist in the understanding of many fundamental concepts in atomic and molecular structure. To illustrate, the ***molecular electron density***, defined as the volume around the atom that contains greater than 95% of the electron density of an atom or molecule. Thus the molecular electron density (or MED) will effectively define the size of an atom or molecule.

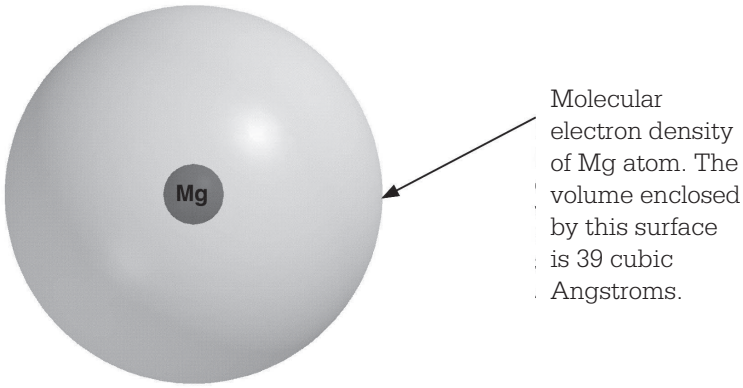
Question 1:

Based on what you have learned about quantum mechanics of atoms and molecules, what volume would the MED have to surround all the electrons of an atom or molecule? Explain.

The volume of an MED would have to be infinite. Because electrons have wavelike properties, we cannot define a single finite volume that would contain all the electrons in atom or molecule.

Question 2:

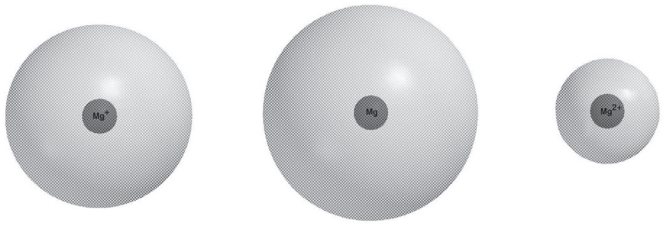
Examine the MED for the magnesium atom:



Note the volume enclosed by this surface is 39 Angstroms^3. Based on this, calculate the **radius** of this sphere and compare it to the radius of the magnesium atom given in your textbook. Based on your calculations, does the MED estimate the size of an atom? Calculate the radius of the MED:

Volume = 4/3*pi*r^3 = 39 Ang^3; r = 2.1 Angstroms. Many texts list the radius of Mg as approximately 1.5–1.6 Angstroms. Thus, the MED slightly overestimates the size of the atom, as compared to text values.

Magnesium being an alkaline earth metal, we expect to lose two electrons when it is the cation in ionic compounds. Let us examine the MEDs of Mg^+ and Mg^{2+} in addition to the MED of magnesium. To test your understanding of what MEDs can illustrate, look at the data below and then answer the following questions. As part of your answers, write down the complete electron configurations of each of the atoms or ions discussed.



MEDs of Mg^+, Mg and Mg^{2+} respectively.

Volumes of MEDs in the Figure

Atom or Ion	MED Volume (Angstroms^3)
Mg	39.4
Mg^+	23.3
Mg^{2+}	4.4

Question 3:

Explain why the MED of the magnesium cation is 59% as large as that of magnesium.

The magnesium cation has the same number of protons as Mg, and thus the same attractive forces are acting on the electrons of both species. However, Mg^+ has one fewer electron. Consequently, there is less electron–electron repulsion in the cation as compared to the neutral atom. Consequently, the cation's electrons feel a slightly greater net attractive force, causing the cation to contract.

Question 4:

Explain why the MED of Mg^{2+} is only 11% of the size of the magnesium atom and 19% the size of the magnesium cation.

Mg^{2+} has lost all of its valence electrons, and its "outermost" energy level is now the n=2 level. These electrons are in a lower energy level than the electrons in either Mg^+ or Mg. In addition, less electron shielding exists in Mg^{2+} than Mg or Mg^+. Consequently, the significantly higher effective nuclear charge in Mg^{2+} coupled with the outermost electrons being in a lower energy level results in a much smaller ion than either Mg^+ or Mg.

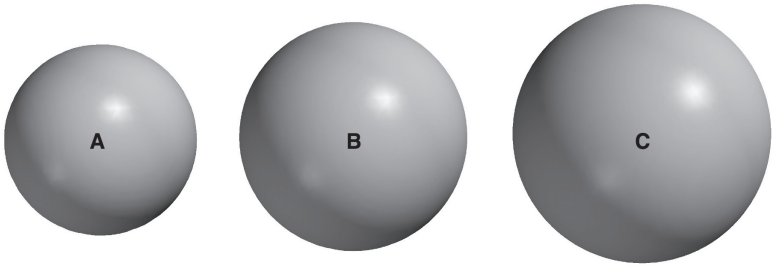
Question 5:

If you examined the MED of **Mg^{+3}**, how do you think it would compare to that of Mg^{+2}? Explain. (Your teacher has pictures of each to verify your prediction).

The size of Mg^{3+} would be smaller than, but not significantly different from, than Mg^{2+}, as Mg^{3+} has lost another core electron, so the outermost energy level for Mg^{2+} and Mg^{3+} is the same. However, the smaller amount of electron repulsion in Mg^{3+} will result in a slightly smaller ion.

Summary Question:

Shown below are the MEDs for three **isoelectronic** species, Be, B^+ and Li^-. The isosurfaces are labeled A, B and C.



(a) Write down the electron configurations of each species.

All have the same electron configuration: $1s^2 2s^2$

(b) Identify which MED corresponds to Be, B^+ and Li^-. Justify your choices.

A = B^+, B = Be, C = Li^-
Explanation: All of the species have the same electron configuration. Hence, the repulsion each electron experiences is identical. Therefore, differences in attraction, due to the number of protons in each atom, determine the size of the atom or ion. The order of number of protons is B^+ > Be > Li^-. Fewer protons mean less attractive force, which implies greater size of the atom or ion.

(c) Would the species represented by the MEDs above be paramagnetic or diamagnetic? Explain.

Paramagnetic substances are attracted to a magnetic field, while diamagnetic substances are repelled. In the case of paramagnetic atoms, this attraction is caused by the interaction of unpaired electrons in the atom with a magnetic field. In contrast, the interaction of paired electrons with a magnetic field causes a slight repulsion. Since all species have paired electrons, they should all be diamagnetic.

(d) Which of the above MEDs would have the **lowest** ionization energy? Explain.

The species in which the valence electrons are attracted the least should have the lowest ionization energy. As all atoms or ions experience the same repulsive forces among electrons, since they all have the same electron configuration, the atom with the fewest number of protons will exert the smallest attractive forces on the valence electrons. Hence, Li^-, with only 3 protons, has the smallest hold on valence electrons and the lowest first ionization energy.

Electron Density of Molecules — Sample Student Answers

The diagrams you have looked at for the electron density of various atoms and ions can be used to begin to glean ideas about the electron density of molecules as well. In the simplest approximation, molecules form because two nuclei are attracted to the electrons that form the bond, and the electrons that will participate in the bonding will be those with the highest energy: the **valence electrons**. Consequently, the closer the **valence electrons** are to the nucleus of each respective atom, the smaller (and stronger) the resulting bond will be in the molecule.

There are two main bonding theories that chemists use to understand quantitatively how molecules are held together. In upper division courses in chemistry, **molecular orbital** theory is used. This theory assumes that the electrons are found in orbitals that span the entire molecule. Although this theory is very easy for computers to work with, the properties of molecular orbitals can be difficult for beginning students to visualize. Hence, an equivalent theory, **valence bond** theory, is typically used in AP Chemistry (and first-year college chemistry). This theory assumes that bonds are formed when the valence orbitals of various atoms *overlap*, with a higher amount of overlap resulting in a stronger bond. Since molecular electron densities describe the size and shape of all the valence orbitals in the molecule, they can be used to estimate the geometry of the molecule.

Consider a diagram illustrating the MEDs of the hydrogen atom, as shown below. Since the valence electrons of each atom have the electron configuration $1s^1$, the MED of each hydrogen atom is that of a small sphere. The MED of the molecule would be formed when the atomic electron densities overlap.

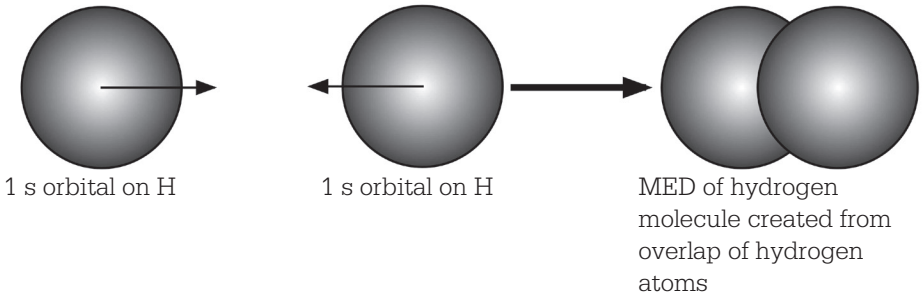


Figure 1: A schematic of the molecular electron density of the hydrogen molecule created by the overlap of the electron density of each 1s hydrogen orbital.

Figure 2: The actual MED of the hydrogen molecule from quantum mechanical calculations.

Knowledge of atomic MEDs can immediately lead to useful information about molecules. Shown below are the MEDs for the atoms of fluorine, chlorine and iodine. From these shapes, **sketch** what the MEDs of F_2, I_2, ClF and IF will look like in the space below.

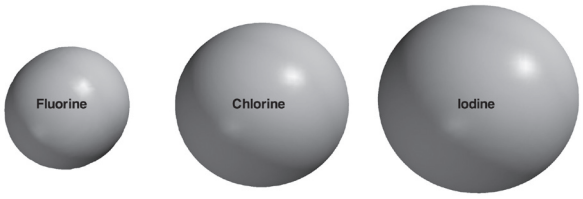
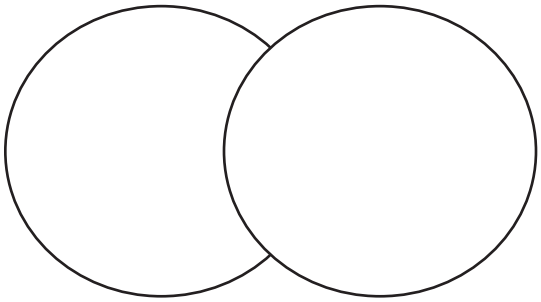
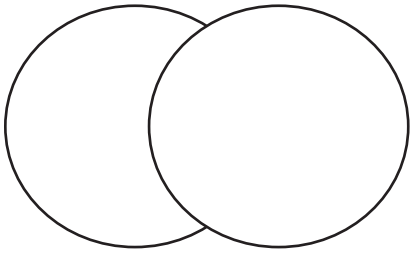


Figure III: The MEDs of the fluorine, chlorine and iodine atoms.

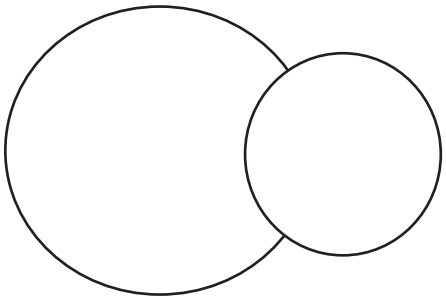
Sketches of I_2, Cl_2, IF and ClF



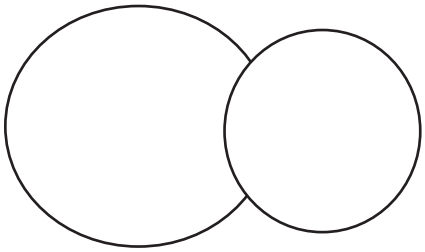
I_2



Cl_2



IF



ClF

Because the size of the molecule is reflected in the MED, **predict** the order of bond lengths of each of the molecules whose densities you have sketched above. Your textbook has the average values of each bond length for comparison. Look up these lengths and compare them with your choices.

Table I: Ranking of the Bond Lengths for Cl_2, I_2, ClF and IF

Molecule	My Ranking of Bond Length (1–4 where 1 is shortest)	Average Bond Length from Text (pm)	Average Bond Energy from Text (kJ/mol)
Cl_2	3 (some students may flip with IF)	200	242
I_2	4	266	151
ClF	1	163	253
IF	2 (some students may flip with Cl_2)	197	278

*Values taken from Kotz, Treichel and Weaver, ***Chemistry and Chemical Reactivity***, 6th ed.

Another important parameter for any bond is its **bond energy**, which is defined as the amount of energy necessary to break the covalent bond and completely separate two atoms. Look up the bond energies of each of the diatomic molecules above and place their values in Table I.

Figure II shows the MED for H_2. For this molecule, the bond length is 74 pm and the bond energy is 432 kJ/mol. Based on this information and the data in the table above, what can you say about the bond lengths and bond strengths for **homonuclear** diatomic molecules? Explain in your own words why any relationship makes sense in light of attraction and repulsion between protons and electrons.

Explanation:

For homonuclear diatomics, it appears that the shorter bonds are stronger bonds. This makes sense in light of the fact that when smaller atoms make covalent bonds, the bonding electrons are closer to the nucleus than the bonding electrons in larger atoms. These closer electrons experience a greater attraction to the protons of the molecule, resulting in a stronger bond.

The hydrogen atom covalently bonds to each of the halogens listed above, forming HF, HCl and HI. The table below shows both the bond lengths and average bond energies for these molecules.

Table II: Average Bond Lengths and Bond Energies for Some Hydrogen Halides

Molecule	Average Bond Length (picometers)	Average Bond Energy (kJ/mol)
HF	92	565
HCl	127	432
HI	161	299

Based on this data and that in Table I, is there any visible relationship between bond length and bond energy for these **heteronuclear** molecules? As part of your analysis, you may wish to consider the hydrogen halides and the interhalogen compounds (IF and ICl) separately.

Explanation of Any Relationship Discovered:

For the hydrogen halides (HF, HCl, HI), it again appears that the smaller atoms have greater attraction, for the same reasons given in the previous explanation. However, there seems to be a problem in the interhalogen compounds, as the larger molecule (IF) has the stronger bond. If students have little experience with polarity, they may not be able to explain this contradiction (nor be able to explain why the bond energies of the hydrogen halides are so much larger than the corresponding homonuclear compounds).

Electrostatic Potential Maps and Bond Polarity

Taken as a group, the examination of bond energy as a function of length for the heteronuclear compounds above seems to suggest the same trend found for homonuclear compounds. Specifically, it seems that as the bond length increases, the bond energy drops. However, if one focuses on the interhalogen compounds only, that trend reverses, as the longer molecule, IF, has a significantly larger bond energy than ClF.

Applying electron density can help us rationalize this contradiction. We know that covalent bonds are formed when electrons are shared between atoms. However, each atom, due to the combination of the number of protons in the nucleus and energy level of the valence electrons, can exert different forces on the bonding electrons. The combination of these different forces can distort the electron density, causing valence electrons to be more attracted to one atom over the other in the molecule. Consequently, the MED will not be *symmetric*, as electrons will effectively be drawn to one side of the diatomic molecule.

Recall that MEDs display the **total** volume over which the electrons in a molecule can be found. Consequently, they alone **do not show** if, on average, the distribution of electrons is distorted toward one atom or another. To illustrate this asymmetry of electron distribution, we need the concept of *electrostatic potential*. To understand what this is, consider just a proton by itself, with no other objects nearby:

Figure IV: A lone proton in space.

How could we determine that this object had a positive charge? The easiest way to do this would be to hold another charged object next to the proton, let it go and see what happens. Consider what would occur if a positive charge of +1 coulomb (henceforth called a *test charge*) was brought next to the proton.

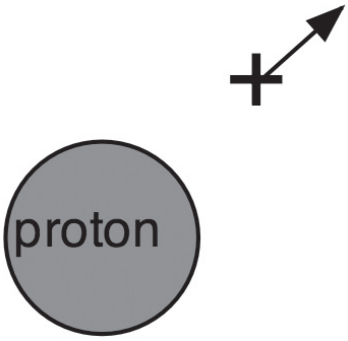


Figure V: A proton with a positive charge brought nearby. The arrow illustrates the force on the positive charge, indicating that it is repelled by the proton.

Because both objects are positively charged, the proton will repel the test charge. Thus the force the test charge experiences lets us know that the proton is positive. In contrast, if we brought the test charge near an electron, the charge would be attracted, as shown in the figure below. Note that as long as the test charge is kept at the same distance from the proton or the electron, it will always experience the same force.

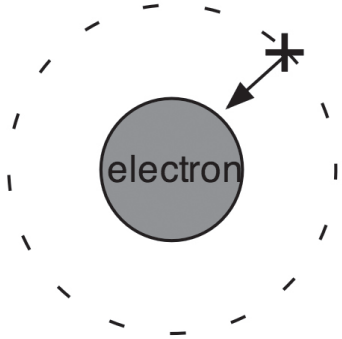


Figure VI: An electron with the test charge brought nearby. The arrow illustrates the force on the test charge, indicating that it is attracted by the electron. *Any* test charge on the dashed ring experiences the same force of attraction.

Clearly in the case of the electron, it would take a lot of energy to push the test charge very far away. In contrast, it would also take a lot of energy to bring the test charge closer to the proton. This **electrostatic potential** formally measures the potential energy change the test charge experiences as it is brought near another object (in this case the proton or the electron) from far away. In the case of the proton, the electrostatic potential is ***positive***, because the test charge is repelled by the proton. In contrast, the electrostatic potential of the electron is ***negative***, because the test charge is attracted to the electron.

Consider a molecule that, because of the different forces the nuclei exert, has an asymmetric distribution of electrons. In order to visually describe this distribution, we **map** the electrostatic potential onto the molecular electron density, determining the relative amount of attraction or repulsion the test charge will experience at every point on the MED. Areas where the test charge has high attraction, and hence are electron rich, are colored in red. Areas of lesser attraction or repulsion that are electron poor are colored blue.

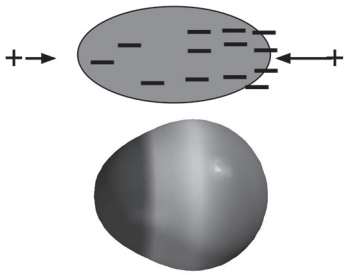


Figure VII: A molecule with an asymmetric distribution of electrons. The side that is electron rich is indicated by a red color. The scale gradually shifts to blue, illustrating the side of the molecule that is electron deficient.

A molecule that contains a symmetric distribution of electrons will cause the test charge to experience the same force on either side of the MED. Consequently, as there are no areas of electron deficiency or excess, the map of the electrostatic potential onto the electron density (referred to hereafter as the MEP) is green.

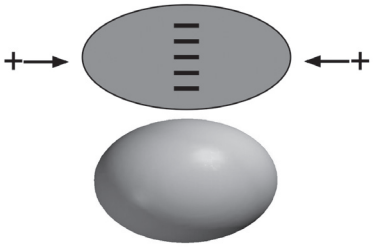


Figure VIII: A molecule with a symmetric distribution of electrons in which a test charge experiences the same force on either side of the molecule. The symmetry of the electron distribution is illustrated by the green color (green being in between red and blue on the color scale) of the MEP.

With these concepts in hand, let us examine the MEPs for both ClF and IF.

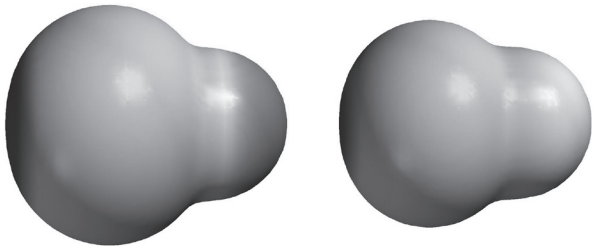


Figure IX: MEPs of IF (left) and ClF (right). Notice the difference in electron distribution.

We immediately see that the electron distribution is much more asymmetrical in IF than in ClF, as the fluorine atom is much more "red" in IF. Thus fluorine is doing a better job of pulling electrons in the molecule toward itself when it engages in bonding with iodine as opposed to chlorine. This asymmetry in the electron distribution has a profound impact on the strength of the bond, as now the fluorine end of the molecule has a slight negative charge, while the iodine possesses a slight positive charge. The two "poles" of the molecule, positive for iodine and negative for fluorine, are attracted to each other in an ionic-type interaction, and the bond is *polar*. We also see that the bond in ClF is also polar, but fluorine is not as successful in pulling electron density away from the chlorine atom. The additional electrostatic interaction between the ends of the IF molecule offsets the longer bond length of the molecule, and IF possesses a greater bond energy than ICl.

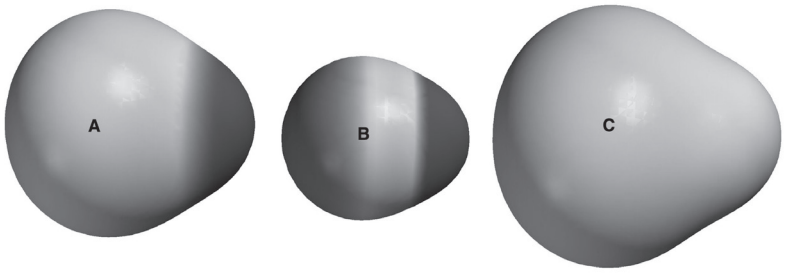
Linus Pauling was one of the first chemists to quantify this "ionic" effect on bonding in covalent compounds using the concept of electronegativity. Electronegativity, defined as the ability of atoms to pull electrons in bonds toward itself, was rated by Pauling on a 0–4 scale. Fluorine is the most electronegative element, with a value of 4. As one moves down a family of the periodic table, the electronegativity of the elements decreases as higher energy levels of electrons and increasing electron shielding lessen the ability of nuclei to distort electron density. Consequently, chlorine has an electronegativity of 3.0, while bromine has an electronegativity of 2.8.

Table III: The Electronegativity Differences in ClF and IF

Compound	Electronegativity Difference
ClF	1.0
IF	1.2

As shown in the table, the greater the electronegativity difference, the more polar the bond.

Below are three MEPs labeled A, B and C, each representing the MEPs of HF, HCl and HI in random order. Answer the questions that follow.



(a) Which of the molecules has the greatest polarity? Justify your answer.

From MEP it is apparent that molecule B has the greatest polarity. The tremendous color spectrum implies that one end of the molecule is very electron rich, while the other is very electron deficient.

(b) Determine which structure belongs to each molecule. Again, justify your answer.

Size differences alone here should allow students to determine which is which. As H is the smallest atom on the periodic table, students should see that the right-hand side of each MEP corresponds to H. As the halogens increase in size down a family, A must represent HCl, B HF and C HI. Students can also use electronegativity arguments and the color scale on the MEPs to rationalize the same result.

(c) Finally, using your answers from parts (a) and (b) in addition to your discussion about bond strength in homonuclear molecules, rationalize the trends in bond energy among the hydrogen halides.

Clearly these bonds have some "ionic" character to them, as charge is separated between the H and the halogen due to the differences in electronegativity. The greater this difference, the greater the attraction between the atoms due to electrostatic forces and the more ionic they become. As HF is both small and has a tremendous electronegativity difference, this bond is extremely strong. The molecules get bigger and the electronegativity difference is less as you move down the family, but the existence of polarity in each bond makes each stronger than one would expect by simply averaging bond energies in tables.

(d) Finally, let us consider polyatomic molecules CO_2, CS_2 **and** OCS. In the space below, draw the Lewis diagrams for each of these molecules. In addition, look up the electronegativities of C, O and S and place their values below the atom in the Lewis diagram for each compound.

Lewis Diagrams with Electronegativities for CO_2, CS_2 and OCS

O=C=O S=C=S S=C=O

(unshared pairs around O and S are not drawn but should be in student structures)

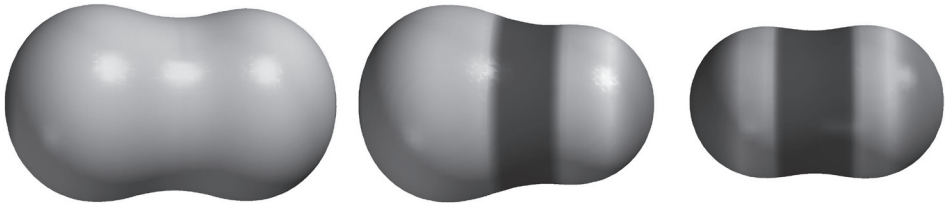
E.N. of C = 2.5

E.N. of O = 3.5

E.N. of S = 2.6

*Values taken from Kotz, Treichel and Weaver, *Chemistry and Chemical Reactivity*, 6th ed.

Shown below are the MEPs for the Lewis diagrams drawn above, again in random order.



Answer the following questions.

(e) Identify which MEP corresponds to each Lewis diagram. Justify your answer.

Again, students can use size differences to determine the MEPs. CO_2 will be the molecule on the right, as it is the smallest. OCS is in the middle, while CS_2 is the molecule on the left. Students should be able to back up these assignments by looking at the color scale of the MEP.

(f) Do the MEPs indicate that any of the **bonds** in each molecule are polar? Explain.

The MEPs indicate all the bonds are polar in each molecule. We see a distinct difference in color (and hence electron distribution) in both CO_2 and OCS, and a very slight difference in the MEP for CS_2.

(g) If your answer to (b) was yes, which of the bonds does the MEP say is *most* polar? Do the electronegativities of the atoms support this?

These polarities equate well with electronegativity values. Looking at the differences, we would expect the C=O bond to be the most polar, followed by the C=S bond. In CS_2 this slight difference in electron attraction in bonds is visible with the carbon "losing out" to the slightly more electronegative sulfur atom.

(h) CO_2 and CS_2 are nonpolar molecules. How do the MEPs illustrate this?

The symmetries in the MEPs illustrate nonpolar molecules. In CO_2, although each O individually pulls on the electrons in the bonds with carbon, the sum of the two pulls cancels, resulting in a nonpolar molecule. We see the same effect in CS_2.

(i) Is OCS polar or nonpolar? Explain.

Because of the differences in electronegativity between O and S, the two atoms distort the electron density of OCS differently, resulting in an asymmetric MEP. Here O is more negative than S, resulting in O being the negative end of the molecule, with S having a slightly positive end.

References

Getting Started with Spartan, 3rd ed., Irvine, CA: Wavefunction, 2004.

http://academic.reed.edu/chemistry/roco/index.html (Accessed Jan. 2008)

Shusterman, G. P., and A. J. Shusterman. "Teaching Chemistry with Electron Density Models." *Journal of Chemical Education* 74 (1997): 771–776.

Appendix 1

Electron Density and Sizes of Atoms and Ions — Handout for Students

You have just watched a video depicting the **electron density** of the argon atom. Remember, the electron density is a mathematical function that describes the number of electrons of an atom or molecule that can be found within a small volume at a certain distance from the nucleus. To visualize the density, we frequently look at *isosurfaces*, which are a set of points from the nuclei of atoms or molecules that have a constant value of the electron density.

Consider the forces acting on an electron: If every electron had a "choice," which orbital would it choose? In accordance with the Aufbau principle, each electron would have the lowest energy (and greatest attraction to the nucleus) if it were in the 1s orbital. Only repulsion between electrons and the Pauli Exclusion Principle prevent more than two electrons from occupying an orbital. As electrons continue to fill orbitals, the electrons fill so that they will maintain the lowest total energy possible. Consequently, the **density** of electrons should be higher at closer distances to the nucleus. This is depicted in the video, as each successive picture illustrates larger and larger values of electron density.

Electron density can assist in the understanding of many fundamental concepts in atomic and molecular structure. To illustrate, the ***molecular electron density***, defined as the volume around the atom that contains greater than 95% of the electron density of an atom or molecule. Thus the molecular electron density (or MED) will effectively define the size of an atom or molecule.

Question 1:

Based on what you have learned about quantum mechanics of atoms and molecules, what volume would the MED have to surround all the electrons of an atom or molecule? Explain.

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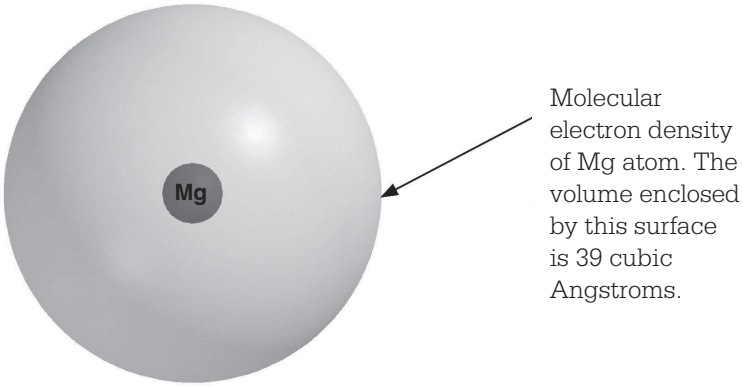
Question 2:

Examine the MED for the magnesium atom (the sphere in the middle indicates the position of the magnesium nucleus):



Note the volume enclosed by this surface is 39 Angstroms^3. Based on this, calculate the **radius** of this sphere and compare it to the radius of the magnesium atom given in your textbook. Based on your calculations, does the MED estimate the size of an atom? Calculate the radius of the MED:

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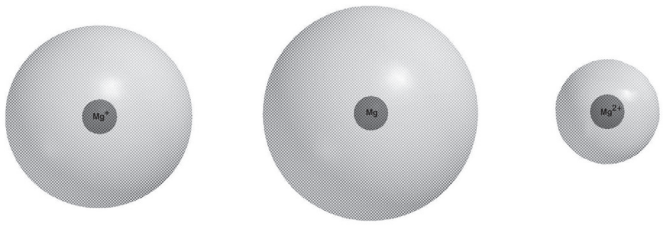
Magnesium being an alkaline earth metal, we expect to lose two electrons when it is the cation in ionic compounds. Let us examine the MEDs of Mg^+ and Mg^{2+} in addition to the MED of magnesium. To test your understanding of what MEDs can illustrate, look at the data below and then answer the following questions. As part of your answers, write down the complete electron configurations of each of the atoms or ions discussed.



MEDs of Mg^+, Mg and Mg^{2+} respectively.

Volumes of MEDs in the Figure

Atom or Ion	MED Volume (Angstroms^3)
Mg	39.4
Mg^+	23.3
Mg^{2+}	4.4

Question 3:

Explain why the MED of the magnesium cation is 59% as large as that of magnesium.

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Question 4:

Explain why the MED of Mg^{2+} is only 11% of the size of the magnesium atom and 19% the size of the magnesium cation.

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Question 5:

If you examined the MED of **Mg^{+3}**, how do you think it would compare to that of Mg^{+2}? Explain. (Your teacher has pictures of each to verify your prediction.)

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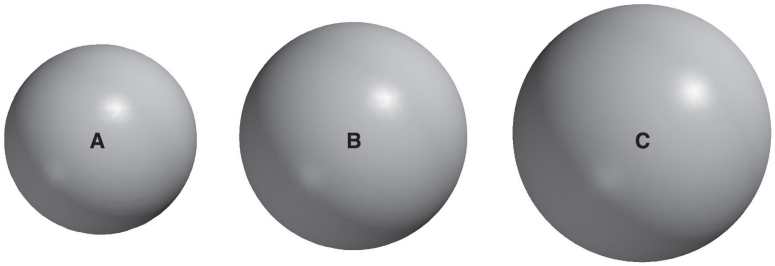
Summary Question:

Shown below are the MEDs for three **isoelectronic** species, Be, B^+ and Li^-. The isosurfaces are labeled A, B and C.



(a) Write down the electron configurations of each species.

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(b) Identify which MED corresponds to Be, B^+ and Li^-. Justify your choices.

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(c) Would the species represented by the MEDs above be paramagnetic or diamagnetic? Explain.

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(d) Which of the above MEDs would have the **lowest** ionization energy? Explain.

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Appendix 2

Electron Density of Molecules — Teacher's Handout

The diagrams you have observed show the electron density of various atoms and ions, and they are also useful to glean ideas about the electron density of molecules. In the simplest approximation, molecules form because two nuclei are attracted to the electrons that form the bond, and the electrons that participate in the bonding are those with the highest energy: the **valence electrons**. Consequently, the closer the **valence electrons** are to the nucleus of each respective atom, the smaller (and stronger) the resulting bond in the molecule.

There are two main bonding theories that chemists use to understand quantitatively how molecules are held together. In upper-division courses in chemistry, **molecular orbital** theory is used. This theory assumes that the electrons are found in orbitals that span the entire molecule. Although this theory is very easy for computers, the properties of molecular orbitals can be difficult for beginning students to visualize. Hence, an equivalent theory, **valence bond** theory, is typically used in AP Chemistry (and first-year college chemistry). This theory assumes that bonds are formed when the valence orbitals of various atoms *overlap*, with a higher amount of overlap resulting in a stronger bond. Since molecular electron densities describe the size and shape of all valence orbitals in the molecule, they are used to estimate the geometry of the molecule.

Consider a diagram illustrating the MEDs of the hydrogen atom, as shown below. Since the valence electrons of each atom have the electron configuration $1s^1$, the MED of each hydrogen atom has the shape of a small sphere. The MED of the molecule forms when the atomic electron densities overlap.

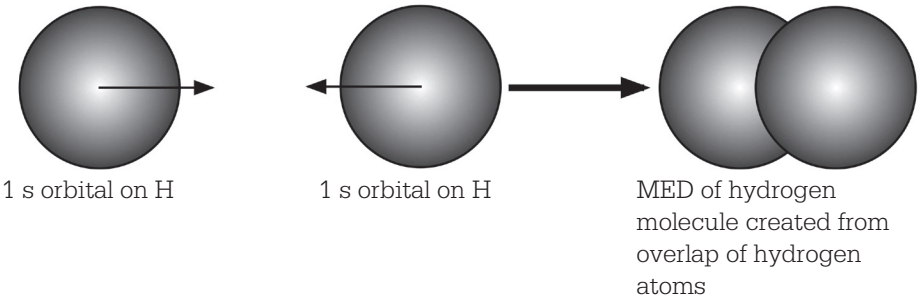

Figure I: A schematic of the molecular electron density of the hydrogen molecule created by the overlap of the electron density of each 1s hydrogen orbital.

Figure II: The actual MED of the hydrogen molecule from quantum mechanical calculations.

Knowledge of atomic MEDs can immediately lead to useful information about molecules. Shown below are the MEDs for the atoms of fluorine, chlorine and iodine. From these shapes, **sketch** the shape of the MEDs of F_2, I_2, ClF and IF in the space below:

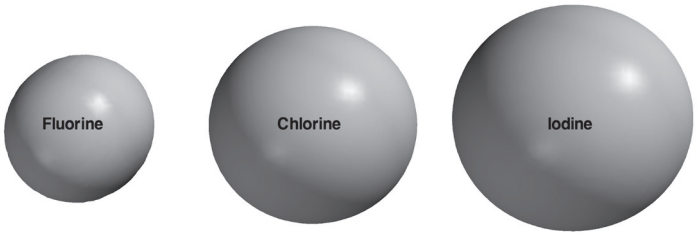

Figure III: The MEDs of the fluorine, chlorine and iodine atoms.

Sketches of I_2, Cl_2, IF and ClF

Because the size of the molecule is reflected in the MED, **predict** the order of bond lengths of each of the molecules whose densities you sketched above. Your textbook has the average values of each bond length for comparison. Look up these lengths and compare them with your choices.

Table I: Ranking of the Bond Lengths for Cl_2, I_2, ClF and IF

Molecule	My Ranking of Bond Length (1–4 where 1 is shortest)	Average Bond Length from Text (pm)	Average Bond Energy from Text (kJ/mol)
Cl_2			
I_2			
ClF			
IF			

Another important parameter for any bond is its **bond energy**, which is defined as the amount of energy necessary to break the covalent bond and completely separate two atoms. Look up the bond energies of each of the diatomic molecules above and place their values in Table I.

Figure II shows the MED for H_2. For this molecule, the bond length is 74 pm and the bond energy is 432 kJ/mol. Based on this information and the data in the table above, what can you say about the bond lengths and bond strengths for **homonuclear** diatomic molecules? Explain in your own words why any relationship makes sense in light of the attraction and repulsion between protons and electrons.

Explanation:

The hydrogen atom covalently bonds to each of the halogens listed above, forming HF, HCl and HI. The table below shows both the bond lengths and average bond energies for these molecules.

Table II: Average Bond Lengths and Bond Energies for Some Hydrogen Halides

Molecule	Average Bond Length (picometers)	Average Bond Energy (kJ/mol)
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Based on this data and Table I, is there a visible relationship between bond length and bond energy for these **heteronuclear** molecules? As part of your analysis, consider the hydrogen halides and the interhalogen compounds (IF and ICl) separately.

Explanation of Any Relationship Discovered:

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Electrostatic Potential Maps and Bond Polarity

Taken as a group, the examination of bond energy as a function of length for the heteronuclear compounds above may suggest the same trend found for homonuclear compounds. Specifically, it seems that as the bond length increases, the bond energy drops. However, if one focuses on the interhalogen compounds only, that trend reverses, as the longer molecule, IF, has a significantly larger bond energy than ClF.

Applying electron density can help us rationalize this contradiction. We know that covalent bonds are formed when electrons are shared between atoms. However, each atom, due to the combination of the number of protons in the nucleus and energy level of the valence electrons, can exert different forces on the bonding electrons. The combination of these different forces can distort the electron density, causing valence electrons to have more attraction to one atom over the other in the molecule. Consequently, the MED will not show symmetry, as electrons are effectively drawn to one side of the diatomic molecule.

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Figure IV: A lone proton in space.

How could we determine that this object had a positive charge? The easiest way to check this is to hold another charged object next to the proton, let it go and observe what happens. Consider what would occur if a positive charge of +1 coulomb (henceforth called a *test charge*) was brought next to the proton.

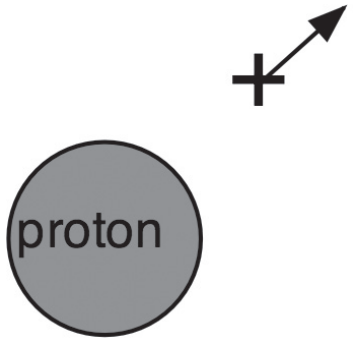
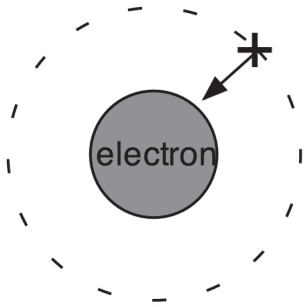


Figure V: A proton with a positive charge brought nearby. The arrow illustrates the force on the positive charge, indicating that it is repelled by the proton.

Since both objects are positively charged, the proton repels the test charge. Thus the force experienced by the test charge indicates that the proton is positive. In contrast, if we brought the test charge near an electron, the charge would be attracted, as shown in the figure below. Note that as long as the test charge is kept at the same distance from the proton or the electron, it will always experience the same force.



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Clearly in the case of the electron, it would take a lot of energy to push the test charge very far away. In contrast, it would also take a lot of energy to bring the test charge closer to the proton. This **electrostatic potential** formally measures the potential energy change the test charge experiences as it is brought near another object (in this case the proton or the electron) from far away. In the case of the proton, the electrostatic potential is ***positive***, because the test charge is repelled by the proton. In contrast, the electrostatic potential of the electron is ***negative***, as the test charge is attracted to the electron.

Consider a molecule that, because of the different forces the nuclei exert, has an asymmetric distribution of electrons. In order to visually describe this distribution, we **map** the electrostatic potential onto the molecular electron density, determining the relative amount of attraction or repulsion the test charge will experience at every point on the MED. Areas where the test charge has high attraction, and hence are electron rich, are colored in red. Areas of lesser attraction or repulsion are electron poor and are colored blue, as shown below.

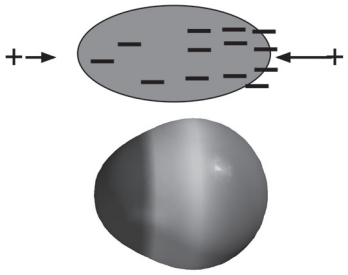


Figure VII: A molecule with an asymmetric distribution of electrons. The side that is electron rich is indicated by a red color. The scale gradually shifts to blue, illustrating the side of the molecule that is electron deficient.

A molecule that contains a symmetric distribution of electrons will cause the test charge to experience the same force on either side of the MED. Consequently, there are no areas of electron deficiency or excess, the map of the electrostatic potential onto the electron density (referred to hereafter as the MEP) is green.

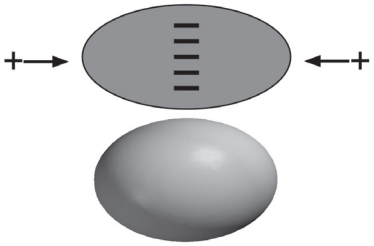


Figure VIII: A molecule with a symmetric distribution of electrons in which a test charge experiences the same force on either side of the molecule. The symmetry of the electron distribution is illustrated by the green color (green being in between red and blue on the color scale) of the MEP.

With these concepts in hand, let us examine the MEPs for both ClF and IF.

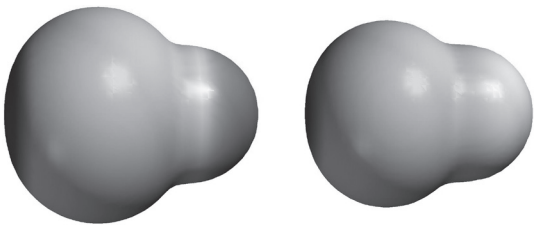


Figure IX: MEPs of IF (left) and ClF (right). Notice the difference in electron distribution.

We immediately see that the electron distribution is more asymmetrical in IF than in ClF, as the fluorine atom is more "red" in IF. Thus fluorine does a better job of pulling electrons in the molecule toward itself when it engages in bonding with iodine as opposed to chlorine. This asymmetry in the electron distribution has a profound impact on the strength of the bond, as the fluorine end of the molecule has a slight negative charge, while the iodine end possesses a slight positive charge. The two "poles" of the molecule, positive for iodine and negative for fluorine, are attracted to each other in an ionic-type interaction, and the bond is *polar*. We also see that the bond in ClF is also polar, but fluorine is not as successful in pulling electron density away from the chlorine atom. The

additional electrostatic interaction between the ends of the IF molecule offsets the longer bond length of the molecule, and IF possesses a greater bond energy than ICl.

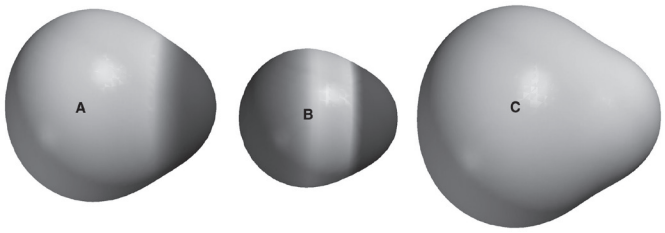
Linus Pauling was one of the first chemists to quantify this "ionic" effect on bonding in covalent compounds using the concept of electronegativity. Electronegativity, defined as the ability of atoms to pull electrons in bonds toward itself, was rated by Pauling on a 0–4 scale. Fluorine is the most electronegative element, with a value of 4. As one moves down a family of the periodic table, the electronegativity of the elements decreases as higher energy levels of electrons and increasing electron shielding lessen the ability of nuclei to distort electron density. Consequently, chlorine has an electronegativity of 3.0, while bromine has an electronegativity of 2.8.

Table III: The Electronegativity Differences in ClF and IF

Compound	Electronegativity Difference
ClF	1.0
IF	1.2

As shown in the table, the greater the electronegativity difference, the more polar the bond.

Below are three MEPs labeled A, B and C, each representing the MEPs of HF, HCl and HI in random order. Answer the questions that follow.



(a) Which of the molecules has the greatest polarity? Justify your answer.

_____

_____

(b) Determine which structure belongs to each molecule. Again, justify your answer.

_____

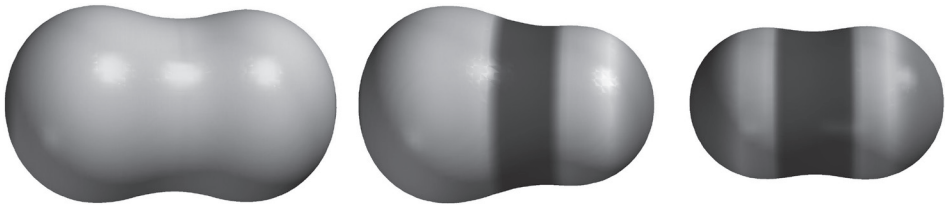
_____

(c) Finally, using your answers from parts (a) and (b) in addition to your discussion about bond strength in homonuclear molecules, rationalize the trends in bond energy among the hydrogen halides.

(d) Finally, let us consider polyatomic molecules CO2, CS2 and OCS. In the space below, draw the Lewis diagrams for each of these molecules. In addition, look up the electronegativities of C, O and S and place their values below the atom in the Lewis diagram for each compound.

Lewis Diagrams with electronegativities for CO_2, CS_2 and OCS

Shown below are the MEPs for the Lewis diagrams drawn above, again in random order.



Answer the following questions.

(e) Identify which MEP corresponds to each Lewis diagram. Justify your answer.

(f) Do the MEPs indicate that any of the **bonds** in each molecule are polar? Explain.

(g) If your answer to (b) was yes, which of the bonds does the MEP say is *most* polar? Do the electronegativities of the atoms support this?

_____

_____

_____

_____

(h) CO_2 and CS_2 are nonpolar molecules. How do the MEPs illustrate this?

_____

_____

_____

_____

(i) Is OCS polar or nonpolar? Explain.

_____

_____

_____

_____

About the Contributors

Carol Brown teaches honors chemistry and AP Chemistry at Saint Mary's Hall in San Antonio, Texas, where she is also the academic contest adviser and chair of the Science Department. She has taught all levels of science from fourth grade through graduate school. She earned a Bachelor of Arts from Trinity University and a Master of Science in chemistry from the University of Texas at San Antonio. She has been a faculty consultant (AP Exam Reader) for ETS for 10 years and, after serving on the AP Chemistry Development Committee for five years, is now the College Board adviser to the committee. Brown was named 1994 Outstanding Chemistry Teacher in Texas by the Associated Chemistry Teachers of Texas and received the College Board Special Recognition Award for Outstanding Teaching and Participation in the Advanced Placement Program® in 1987 and 1997. She is a 1999 recipient of the Siemens Award for Advanced Placement® and received a 2005 Educator of Distinction award from the Coca-Cola Company. She is a contributing author of the Laying the Foundation resource and strategies guides.

Lisa McGaw received her Master of Science in chemistry at West Texas A&M University in Canyon, Texas. She recently moved to Oklahoma from Texas, where she taught chemistry at Saint Mary's Hall in San Antonio. She currently teaches freshman chemistry lecture and laboratories at the University of Central Oklahoma in Edmond. Her background includes acting as the science program coordinator for Advanced Placement Strategies Inc. and teaching at Bryan High School, West Texas A&M University, Canyon High School, Hereford Junior High, Hereford High School, Mabank Middle School and Mabank High School. McGaw's professional activities include involvement in the AP Chemistry program, where she has served as an AP Reader, Table Leader and Question Leader for the AP Exam Reading held each summer. She has been a member of the National Science Academic Advisory Council since 1999 and has conducted many types of workshops for the College Board, including parent presentations and one-day, two-day and weeklong institutes since the early 1990s.

McGaw received the Southwest Regional Award for AP Chemistry in 1997. Her other professional activities include serving as an officer for the Associated Chemistry Teachers of Texas; making presentations at CAST, ACS, ICE, ACT_2-Welch, and Panhandle Area Math and Science Conferences; Laying the Foundation training; reading proposals for the National Science Foundation; planning for AP two-day conferences; Science Safety Committee; and textbook reviews. She also served on the Lighthouse Committee for Vertical Alignment in the Sciences for the state of Texas. Her writing activities and projects include serving as coeditor for Laying the Foundation guides in science; and as a participant in writing the College Board Science Framework, SAT Subject Test in Chemistry review book for SparkNotes, AP Chemistry Power Pack for SparkNotes and, most recently, the AP Chemistry multiple-choice review for McGraw-Hill.

Paul D. Price is the science department chairman at Trinity Valley School in Fort Worth, Texas, where he has taught chemistry, AP Chemistry and physics since 1998. He earned a Bachelor of Science in chemistry and mathematics from Southwestern University in Georgetown, Texas, and a Master of Science in chemistry from the University of Wisconsin at Madison. In 2004, the Dallas–Fort Worth Section of the American Chemical Society honored him with the Werner Schulz Award for Outstanding High School Chemistry Teaching, and he was named the Southwest Regional ACS Teacher of the Year in 2005. Price is a frequent presenter at regional and national conferences, often discussing techniques to improve molecular-level, problem-solving skills. He is also currently serving as a member of the AP Chemistry Development Committee.

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