

ACID-BASE EQUILIBRIA

INTRODUCTION

How about the chemical workers - are they unionized or ionized?

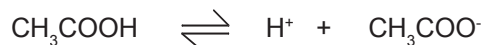


What are acids and bases? Svante Arrhenius noticed that acids release hydrogen ions in solution. He classified acids and bases in this way: acids are compounds that dissociate, or break up, in water to give a proton; bases are compounds that dissociate in water to accept a proton.

Acids that break up completely in water; these are strong acids. Acids that do not dissociate completely in water are called weak acids. Can you guess what bases that dissociate completely are called? Do you think weak bases dissociate completely?

Things that don't dissociate completely are most interesting - and often overlooked when it comes to safety! Take vinegar, for example. Did you know that this common kitchen item is actually a weak acid called acetic acid? While it's not dangerous in the form you buy at the grocery store because it's very dilute (about 4-5% acetic acid), more concentrated solutions of acetic acid can be quite dangerous even though it's a weak acid.

Take a look at the dissociation of acetic acid in water.

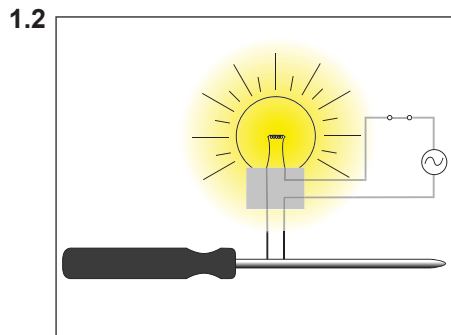
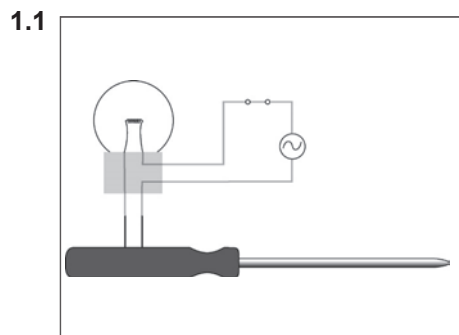


Consider an acetic acid burn on your skin. Because acetic acid is neutral, it can be absorbed into the skin readily. Now you've got acetic acid in your hypodermis - the lower layer of your skin! If it were to remain neutral and not dissociate, this wouldn't be a problem, but it does dissociate. The ions then attack the layers of skin and burn it. All the while, more weak acid can enter the hypodermis causing further damage, and a very severe burn.

ACID-BASE EQUILIBRIA

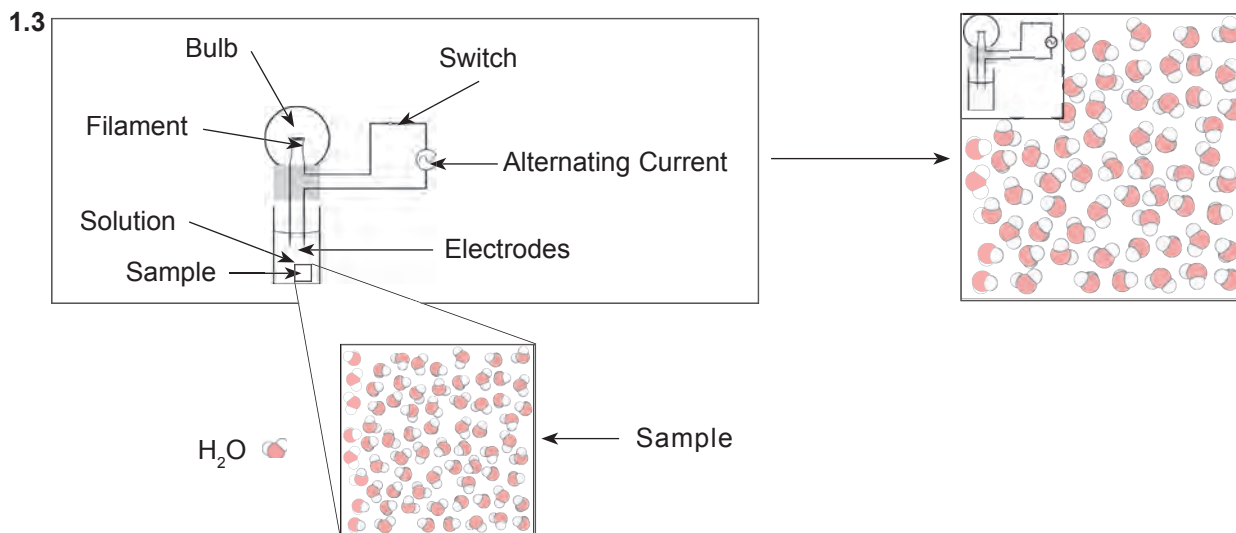
ELECTROLYTES

A simple conductivity experiment is the following:
A plastic screwdriver handle is placed against the electrodes - no light!
When the metal part is used - bulb lights brightly!
The handle is an insulator, whereas the metal is a conductor!



We can do the same type of experiment with solutions. Solutions are homogeneous mixtures of a solute dissolved in a solvent (module #). When substances are dissolved in water, the solutions can be tested by seeing if the solution conducts electricity, just as the metal of the screwdriver does. An electrolyte is a substance whose aqueous solutions conduct electricity. Electrolytes are often identified by experiments testing the conductivity of solutions.

► The diagram below represents the apparatus with electrodes dipped into liquid water. Is liquid water a conductor? Look at the top left-hand corner of the conductivity experiment (the light bulb) to answer the question.



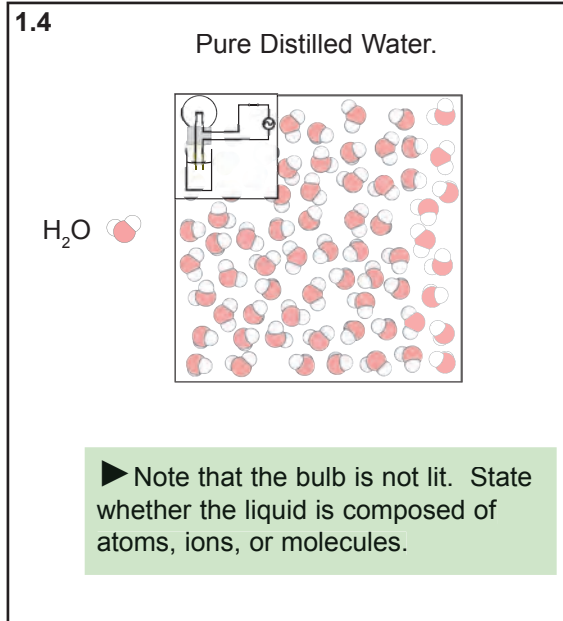
In the following pictures, you will be asked to determine if the solutions are conductors or non-conductors. These pictures will help you realize the definitions of some key chemical terms, and hopefully some chemical concepts!

Be aware of the potential danger of alternating current electricity. Do not attempt any of these experiments without appropriate supervision.

ACID-BASE EQUILIBRIA

ELECTROLYTES

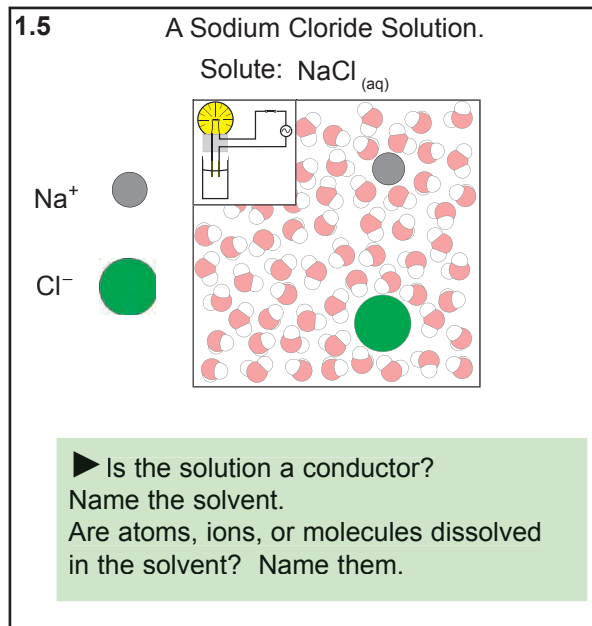
1.4 Pure Distilled Water.



H_2O

► Note that the bulb is not lit. State whether the liquid is composed of atoms, ions, or molecules.

1.5 A Sodium Chloride Solution.
Solute: $\text{NaCl}_{(\text{aq})}$

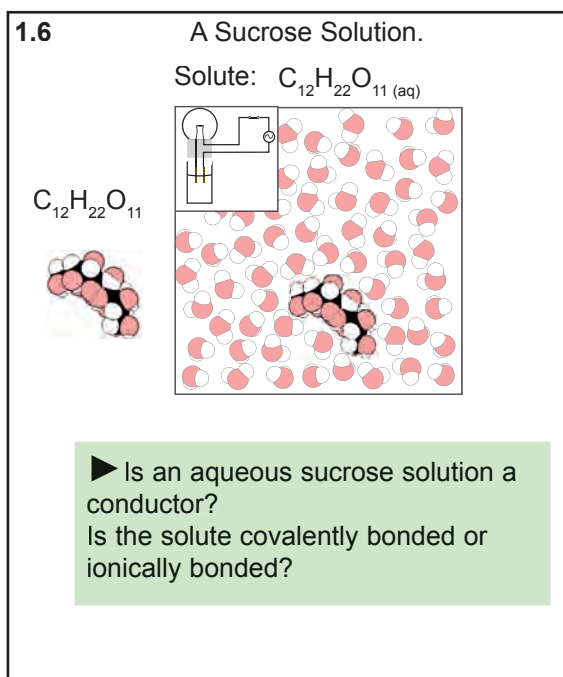


Na^+

Cl^-

► Is the solution a conductor? Name the solvent. Are atoms, ions, or molecules dissolved in the solvent? Name them.

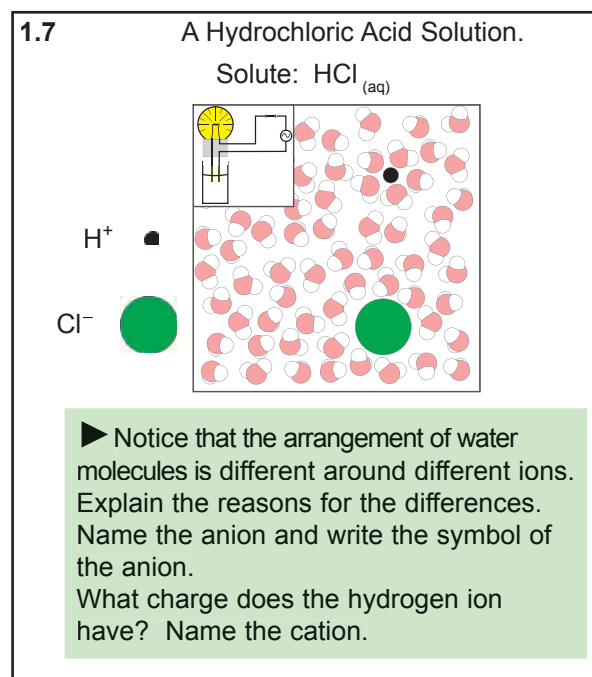
1.6 A Sucrose Solution.
Solute: $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$



$\text{C}_{12}\text{H}_{22}\text{O}_{11}$

► Is an aqueous sucrose solution a conductor? Is the solute covalently bonded or ionically bonded?

1.7 A Hydrochloric Acid Solution.
Solute: $\text{HCl}_{(\text{aq})}$



H^+

Cl^-

► Notice that the arrangement of water molecules is different around different ions. Explain the reasons for the differences. Name the anion and write the symbol of the anion. What charge does the hydrogen ion have? Name the cation.

Solutes dissolved in water to give solutions that conduct are called ELECTROLYTES. Solutes dissolved in water to give solutions that do not conduct are called NON-ELECTROLYTES.

► List the electrolytes for pictures 4-7.

► List the non-electrolytes for pictures 4-7.

ACID-BASE EQUILIBRIA

ELECTROLYTES

1.8 An Ammonium Chloride Solution.
Solute: $\text{NH}_4\text{Cl}_{(aq)}$

NH_4^+

Cl^-

► Name the ions in solution. Which species is the anion? Which species is the cation? Is the solute an electrolyte?

1.9 A Carbon Dioxide Solution.
Solute: $\text{CO}_{2(aq)}$

H^+

CO_2

HCO_3^-

► Name the ions in solution. Name the molecules in solution. Is the solute an electrolyte?

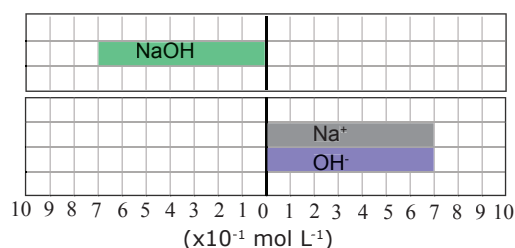
1.10 0.7 M Sodium Hydroxide Solution.
Solute: $\text{NaOH}_{(aq)}$

Na^+

OH^-

► Write the formula for the anion. Write the formula for the cation. Write the formula for the solute. Write the formula for the solvent.

Let's do some ChemLogs in order to further understand strong electrolytes.



Dissociation is the separation of ions that occurs when an ionic compound dissolves.

Notice the solutes which dissociate completely cause the light to shine brightly. The dim light is caused by partial dissociation. Solutes that dissociate completely are called **STRONG ELECTROLYTES**. Solutes that dissociate only partially are called **WEAK ELECTROLYTES**.

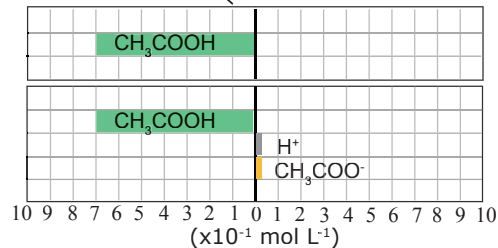
1.11 0.7 M Acetic Acid Solution.
Solute: $\text{CH}_3\text{CO}_2\text{H}_{(aq)}$

H^+

$\text{CH}_3\text{CO}_2\text{H}$

► Is the solute completely dissociated? Complete the list above of the chemical species in solution.

Let's do some ChemLogs in order to further understand weak electrolytes.



► Why is the equilibrium arrow used for this weak electrolyte dissociation?

► List the weak electrolytes. List the strong electrolytes.

An **ACID** is a proton (H^+ ion) donor. A **BASE** is a proton acceptor. This is called the **Bronsted-Lowry system**.

ACID-BASE EQUILIBRIA

ELECTROLYTES

► Fill in the “empty” ChemLogs for each of the following experiments:

1.12 0.8 M Sulfuric Acid Solution.
Solute: H_2SO_4 (aq)

$\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}^+ + \text{SO}_4^{2-}$

10	9	8	7	6	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10
(x10 ⁻¹ mol L ⁻¹)																				

1.14 0.8 M Nitric Acid Solution.
Solute: HNO_3 (aq)

$\text{HNO}_3 \longrightarrow$

10	9	8	7	6	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10
(x10 ⁻¹ mol L ⁻¹)																				

► Strong electrolytes that dissociate completely to give H^+ ions are called strong acids. Name the strong acids on this page.

► Strong electrolytes that completely dissociate to give a H^+ acceptor are called strong bases. Name the strong bases on this page.

► There are other solutes that are strong electrolytes. These are called salts. Name the salts on this page.

► Complete the chemical reaction and the chemLog where necessary.

1.13 0.8 M Potassium Chloride Solution.
Solute: KCl (aq)

$\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$

10	9	8	7	6	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10
(x10 ⁻¹ mol L ⁻¹)																				

1.15 0.8 M Potassium Hydroxide Solution.
Solute: KOH (aq)

$\text{KOH} \longrightarrow$

10	9	8	7	6	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10
(x10 ⁻¹ mol L ⁻¹)																				

pH is a measure of the concentration of H^+ .

$$\text{pH} = -\log [\text{H}^+]$$

When pH is between 1 and 7, the solution is acidic. When the pH is between 7 and 14, the solution is basic. The pH of pure water is 7 (neutral pH).

► For each of the solution on this page, state whether the ph is less than 7, greater than 7, or equal to 7.

ACID-BASE EQUILIBRIA

ELECTROLYTES

► Fill in the “empty” ChemLogs for each of the following experiments. Include the chemical reaction and the appropriate arrow for the reaction.

1.16 0.8 M Nitrous Acid Solution
Solute: $\text{HNO}_2(\text{aq})$

HNO_2
 NO_2^-
 H^+

$\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+$

10 9 8 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 8 9 10
($\times 10^{-1} \text{ mol L}^{-1}$)

1.17 0.8 M Ammonia Solution
Solute: $\text{NH}_3(\text{aq})$

NH_3
 NH_4^+
 OH^-

10 9 8 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 8 9 10
($\times 10^{-1} \text{ mol L}^{-1}$)

1.18 0.8 M Caffeine Solution
Solute: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(\text{aq})$

$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
 $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+$
 OH^-

10 9 8 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 8 9 10
($\times 10^{-1} \text{ mol L}^{-1}$)

► Weak electrolytes that dissociate to give H^+ ions are called weak acids. Name the weak acids on this page.

Weak electrolytes that dissociate to give H^+ ion acceptors are called weak bases. Name the weak bases on this page.

► On this page, which solutions are acidic? Is the pH of these solutions less than 7 or greater than 7?

Which solutions are basic? Is the pH of these solutions less than 7 or greater than 7?

Are there any solutions on this page that have a pH equal to 7?

► For review, define a strong electrolyte and a weak electrolyte.

Can a weak base be a strong electrolyte?

ACID-BASE EQUILIBRIA

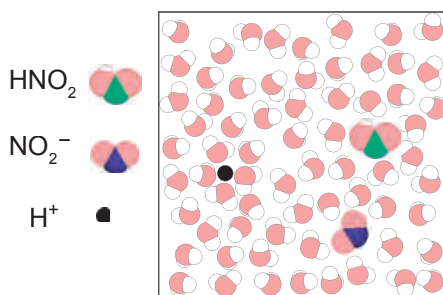
CONJUGATE ACIDS AND BASES

ACIDS

We've already seen the following reaction earlier, but let's study it more.



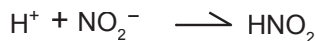
2.1 Nitrous Acid Solution.



We know that HNO_2 is an acid because it gives a H^+ ion;



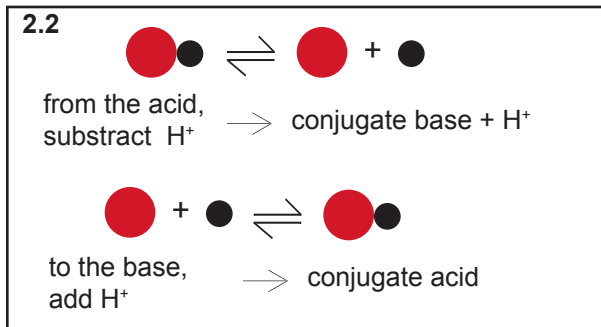
However, at equilibrium, NO_2^- accepts a proton to become HNO_2 . That makes NO_2^- a base;



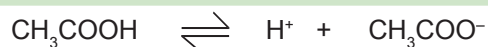
So, HNO_2 is an acid, and NO_2^- is its conjugate base. On the other hand, NO_2^- is a base, and HNO_2 is its conjugate acid.

The species formed when an acid loses a proton is called a CONJUGATE BASE. The species formed when a base gains a proton is called a CONJUGATE ACID.

A simple way to remember how to identify acids and their conjugate bases, and bases and their conjugate acids, is the following table:

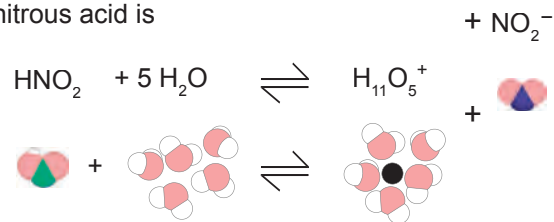


► Identify the acid and conjugate base in the following reaction:

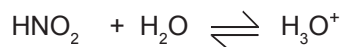


► What do you notice about the arrangement of the water molecules around the H^+ ion in picture 2.1?

The oxygen atoms in the water molecules have a slightly negative charge (negative dipole). The H^+ ion is actually bonded to several water molecules. As you can see from the picture, a more complete way of writing the reaction of the dissociation of nitrous acid is



Obviously, this could get complicated (and long!) very fast. A more common way + NO_2^- to



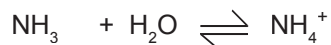
We call the H_3O^+ ion the hydronium ion.

Note: Water must be acting as a base in this reaction (see next section).

We chemists usually just write the most simplified version using H^+ . You may notice that some books do use the hydronium ion. As a student, it is important to recognize that these two versions indicate the same thing - a proton surrounded by water molecules.

BASES

When $\text{NH}_3(\text{g})$ is dissolved in water, it acts as a base. Bases accept protons. $\text{H}^+ + \text{OH}^-$



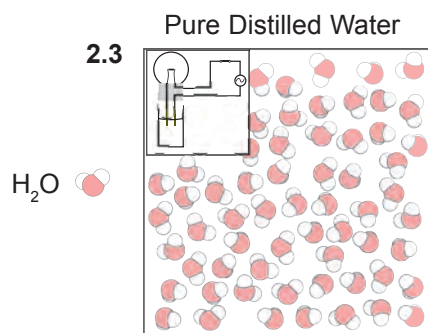
Notice that H_2O is acting as an acid. We cannot exclude H_2O as a reactant because we need to have a balanced chemical reaction.

ACID-BASE EQUILIBRIA

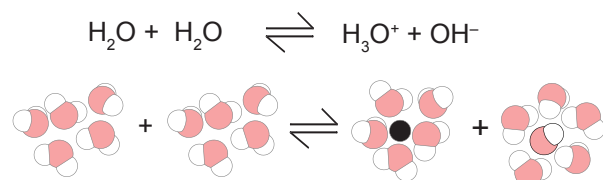
CONJUGATE ACIDS AND BASES

Now that we've seen that acids in water give hydrogen ions, let's look at pure water. We've studied the following picture earlier and determined that water is a non-electrolyte because the light bulb didn't light. While all of this is true, there's more to this story.

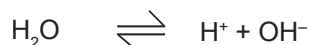
► For a review, state the definition of a non-electrolyte.



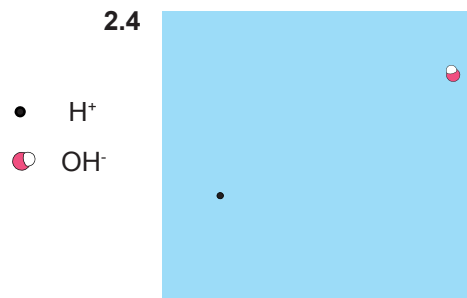
When a very sensitive light is used in the conductivity experiment, the light lights. How can this be? Well, pure water does form ions in solution; it forms protons and hydroxide ions. But, the concentration of these ions is so low that a sensitive light is needed in the conductivity experiment to see evidence of the ions. To show this in the form of a reaction, we write



which can be simplified to



For most purposes, we can simplify pictures of solvent molecules. The neutral water molecules in the following picture are simplified to a blue background. The ions in the water are thus shown more clearly.



► Water is an example of a molecule which gives 2 conjugate acid/base pairs. What are they?

The dissociation of water gives both an acid (substance that provides a proton) and a base (substance that accepts a proton). We call water AMPHIPROTIC.

In the general equilibrium module, we learned to write equilibrium constants. For water,

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since the concentration of H_2O in water is 55.6 M, it can be regarded as a constant. A simplified version of K_c is called the ion-product constant of water.

$$K_w = [\text{H}^+][\text{OH}^-]$$

K_w is a constant. At 25°, the concentrations of both H^+ and OH^- are $1 \times 10^{-7} \text{ mol L}^{-1}$.

$$K_w = (10^{-7})(10^{-7}) = 1 \times 10^{-14}$$

Note that there are no units associated with equilibrium constant values, K . This is standard, and you are not expected to show units.

► Will the value of K_w change at varying temperatures? Explain.

Ion Product of Water.		
° C	K_w	$\text{p}K_w$
0	0.12×10^{-14}	14.93
10	0.29×10^{-14}	14.53
25	1.01×10^{-14}	14.00

Remember the definition of pH from earlier in this module.

$$\text{pH} = -\log [\text{H}^+]$$

This calculation can be used for more than just the concentration of H^+ . The pX of X (where X is any number) is equal to the $-\log$ of X.

Other examples include:

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{p}K_w = -\log K_w$$

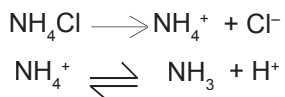
► Determine the pH, pOH, and $\text{p}K_w$ for the dissociation of water. Check your answers by using the fact that $\text{pH} + \text{pOH} = \text{p}K_w$.

► What is the pH of a solution in which the $\text{pOH} = 4$? Which is greater for this solution - the value of $[\text{H}^+]$ or the value of $[\text{OH}^-]$?

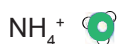
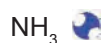
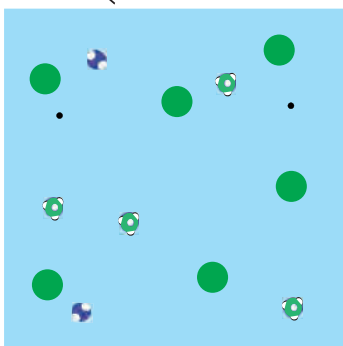
ACID-BASE EQUILIBRIA

CONJUGATE ACIDS AND BASES

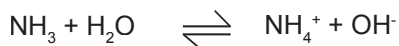
► For each reaction below, identify the acid, base, conjugate acid, and conjugate base.



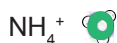
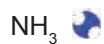
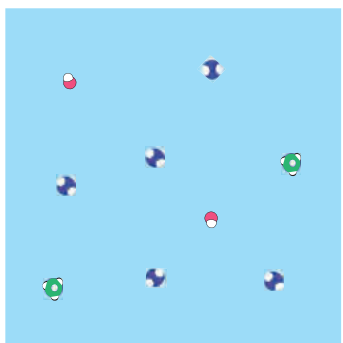
2.5



► Is this solution acidic or basic?



2.6

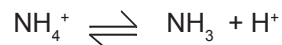


► Is this solution acidic or basic?

► Write the appropriate K_a or K_b for each of the reactions involving ammonia at the left.

For each reaction, we must determine whether the solvent (water) is acting as a base or an acid. Look back at your acid-conjugate base and base-conjugate acid designations for a reminder.

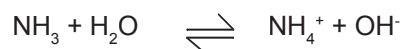
For the dissociation



we write the acid dissociation constant called K_a .

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

For the reaction



we write the base dissociation constant called K_b .

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

An important relationship for (and only for) conjugate acids and bases is $K_w = K_a \times K_b$.

$$K_a \times K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \times \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$= [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} = K_w$$

► K_a for NH_4^+ is 1.0×10^{-9} . Calculate the K_b for NH_3 .

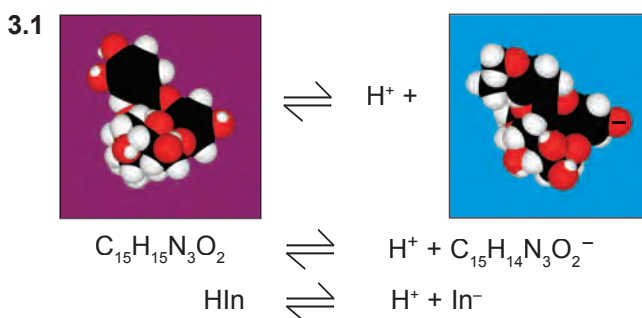
► What is the $\text{p}K_a$ for NH_4^+ and the $\text{p}K_b$ for NH_3 ?

► Another important relationship for conjugate acids and bases is that $\text{p}K_a + \text{p}K_b = 14$. Prove this relationship.

ACID-BASE EQUILIBRIA

INDICATORS

One way to determine the pH of a solution is to use an indicator. An indicator exists in different colored forms depending on whether the compound is protonated or unprotonated. The indicator shown is purple cabbage extract.

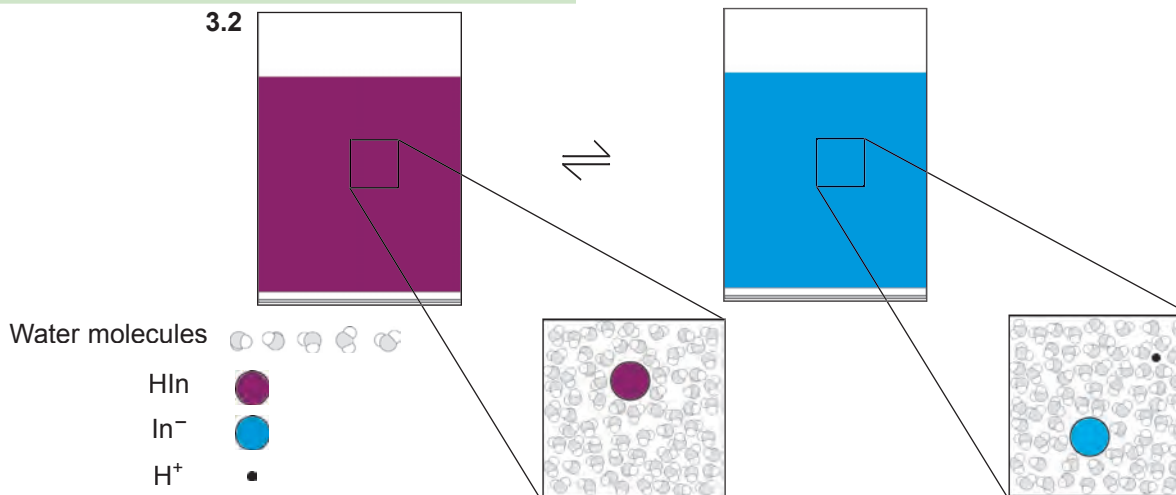


► Is purple cabbage indicator an acid or a base?

► Write the K_a expression for $HIn \rightleftharpoons H^+ + In^-$.

Rearranging the K_a expression gives

$$\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]}$$



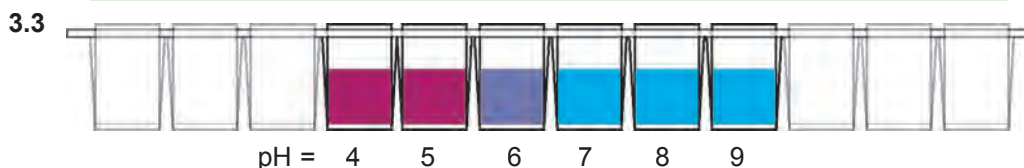
► Which part of the solution causes the color, the solute or the solvent?

► The 1 x 12 array shown below shows the pH where the color changes.

Mark which pH values show $[HIn] > [In^-]$.

Mark which pH values show $[HIn] < [In^-]$.

Mark which pH values show $[HIn] = [In^-]$.



Therefore, when $[HIn] = [In^-]$, $\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]} = 1$, so, $K_a = [H^+]$.

To see "pure" color, $\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]} = \frac{10}{1}$ for blue.

For "pure" purple, $\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]} = \frac{1}{10}$

$$\frac{K_a}{10} = [H^+]$$

$$10 K_a = [H^+]$$

Therefore, the pH range of an indicator is $pK_a \pm 1$.

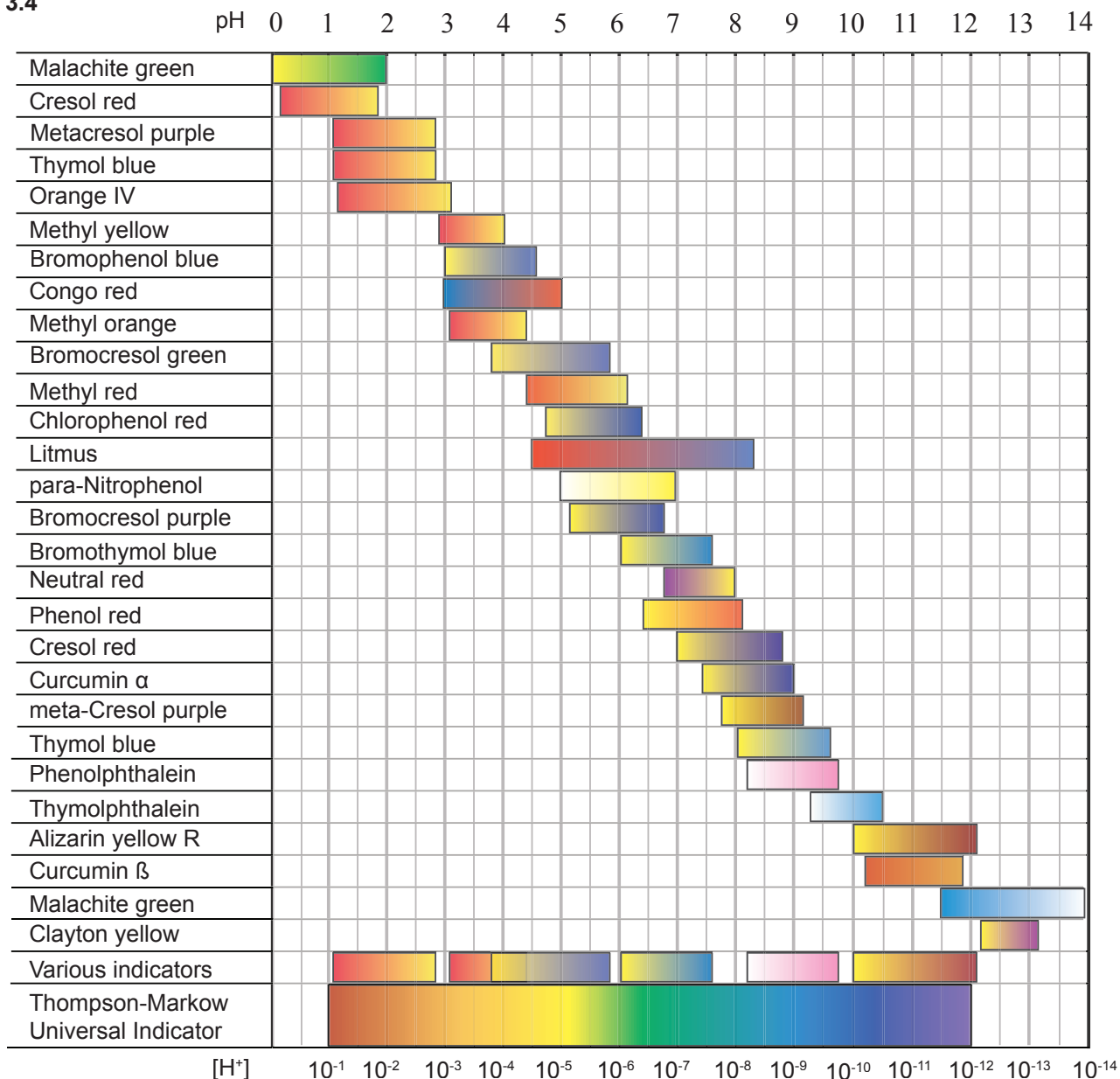
ACID-BASE EQUILIBRIA

INDICATORS

Here is a list of several acid/base indicators and the pH range in which they are useful:

pH Ranges of Indicators

3.4



A universal indicator, shown at the bottom, is a mixture of several indicators. Universal indicators have a wider range of usefulness because they mix indicators.

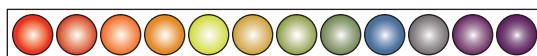
► The Thompson-Markow Universal Indicator is a mixture of six indicators. Metacresol purple is one of them; name the 5 others.

► What is the pH range of the Thompson-Markow universal indicator?
What is $[H^+]$ at pH 0?

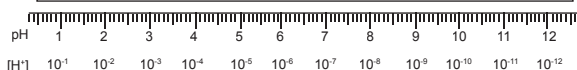
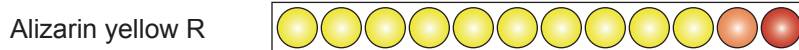
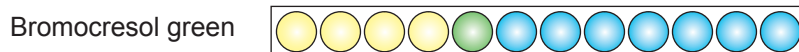
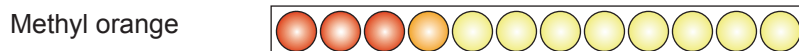
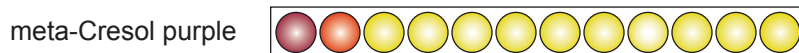
ACID-BASE EQUILIBRIA

THOMPSON-MARKOW UNIVERSAL INDICATORS

3.5 Thompson-Markow Indicator



Individual indicators that make up the Thompson-Markow Universal Indicator:

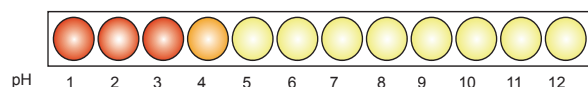
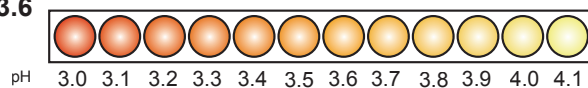


► Determine the K_a and pK_a of each indicator that makes up the Thompson-Markow Universal Indicator.

A more accurate way to determine the K_a and pK_a of each indicator is to decrease the change in each pH interval. For example, instead of measuring methyl orange from pH 1 through pH 12, we could measure it from pH 3 to pH 4.1. Of course, you have to know the general range of where the pK_a lies in order to do this properly.

► Which indicator would be used to determine the pH of a 7.6 buffer solution other than the Thompson-Markow Universal Indicator?

3.6

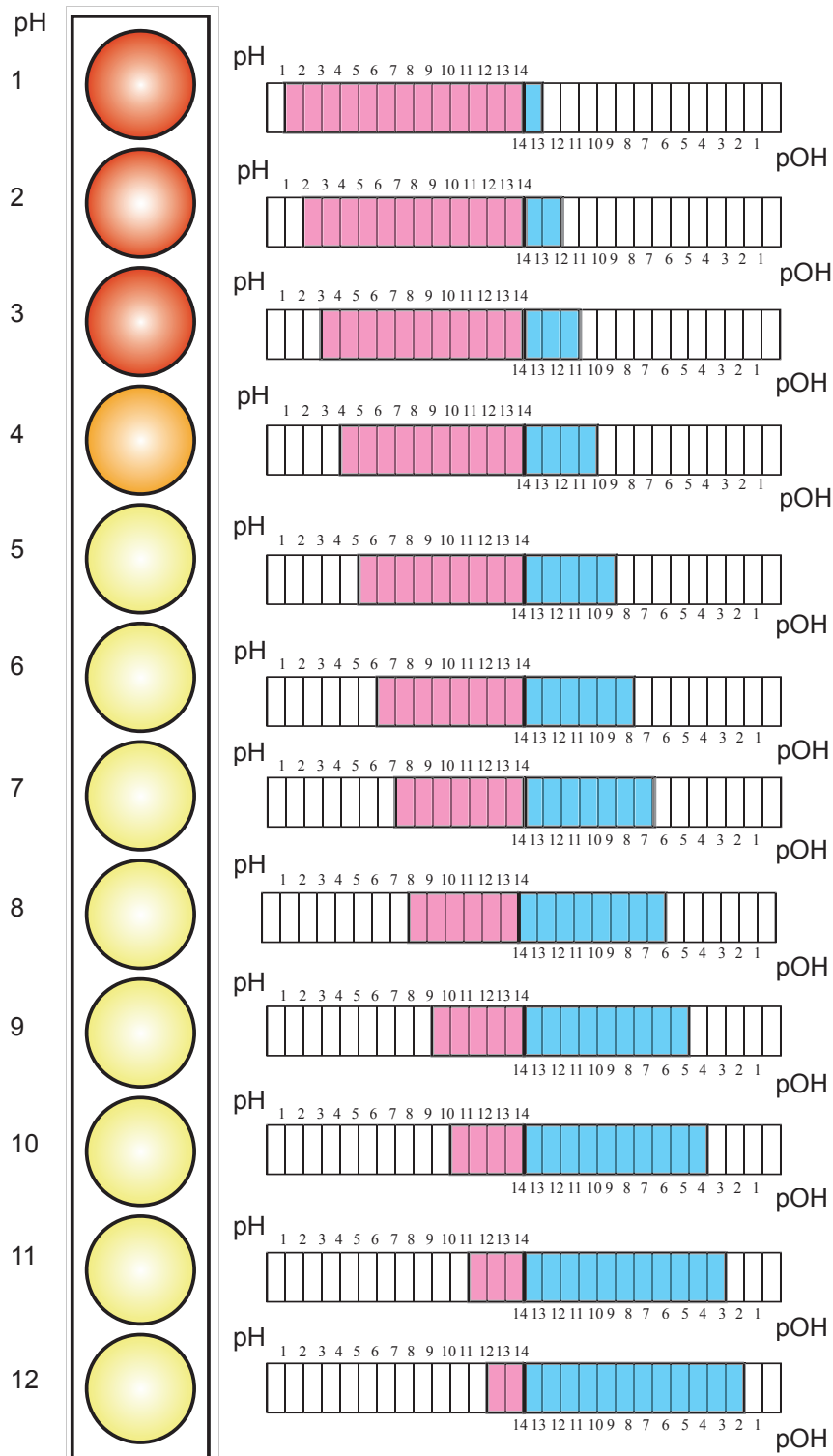


ACID-BASE EQUILIBRIA

INDICATOR WELL TRAYS

Below are several chemLogs showing the pH and pOH for each well. Each well contains a solution of methyl orange at the different pH values listed..

3.7



► What can you determine about the relationship between pH and pOH?

► Complete the following equation:

$\text{pH} + \text{pOH} = \underline{\hspace{2cm}}$

► What is the pK_a of methyl orange?

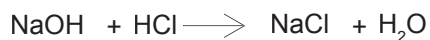
► The approximate pH range of any indicator is the range between the $\text{pK}_a - 1$ and the $\text{pK}_a + 1$. What is the pH range of methyl orange?

► Remember that $K_a \times K_b = K_w$ for any conjugate acid/base pair. What is the pK_b for methyl orange? Using pK_b , determine the pOH range for methyl orange.

ACID BASE EQUILIBRIA

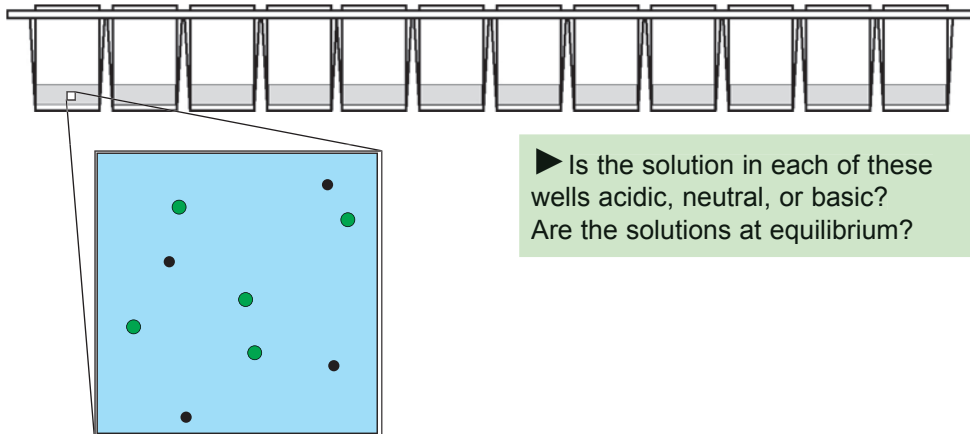
TITRATION

A solution of strong base, NaOH, can be titrated with a solution of strong acid, HCl. The overall chemical reaction for the titration is the following:



Five drops of 0.01 M HCl were added to each of the wells in the 1 x 12 tray.

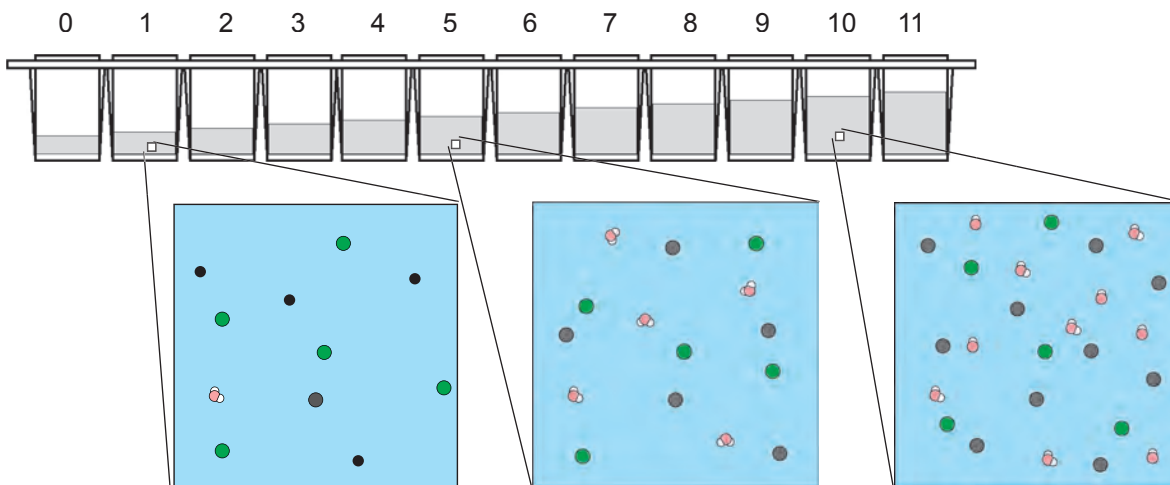
4.1



► Is the solution in each of these wells acidic, neutral, or basic?
Are the solutions at equilibrium?

To each well above, drops of 0.01 M NaOH were added. The numbers above the wells represents the drops of NaOH added.

4.2



4.3



► Which solution is acidic?
Which solution is neutral?
Which solution is basic?
Where are the water molecules that are shown coming from?
Write the net ionic equation for this titration reaction.

Is [H⁺] higher in the well with 1 drop of base added, or 5 drops added? What about pH?
Is [H⁺] higher in the well with 5 drop of base added, or 10 drops added? What about pH?

► So, as [H⁺] increases, pH decreases, and vice versa. What happens to pH as [OH⁻] increases?

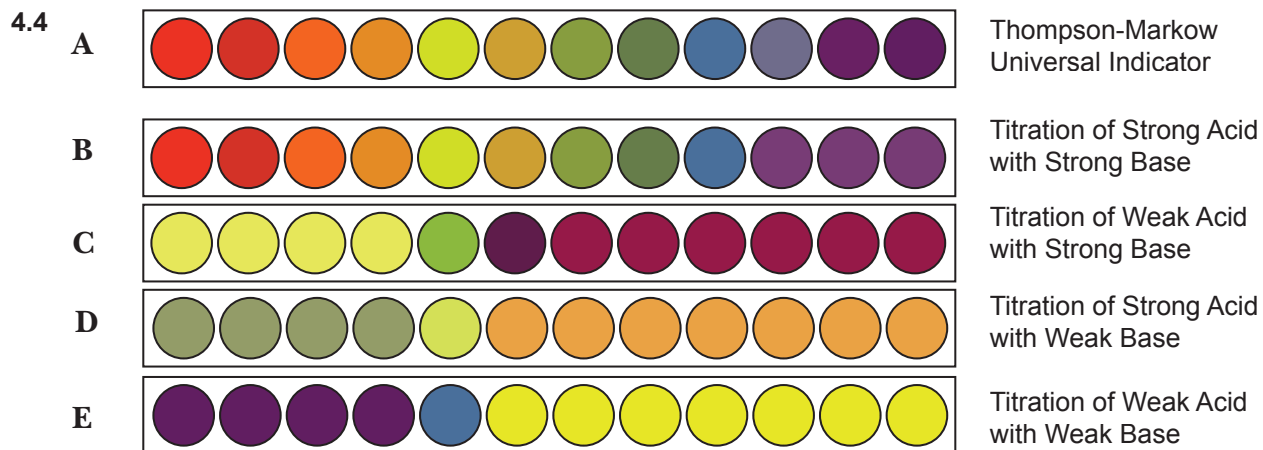
DEFINITION:

$$\text{pH} = -\log [\text{H}^+]$$

► What is the pH of the 0.01 M HCl that we started with?

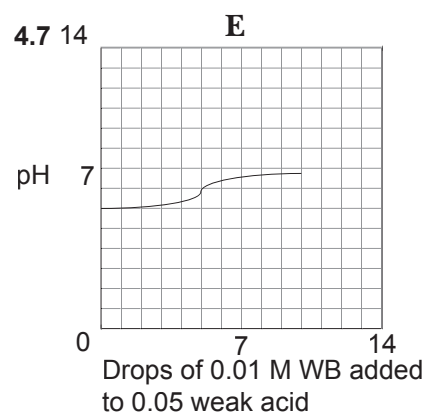
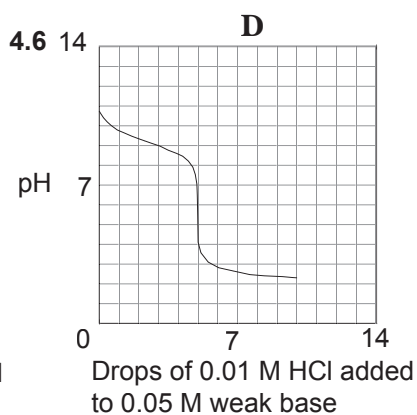
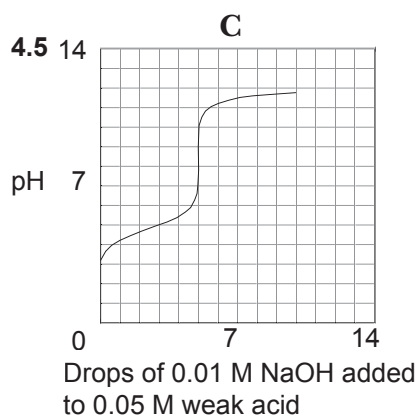
ACID BASE EQUILIBRIA

TITRATION



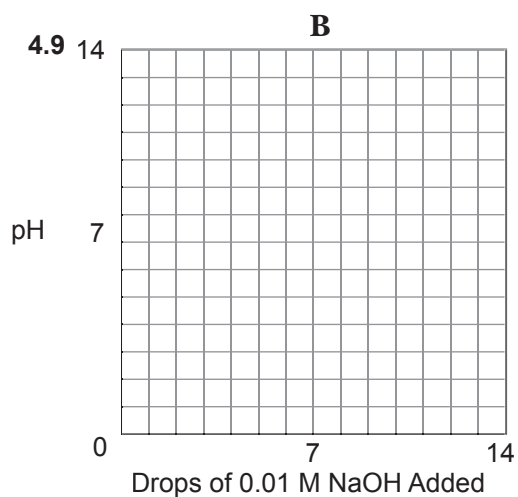
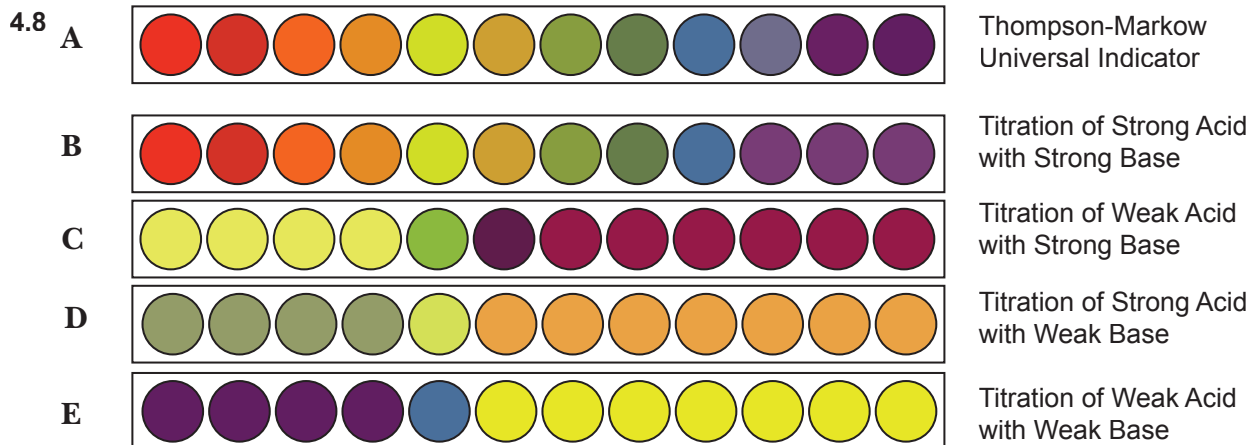
The following graphs show the titration curves of experiments C, D, and E.

► Using the graphs, give a molecular description of each titration from pH 0 to 2, pH 4 to 6, and pH 8 to 10. Describe the molecular changes taking place in the wells at these pH regions.

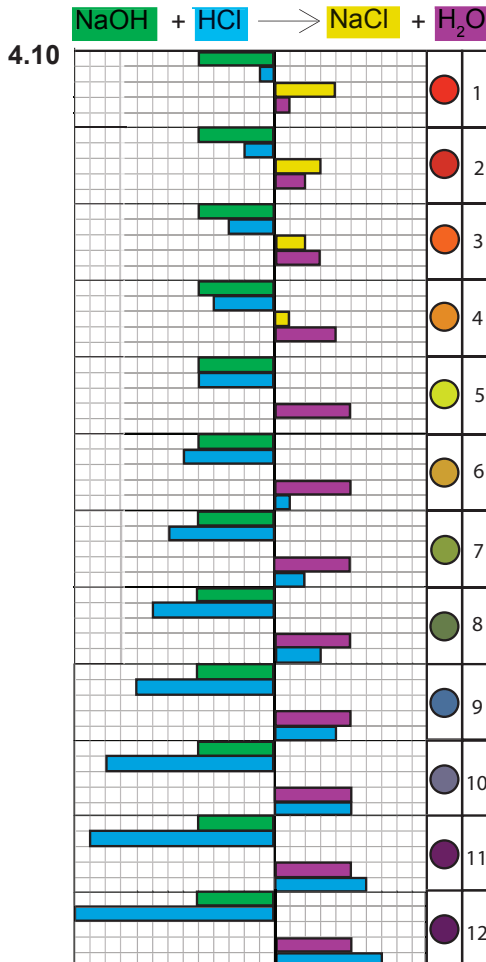


ACID BASE EQUILIBRIA

TITRATION

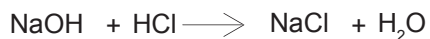


► Experiment B is a strong acid titrated with a strong base. Try to produce the titration curve for this experiment. The chemLog is shown at the right to help you with this.



ACID BASE EQUILIBRIA

TITRATION

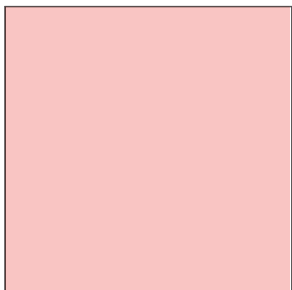
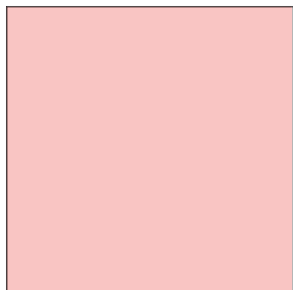
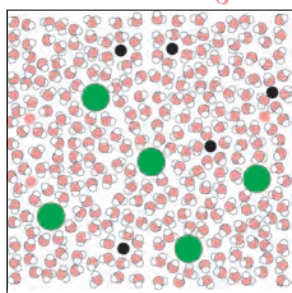
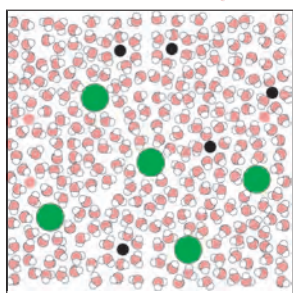


A solution of HCl is shown in each of the drawings.

4.11



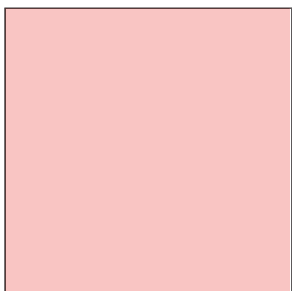
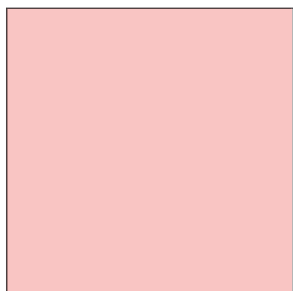
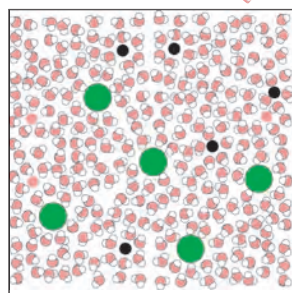
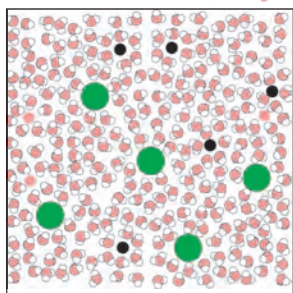
4.12



4.13



4.14



► Draw a sketch for each sample after the NaOH shown has been added. The water molecules are shown for you by the pink background.

► Are the drawings of HCl in solution (before NaOH is added) at equilibrium?

► Which of the sketches that you drew is at equilibrium?

► Is the pH of each of the solutions that you have drawn acidic, neutral, or basic?

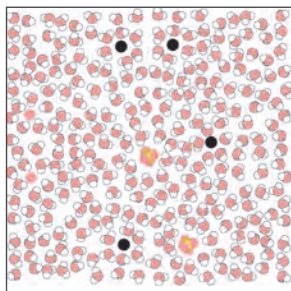
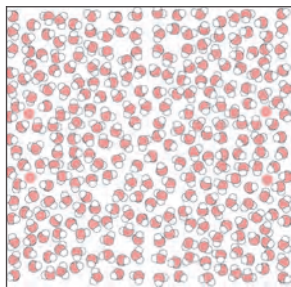
A **LIMITING REAGENT** is a reactant that governs the maximum yield of product that is possible. For example, when 1 NaOH is added to a solution with 10 HCl, the NaOH is the limiting reagent because it governs how many NaCl and water molecules can be formed in the reaction.

► What is the limiting reagent for each of the sketches that you drew?

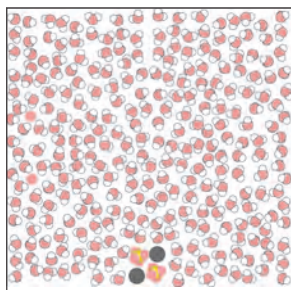
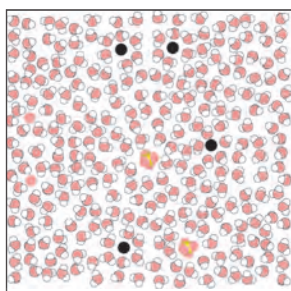
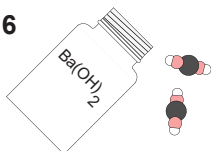
ACID BASE EQUILIBRIA

TITRATION

4.15



4.16

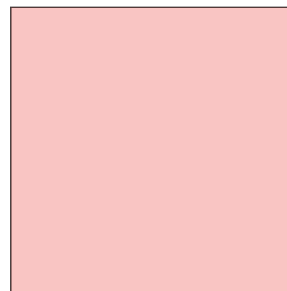


► Write the chemical equations for the process shown in pictures 4.15 and 4.16.

► Is the pH of the final solution greater than 7, equal to 7, or less than 7?

► What is the pH of the water?

► Draw a picture of the final solution after one more $Ba(OH)_2$ is added. Again, the water is shown as a pink background.



► Is the pH of the solution you drew greater than 7, equal to 7, or less than 7? Explain.

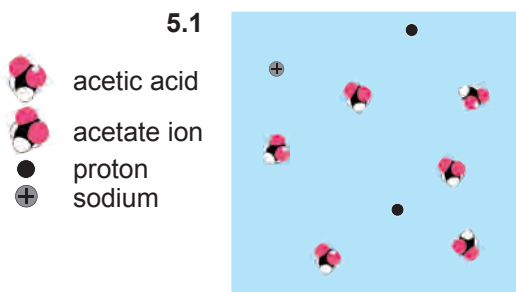
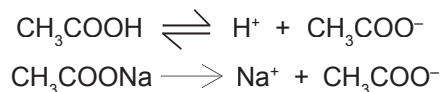
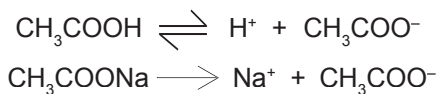
► Is the solution you drew at equilibrium?

ACID-BASE EQUILIBRIA

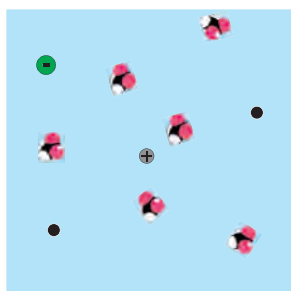
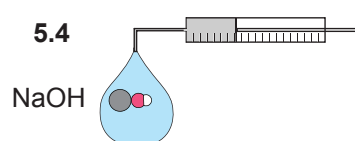
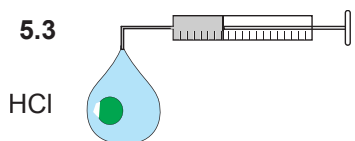
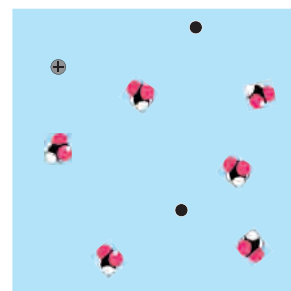
BUFFERS

In experiments, we often need to control the $[H^+]$ of the solution. This is done with buffers. A buffered solution resists changes in $[H^+]$. Buffers can have a predetermined pH, with acidic buffers at any chosen value between pH 0-7, and basic buffers at any chosen value between pH 7-14.

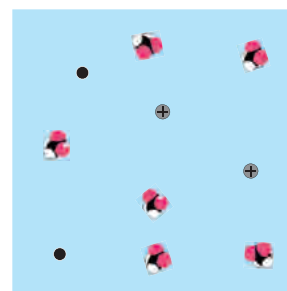
Acidic buffers are solutions containing weak acids and the salts of weak acids, eg. CH_3COOH and CH_3COONa . Basic buffers are solutions containing weak bases and the salts of weak bases, eg. NH_3 and NH_4Cl .



Two dilute solutions of acetic acid at the same concentration.



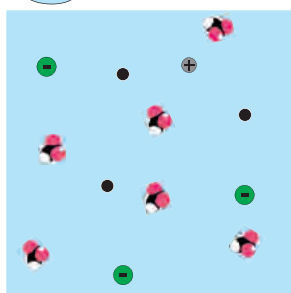
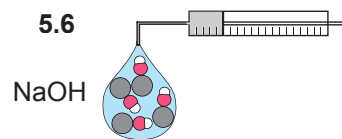
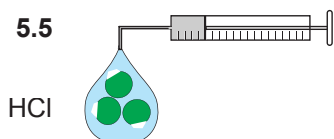
Add acid.



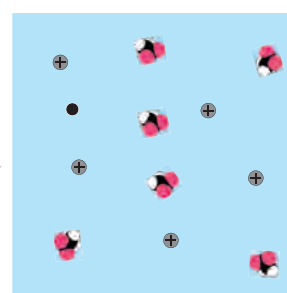
Add base.

When acid is added, the buffer accepts protons.

When base is added, the buffer donates protons.



Add more acid.



Add more base.

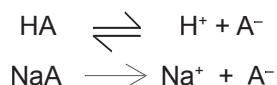
The buffer capacity is an indication of the amount of acid or base that can be added before the buffer loses its ability to resist the pH change.

► At which point in each of the additions above was the buffer capacity exceeded?

ACID-BASE EQUILIBRIA

HENDERSON-HASSELBALCH EQUATION

How can we design a buffer with a specified pH? Let's examine the chemical reaction for solution containing a general weak acid and its salt - a buffer.



► Write the K_a expression for this reaction.

After rearranging the K_a expression to determine what $[\text{H}^+]$ is equal to, we determine that

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

We can now determine the pH. Write the pH expression by taking the negative log of each side of the $[\text{H}^+]$ expression.

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] = -\log \left(K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \right) \\ &= -\log K_a + -\log \left(\frac{[\text{HA}]}{[\text{A}^-]} \right) \\ &= \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \end{aligned}$$

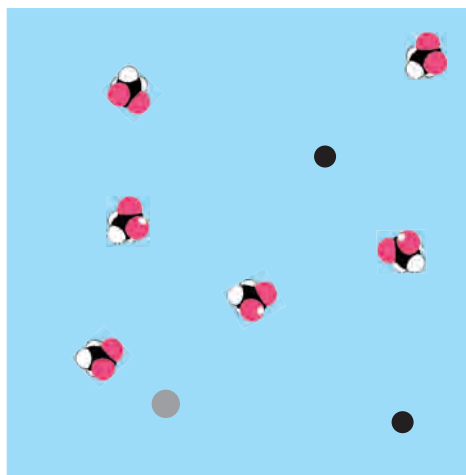
Since acidic buffers are solutions of weak acids and their salt, HA loses only a tiny fraction of its protons. What are the dominant species (the most concentrated) in solution? They HA, because HA is a weak acid, and A^- , because it comes from the complete dissociation of the salt NaA. Because they are so dominant in solution, we can approximate $[\text{HA}]$ and $[\text{A}^-]$ of a buffer by their initial concentrations. The Henderson-Hasselbalch equation states that:

$$\text{pH} \approx \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]_{\text{initial}}} \right)$$

Let's calculate the pH of a buffer solution in which 0.040 M $\text{CH}_3\text{COONa}_{(\text{aq})}$ and 0.080 M $\text{CH}_3\text{COOH}_{(\text{aq})}$ are mixed at 25 °C.

► Identify the acid and its conjugate base in this mixture. Identify the ions from the salt in this mixture.

5.7



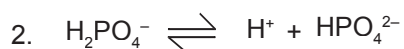
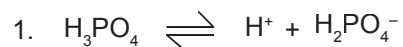
► Write the equilibrium equation for acetic acid, and rearrange the K_a for this equation to give $[\text{H}^+]$.

► Use the Henderson-Hasselbalch equation to find the pH.

ACID-BASE EQUILIBRIA

POLYPROTIC ACIDS AND POLYBASIC BASES

Acids which can donate 2 or more protons are called polyprotic. Bases which can accept 2 or more protons are polybasic bases. Good examples are phosphoric acid (H_3PO_4) and the phosphate ion (PO_4^{3-}). Polyprotic acids release H^+ ions in a step-wise manner:



► Identify and write down the conjugate acids and bases in these dissociations.

► For H_3PO_4 , the $\text{pK}_a = 2.1$.
For H_2PO_4^- , the $\text{pK}_a = 7.2$.
For HPO_4^{2-} , the $\text{pK}_a = 13$.
Calculate the K_a values.

► Write expressions for the K_a 's and K_b 's for all the acids and bases in these dissociation reactions.

► Why are the values of K_a 's and K_b 's very different from each other?

6.1



Thompson-Markow
Universal Indicator

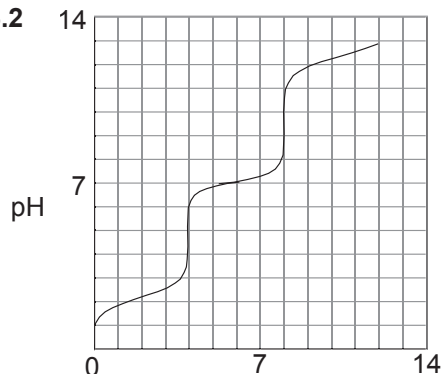


Titration of 1M H_3PO_4
with NaOH

1 2 3 4 5 6 7 8 9 10 11 12

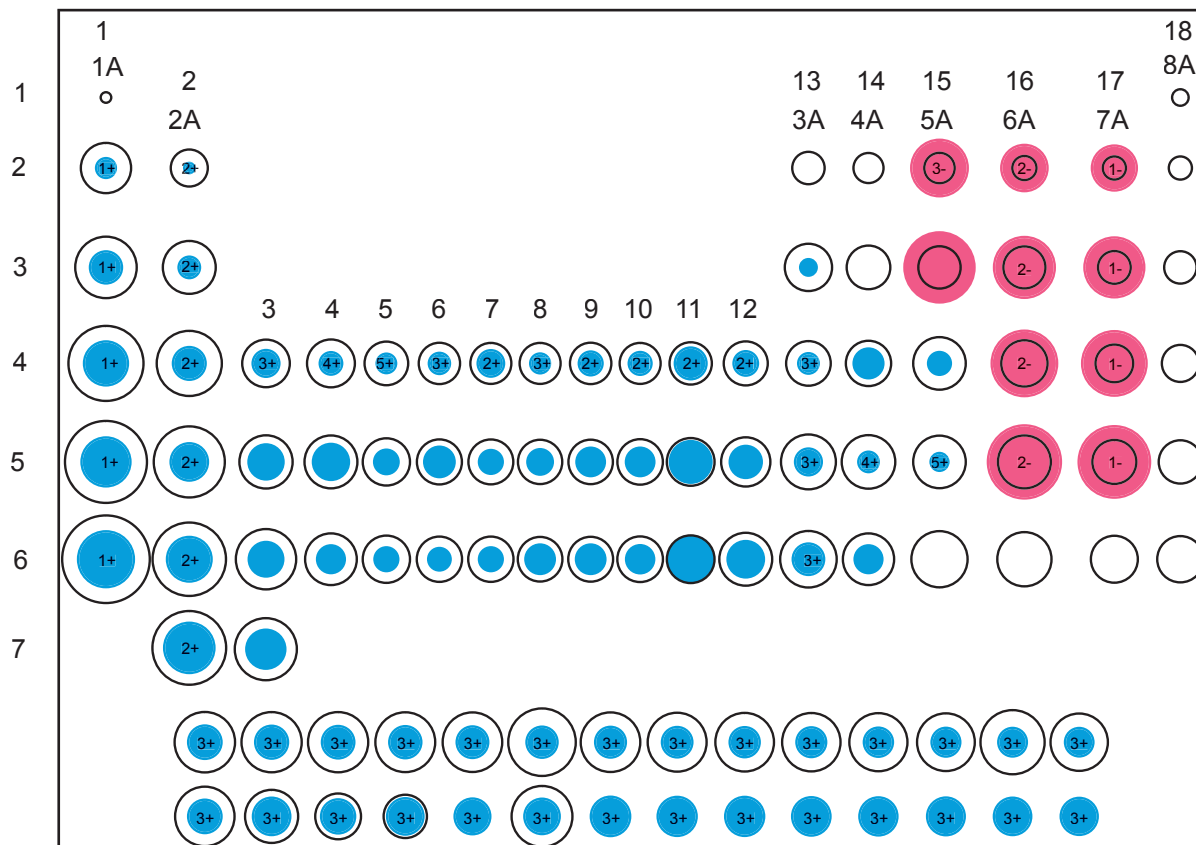
Drops of NaOH added

6.2



Drops of 0.01 M NaOH
added to 0.05 M weak acid

CHEMICAL BONDING



○ Neutral Atom

● Positive Ion

● Negative Ion

by
DR. STEPHEN THOMPSON
MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

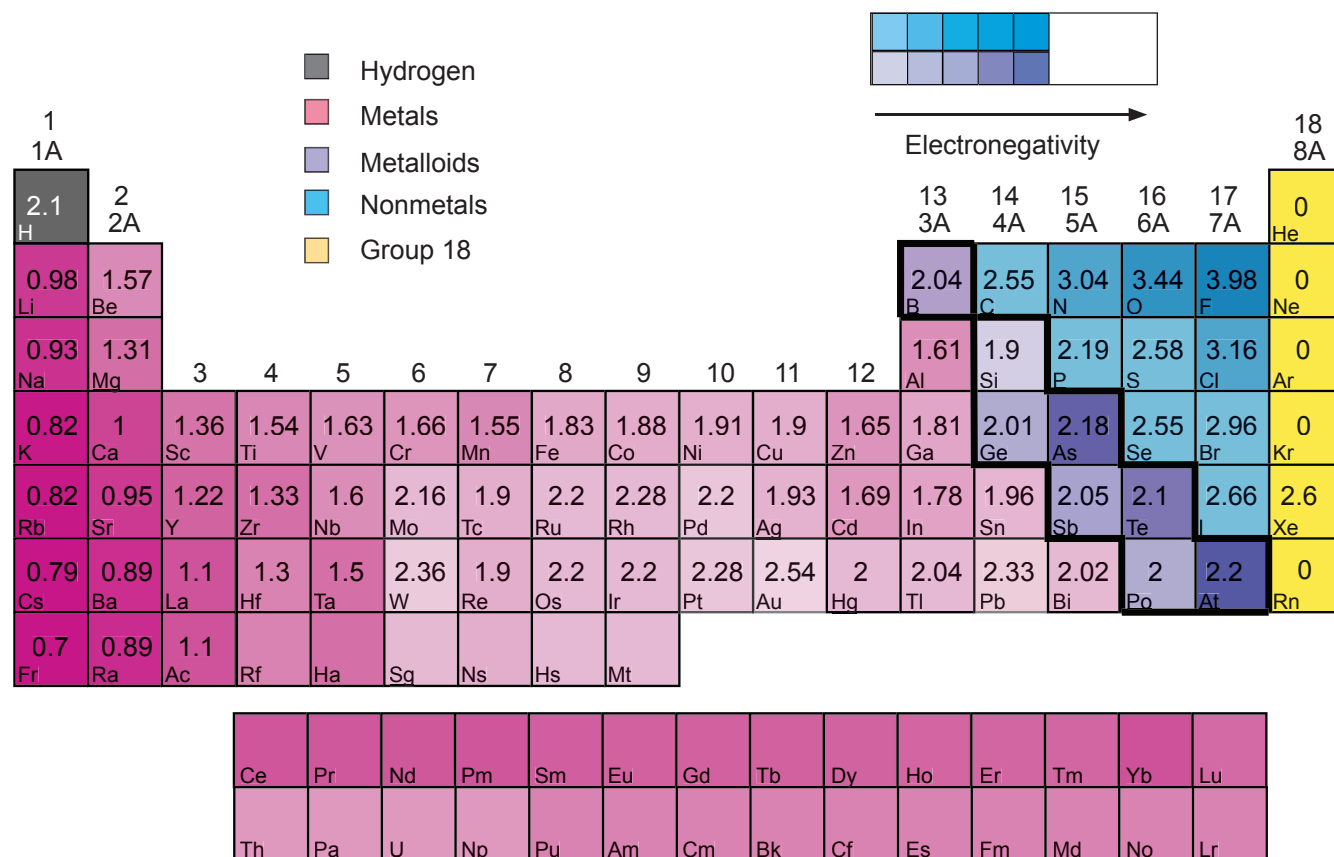
CHEMICAL BONDING

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2	Electronegativity
3	Road Map
4	Types Of Bonding
5	Properties Controlled By Chemical Bond
6	Polar Bonds
7	Metallic Bonding
8	Intermolecular Forces
9	Ions: Counting Electrons And Protons
10	Ionic And Atomic Radii
11	Ions And Energy
12	Lithium Fluoride
13	Crystal Packing
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15	Crystal Packing
16	Covalent H ₂
17	Quantization
18	Bond Length And Strength
19	Strong And Weak Bonds
20	Strong And Weak Bonds
21	Covalent To Metallic
22	Electron Delocalization

CHEMICAL BONDING

ELECTRONEGATIVITY



Electronegativity is the ability of an atom to attract shared electrons to itself. It is largely the difference between the electronegativities of two atoms which determines what kind of bond is formed between them.

What is the most electronegative element?

What is the least electronegative element (aside from the noble gases)?

What is the range of electronegativity for the metals? Metalloids? Nonmetals?

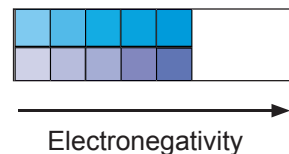
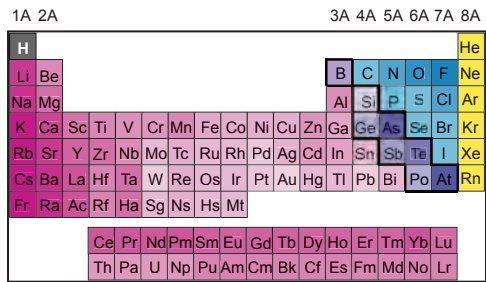
Why is the electronegativity of the noble gases listed as zero?

For an electron shared between hydrogen and chlorine, would you expect the electron to be closer to the hydrogen or the chlorine?

CHEMICAL BONDING

ROAD MAP

- Hydrogen
- Metals
- Metalloids
- Nonmetals
- Group 18

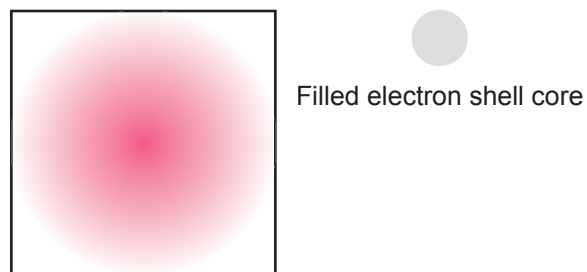


 Groups 1 and 2 Metals	+	 NonMetals and H	→	<h3>Ionic Bonding</h3>
 NonMetals and H	+	 NonMetals and H	→	<h3>Covalent Bonding</h3>
 Other Metals	+	 NonMetals and H	→	<h3>Polar Bonding</h3>
 Non Metalloids	+	 Metalloids	→	<h3>Polar Bonding</h3>
 Metals	+	 Metals	→	<h3>Metallic Bonding</h3>

CHEMICAL BONDING

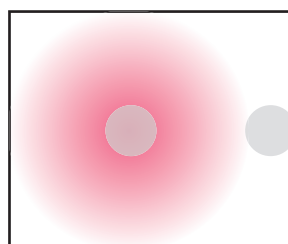
TYPES OF BONDING

The different types of chemical bonding are determined by how the valence electrons are shared among the bonded atoms.



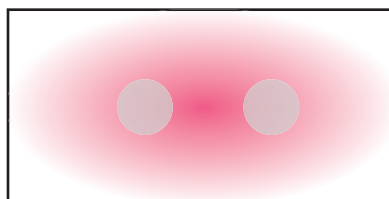
Valence Electron Cloud

In **IONIC BONDING** the valence electrons are completely transferred from one atom to the other atom. Ionic bonds occur between metals and nonmetals when there is a large difference in electronegativity.



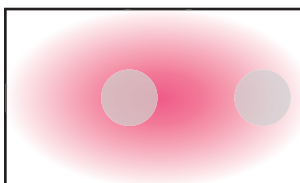
Ionic Bonding

In **COVALENT BONDING** the valence electrons are shared as pairs between the bonded atoms. Pure covalent bonding only occurs when two nonmetal atoms of the same kind bind to each other. When two different nonmetal atoms are bonded or a nonmetal and a metal are bonded, then the bond is a mixture of covalent and ionic bonding called polar covalent bonding.



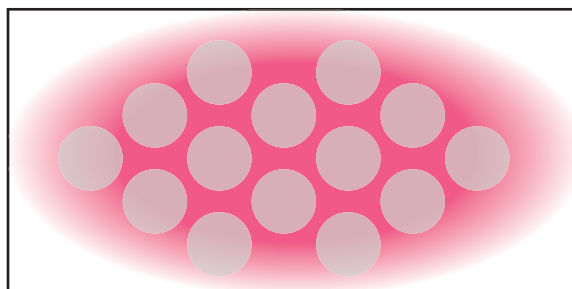
Covalent Bonding

In **POLAR BONDING** the electrons are shared but NOT equally. Many compounds have the characteristics of BOTH ionic and covalent bonding. Electronegativity differences determine the balance of character.



Polar Bonding

In **METALLIC BONDING** the valence electrons are shared among all of the atoms of the substance. Metallic bonding occurs when metals bond to either themselves or mixed with other metals in alloys.



Metallic Bonding

Using the periodic table of electronegativities from the last page, write down examples of atom pairs which you would expect to form covalent bonds, polar covalent bonds and ionic bonds.

CHEMICAL BONDING

PROPERTIES CONTROLLED BY CHEMICAL BOND

Chemical bonding determines the physical properties of substances. These properties are listed below for covalent, ionic and metallic bonding.

Covalent

Gas, liquid, or a soft solid.

Low melting point and low boiling point.

Insoluble in H₂O

Soluble in nonpolar solvents.

Nonconductor of heat and electricity.

Nonlustrous

Using the list of properties on the left, try to assign as many of the common substances in your environment to one of the types of bonding.

Ionic

Crystalline solid.

Very high melting point.

Soluble in H₂O.

Insoluble in nonpolar solvents.

Nonconductor of heat and electricity.

Conducts electricity in aqueous solutions.

Examples: NaCl, CaCO₃

List and describe some substances which do not seem to fit into any of the three types of bonding.

Metallic

Malleable solid.

High melting point and boiling point.

Insoluble in H₂O.

Insoluble in nonpolar solvents.

Conducts heat and electricity.

Lustrous

Examples: gold, copper

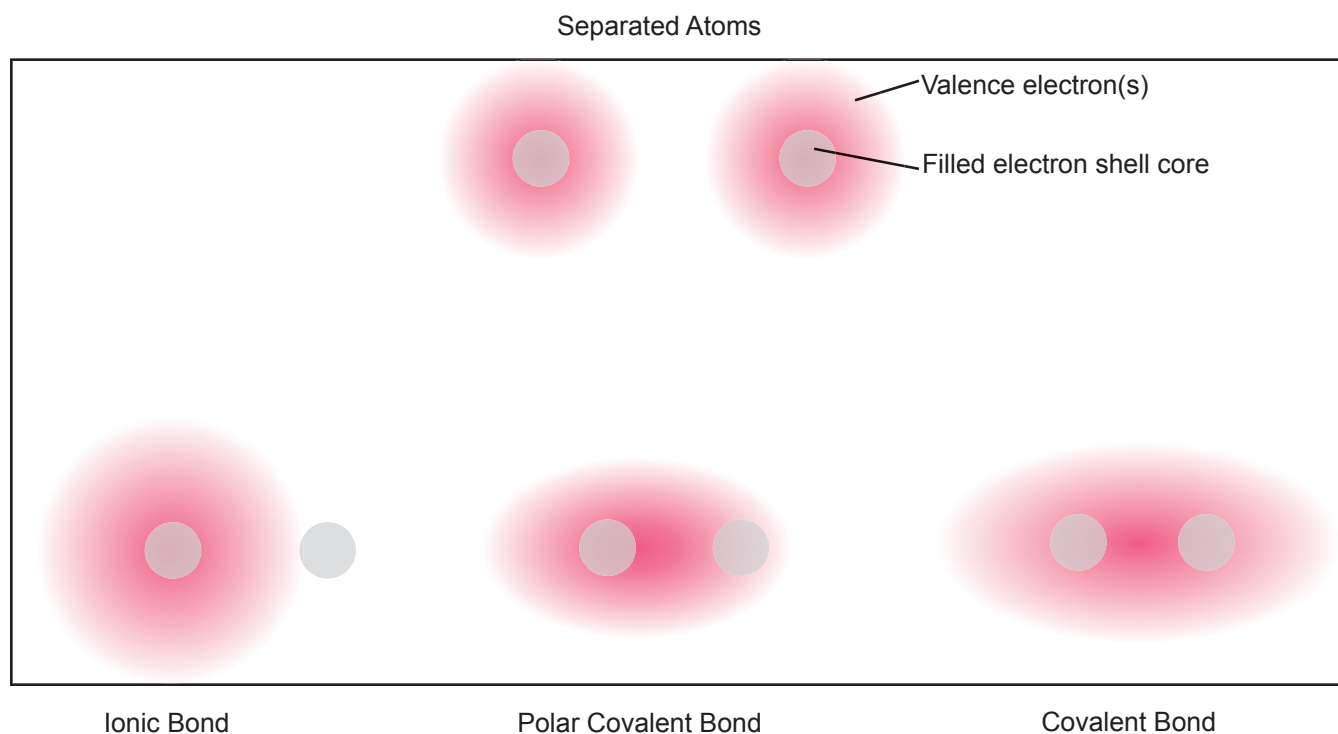
CHEMICAL BONDING

POLAR BONDS

Ionic and covalent bonds are two ideal types.

Many bonds share characteristics of both ionic and covalent bonding. They are called polar covalent bonds and they tend to occur between atoms of moderately different electronegativities.

In polar covalent bonds the electrons belong predominantly to one type of atom while they are still partially shared by the other type, as illustrated in the following pictures of the valence electron densities.



In the picture above, the separated atoms look alike. If, in fact, they are the same kind of atom, which of the three bonds shown is possible? Why only that one? What other type of bonding is possible between identical atoms?

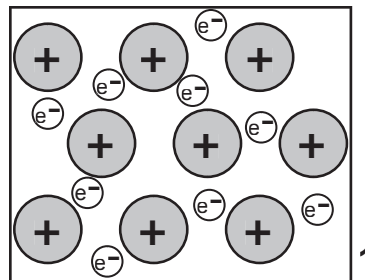
Using the chart of electronegativities, arrange the following compounds in an order from most ionic to most covalent:
 Al_2O_3 , CaCl_2 , NaF , O_2 , NaCl ,

CHEMICAL BONDING

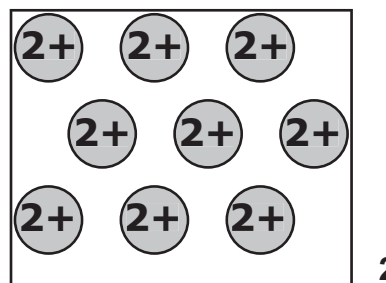
METALLIC BONDING

'ELECTRON SEA' MODEL FOR METALS

Metals are formed from elements on the left hand side of the periodic table. Having generally low electronegativity they tend to lose their valence electrons easily. When we have a macroscopic collection of the same or similar type of metallic atoms, the valence electrons are detached from the atoms but not held by any of the other atoms. In other words, these valence electrons are free from any particular atom and are only held collectively by the entire assemblage of atoms. In a metal the ion cores are held more or less at fixed places in an ordered, or crystal, lattice. The valence electrons are free to move about under applied stimulation, such as electric fields or heat.



Picture 1 presents a regular arrangement of the ion cores for a metal with a single valence electron per atom as well as a snapshot of the location of the freely moving valence electrons.



Picture 2 shows a collection of ion cores for a metal with two valence electrons. Draw in the valence electrons. (Little circles are good enough.)
HINT: Metals are neutral in charge.

What is the origin of electrical and thermal conductivity in sodium metal?

Why do metals exhibit a wide range of melting points and hardness?

CHEMICAL BONDING

INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the stability of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

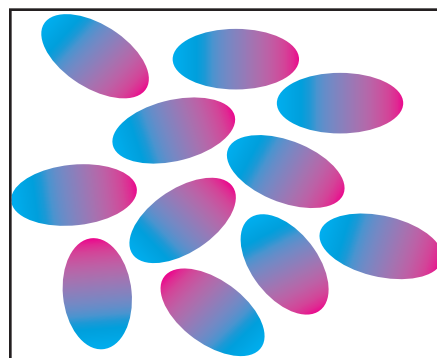
DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?

Why is it more important in liquids than in gases?

Can homonuclear diatomic molecules such as H_2 , O_2 and N_2 have dipole-dipole forces?

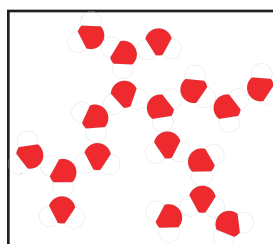


DIPOLE-DIPOLE INTERACTION

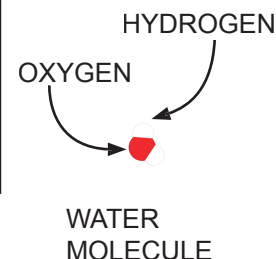
HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom.

Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.

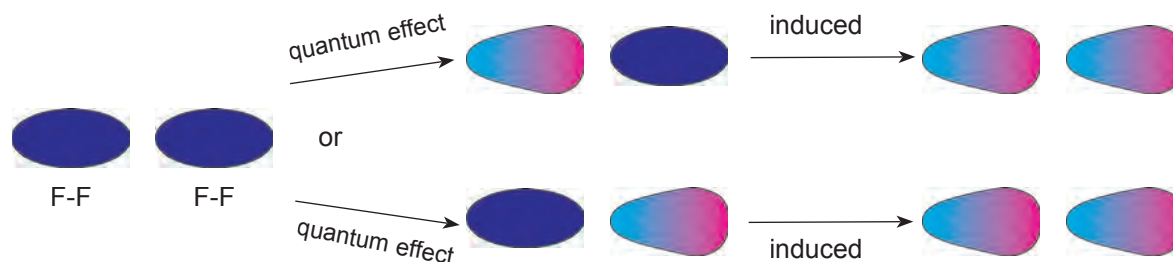


HYDROGEN BONDING



LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecule so that the two molecules have opposite charges on their near sides and attract each other.



CHEMICAL BONDING

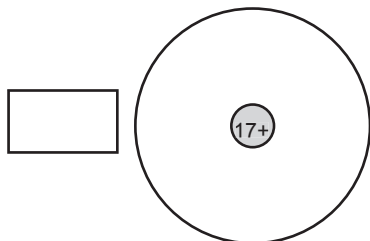
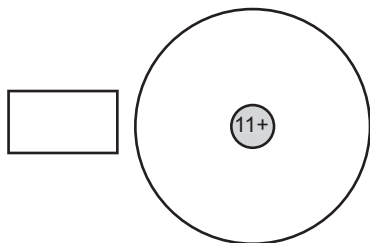
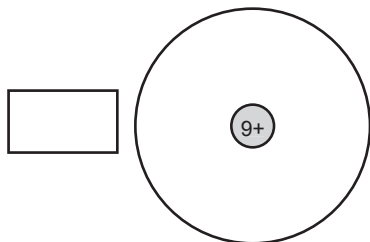
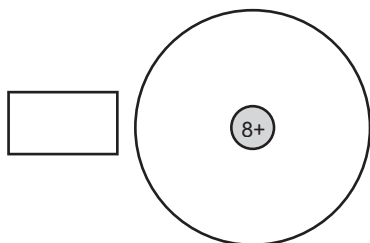
IONS: COUNTING ELECTRONS AND PROTONS

NEUTRAL ATOMS

Neutral atoms have the same number of electrons as protons. In the picture below, the nuclear charge is represented by the gray circle marked 3+, for the 3 protons in the nucleus of lithium. Electrons are marked as horizontal dashes, one for each electron.

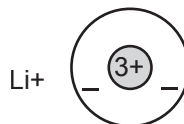


In the pictures below, draw in the number of electrons required to make the atom neutral and write the element symbol in the box to the left of the atom.

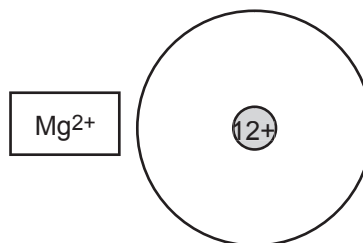
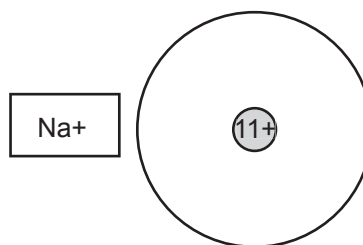


POSITIVE IONS

Positive ions have more protons than electrons. Since the number of protons an atom has is fixed in ordinary chemical reactions, positive ions are produced by removing electrons from the atoms.



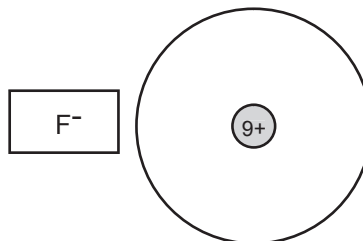
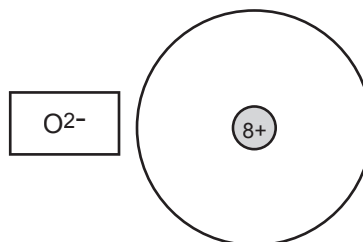
In the pictures below draw in the number of electrons needed to make the ion named in the box.



NEGATIVE IONS

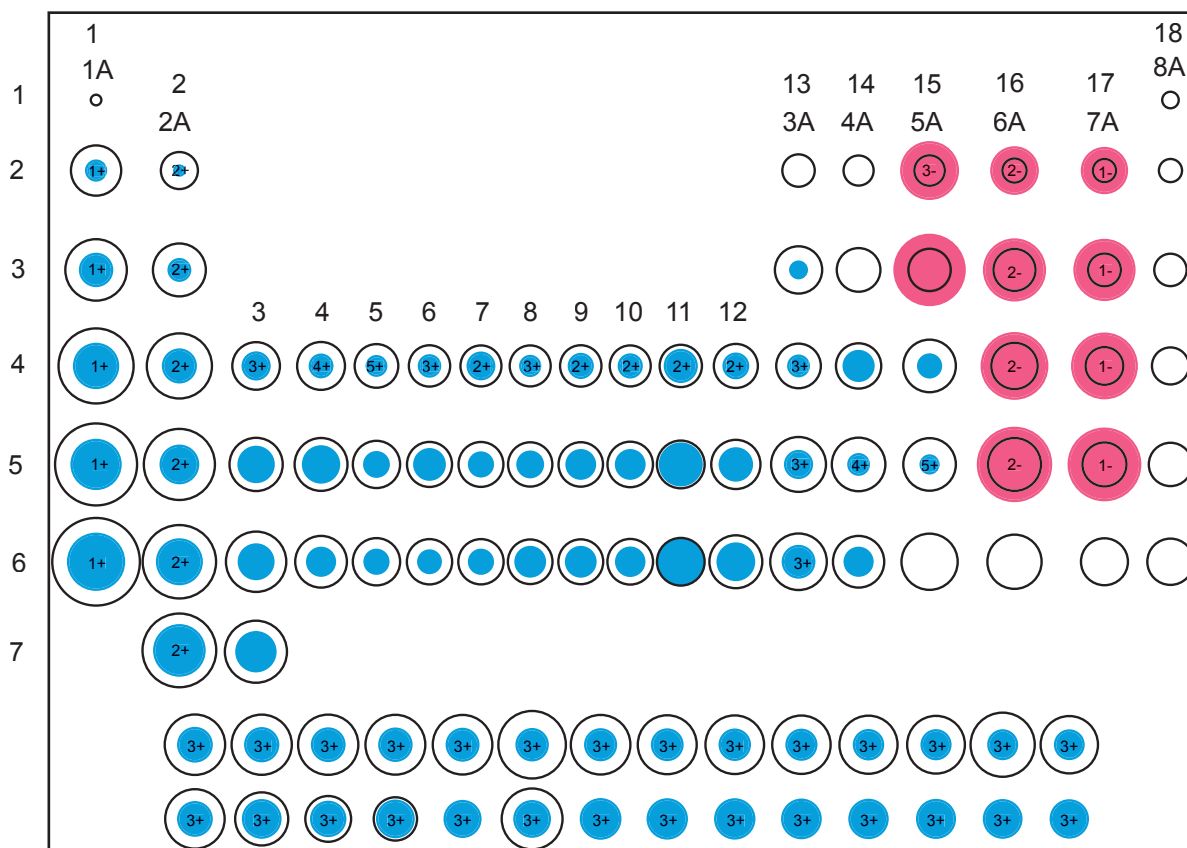
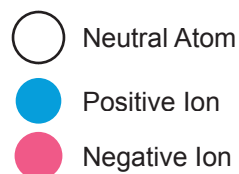
Negative ions have more electrons than protons. Since the number of protons is unchanged from the neutral atom, negative ions are formed by the addition of electrons.

In the pictures below draw in the number of electrons needed to make the ion named in the box.



CHEMICAL BONDING

ATOMIC AND IONIC RADII



In this version of the periodic table the relative sizes of both neutral atoms and of their most common ions are shown, as well as the charges on their ions. The atoms are shown as black outline circles and the ionic diameters are colored blue for positive ions and red for negative ions.

Why are the positive ions smaller than their neutral atoms while the negative ions are larger than the neutral atoms?

Why do both ions and atoms tend to grow larger as we go down the periodic table?

What is the smallest atom? What atom has the smallest ion (too small to show on the table)? Find the largest atom and identify it on a standard periodic table.

What kind of ions do atoms with large electronegativities tend to form?

What makes the atoms and ions in the middle of periods 4, 5 and 6 so small? What makes the samarium atom so large?

Identify the two kinds of atom which appear about the same size as their ion and explain why this is so.

Why are the antimony and beryllium ions so small? Differentiate between the causes.

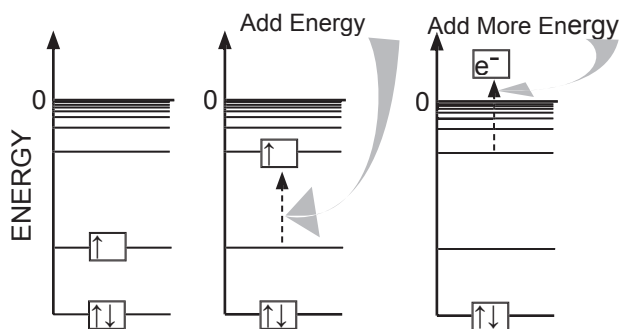
Why are the Lanthanide ions of such similar size?

How might you use the chart of atomic and ionic radii to explain the strengths of ionic bonding between various ions?

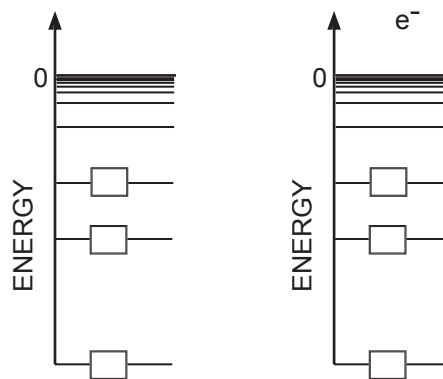
Compare the ionic and atomic radii table above with the chart of electronegativities and attempt to explain as many aspects of the sizes of atoms and ions in terms of electronegativity as possible.

CHEMICAL BONDING

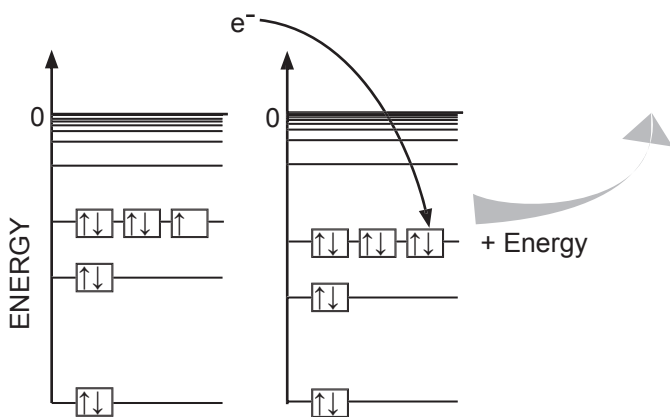
IONS AND ENERGY



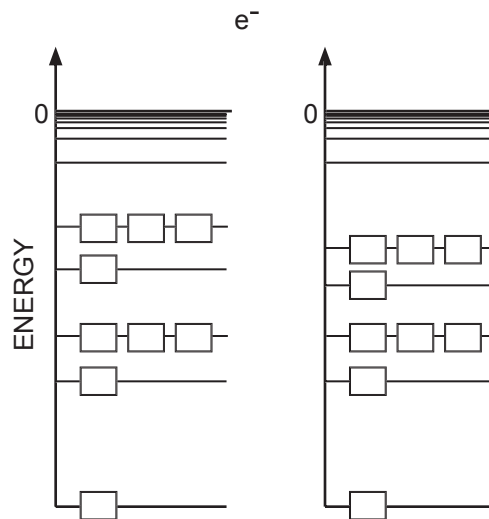
The diagrams above show the ground state of the lithium atom, followed by an excited state, followed by the lithium ion with the free electron. What is the charge of the lithium ion in the right hand drawing?



In the diagrams above, draw in the electrons as arrows which occupy the ground state orbitals of the sodium atom in the left hand picture. In the right hand picture draw in the orbitals and electrons of the sodium ion.



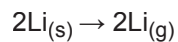
The diagrams above show the ionization of fluorine. What is the charge of the fluoride ion?



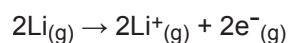
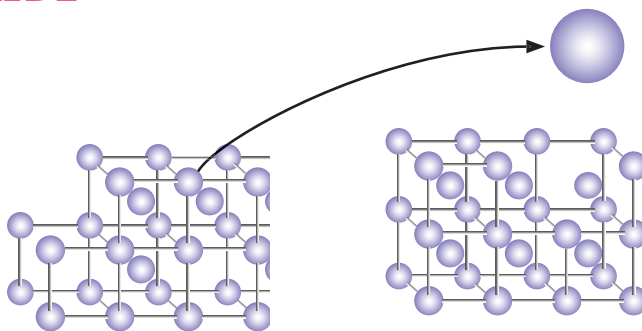
In the diagrams above, draw in the electrons (arrows) for the chlorine atom on the left and for the chloride ion on the right. What is the charge of the chloride ion?

CHEMICAL BONDING

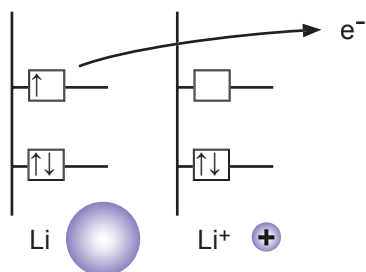
LITHIUM FLUORIDE



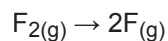
It requires 155 kJ/mol to separate lithium atoms from their body centered cubic crystal structure.



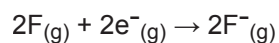
It requires 520 kJ/mol to ionize lithium atoms.



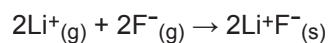
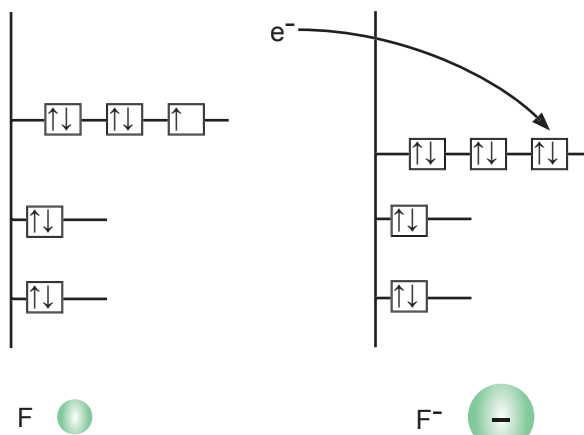
Add the energies which are associated with the process of making lithium fluoride crystal, lithium crystal, and difluoride molecules. Is the net reaction endothermic or exothermic?



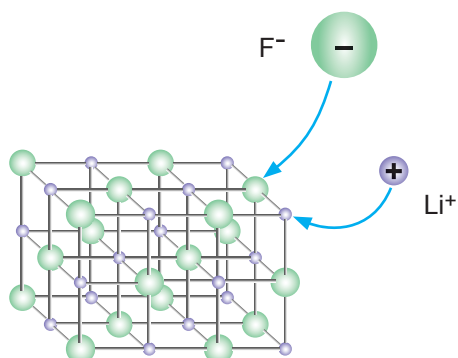
It requires 80 kJ/mol to dissociate the difluoride molecule.



Ionization of the fluorine atom gives off 328 kJ/mol of energy.

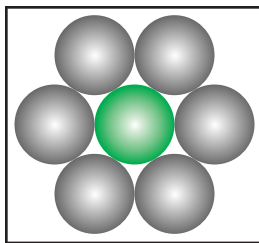


Combining the lithium and fluoride ions into their crystal gives off 1030 kJ/mol of energy.



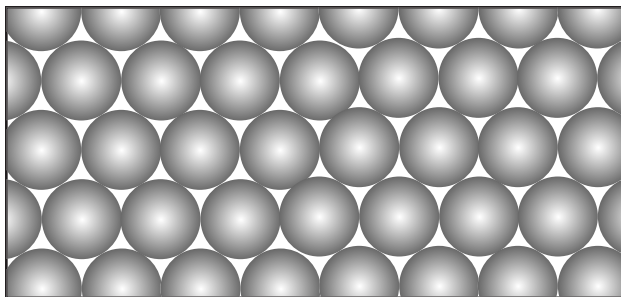
CHEMICAL BONDING

CRYSTAL PACKING



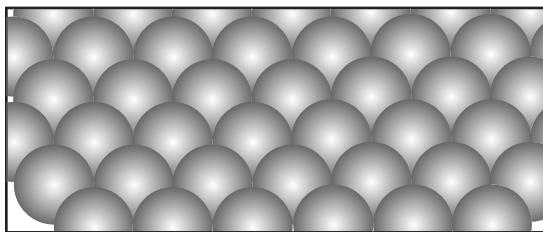
The picture at left shows seven spheres packed as close together as possible in the plane. This is called close packing. How many gray spheres touch the green sphere?

1

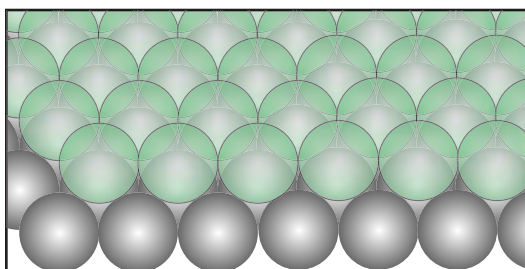


2

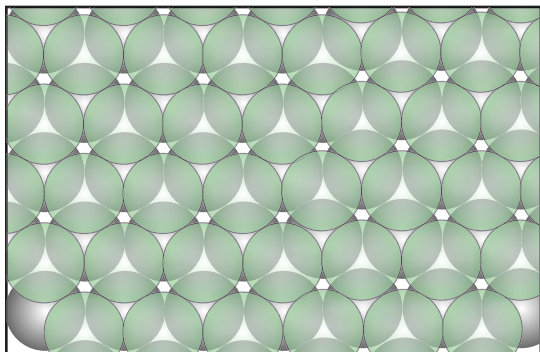
The picture above shows how close packing can fill, or *tile*, the plane. Notice the little triangles (with curved sides) that lie in between the spheres. Some of them point up and some of them point down. Compare the number of each kind of triangle.



3



4



5



Using circles, sketch in the box above another way to tile the plane.

Picture 3 is simply picture 2 looked at through an angle.

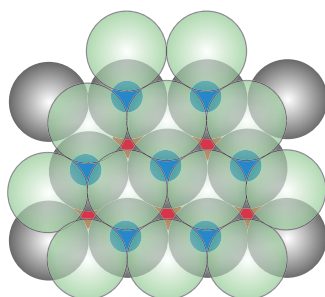
Picture 4 shows the spheres of picture 3 topped by another plane of spheres set to fit as closely as possible into the lower plane. For clarity, the second plane is semitransparent green with a black outline.

Picture 5 shows the same planes of atoms as in picture 4 but viewed from above. What proportion of the triangular spaces between the spheres of the lower (grey) plane are occupied by the second (green) plane of spheres?

CHEMICAL BONDING

CRYSTAL PACKING

Picture 6 shows the same two layers as picture 5 but two different sets of spaces between the green spheres of layer 2 are marked either red or blue. We can construct a third layer by placing spheres either in the blue spaces or the red spaces.



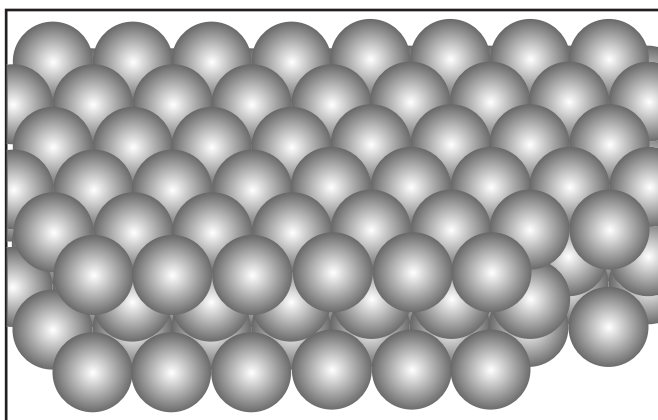
6

Notice that the blue spaces lie directly above the grey spheres of layer 1. If we use these spaces for layer 3 then we get a two level repeating structure. If we name layer 1 A and Name layer 2 B then we can describe the structure as ABABAB....

This is called hexagonal close packing or hcp for short.

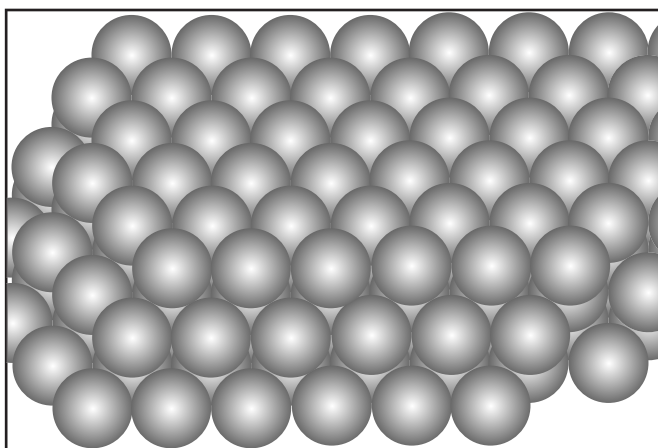
Alternatively we can place the third layer of spheres in the red spaces. Then the third layer is differently located than either of the first two and is named C. We can describe this structure as ABCABC....

It is called cubic close packing or ccp.



7

hcp



8

ccp

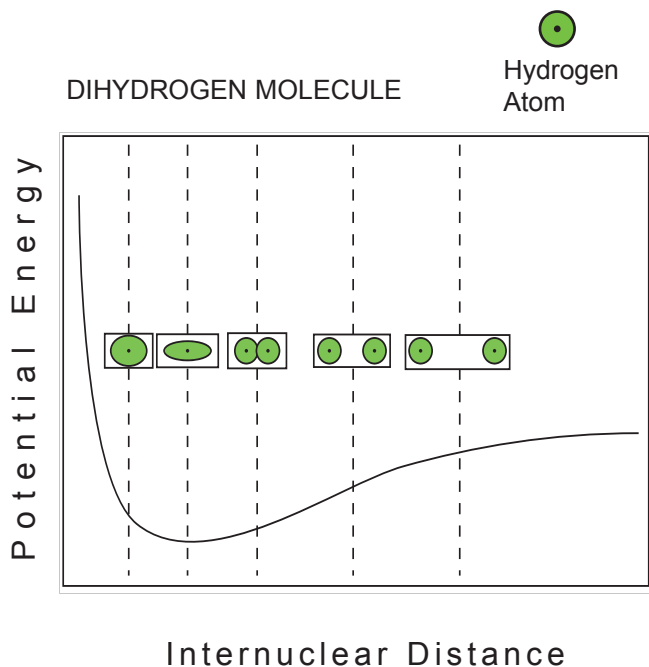
Why can we not use both the red and the blue spaces for placing the layer 3 spheres?

Using colored pencils, pens or crayons, draw circles representing the hcp structure in the box above.

Using colored pencils, pens or crayons, draw circles representing the ccp structure in the box above.

CHEMICAL BONDING

COVALENT H₂



Confining electrons makes them 'dance'. This is part of quantum theory. The tighter electrons are squeezed the harder they dance. Dancing electrons have kinetic energy. But electrons will slow down if they can. When they have more room they can slow down, which means they have less kinetic energy.

In a hydrogen molecule the electrons can move through the space of two atoms instead of one, which means that they have more room and thus can dance slower and have less kinetic energy. (Picture 1)

There are also electric attractions and repulsions between the particles in the molecule. Picture 2 shows the repulsions of like charges as colored arrows and the attractions of opposite charges as black arrows.

The additive combination of the electric and kinetic energy effects gives the covalent bond for hydrogen.

Suppose you have two well separated hydrogen atoms and begin moving them closer together. From the picture above you can see that the energy of the system will decline as they are being moved together until at some distance the system will have a minimum energy.

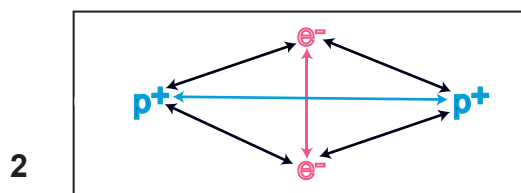
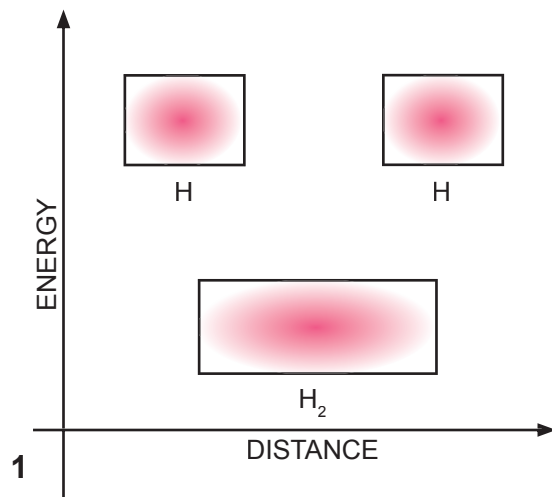
What causes the energy to rise as the atoms are moved closer than the minimum energy?

A dihydrogen molecule consists of two hydrogen nuclei (protons) held a fixed distance apart and surrounded by a probability density cloud of two electrons.

As you can see from the picture above, the separation is that at which the system is in the state of lowest energy. But what are the factors which cause this to be a low energy state?

There are primarily two factors. They are quantum and electrostatic effects.

Quantum theory produces two effects, lowered energy and discrete energy levels.

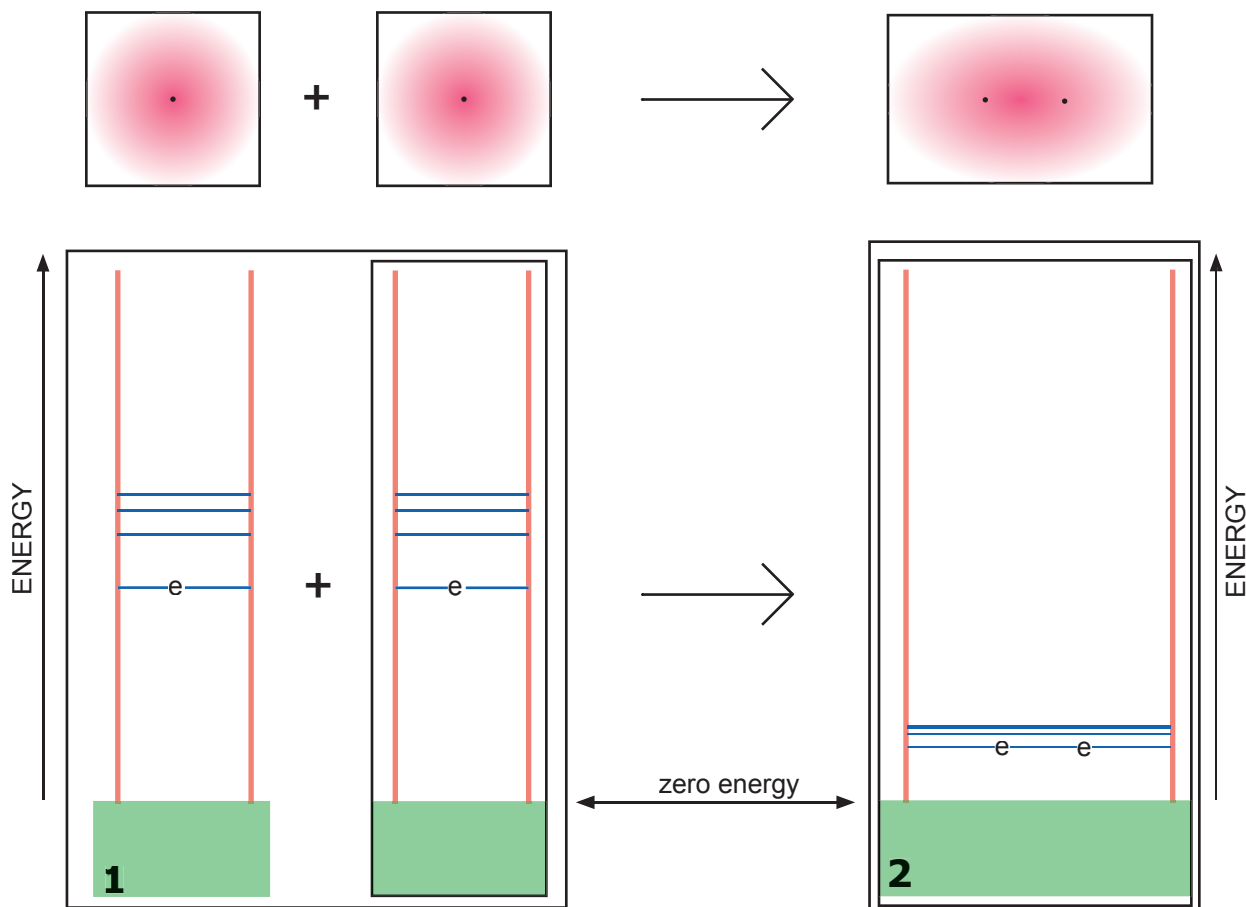


CHEMICAL BONDING

QUANTIZATION

Just below we show two hydrogen atoms and their combination as H₂ on the right.

The red electron cloud represents the probable location of the electrons. Notice that the space for electrons is larger in the H₂ molecule than it is in the separated hydrogen atoms.



One of the basic principles of quantum mechanics is that whenever anything is confined in a finite space, it can only occupy one of a discrete set of energy levels. It is also the case that when the space is made larger the energy states are lower.

In picture 1 the blue lines represent the energy states available for a particle confined between the orange walls.

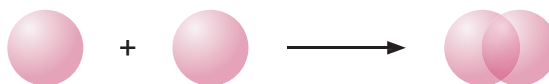
In picture 2 the blue lines show how the energy states are lower when the particles are given more space.

Which picture, number 1 or number 2, has the lowest total energy?

If picture 1 represents the energy states of two separate hydrogen atoms, then what could picture 2 represent?

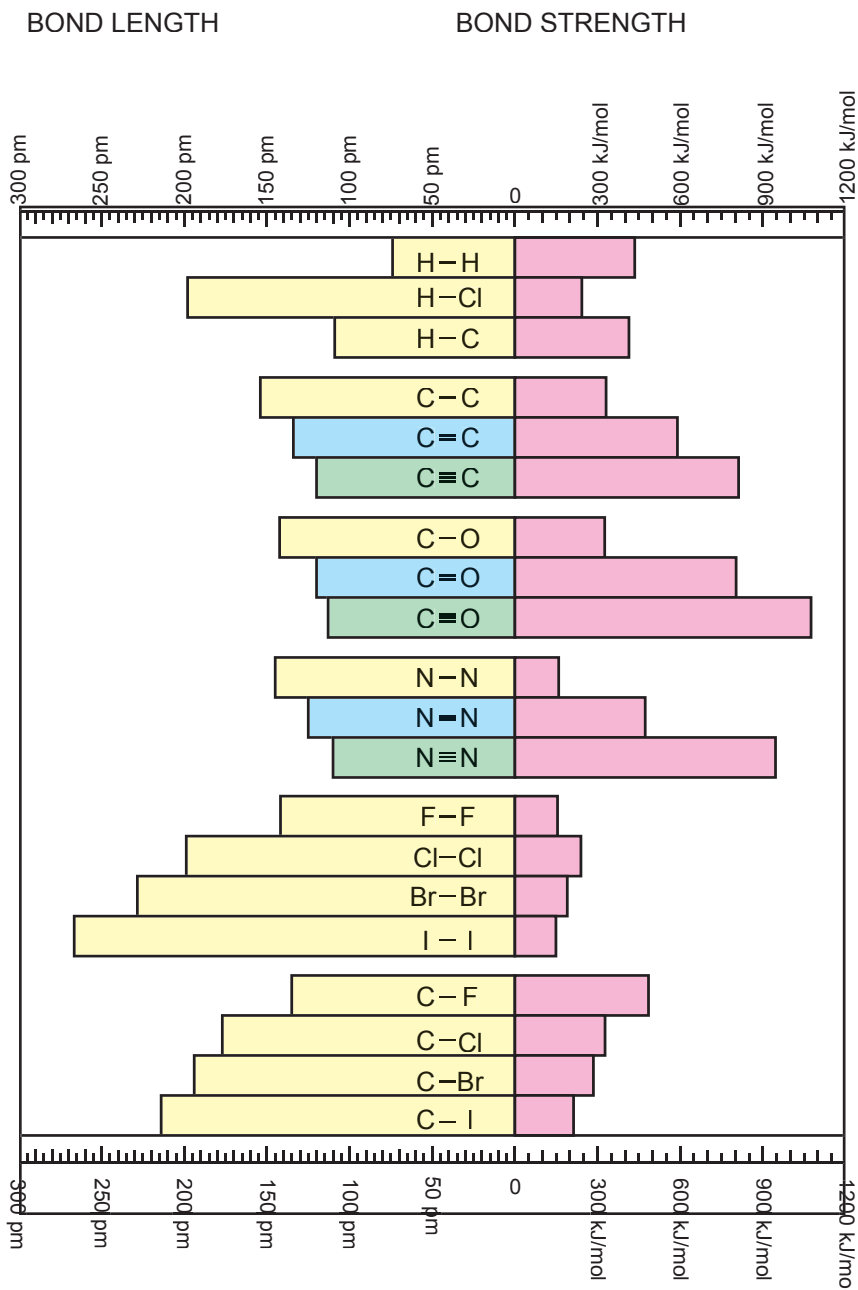
These pictures do not necessarily show that if you move two hydrogen atoms close together they will bond to form a hydrogen molecule but they do show that the hydrogen molecule will be at a lower energy state than the combined energies of the separate atoms and that you would need to add energy to the molecule to get the atoms separated and that therefore the molecule will hold together until you add that energy.

Now that we know why covalent bonding occurs we will use simplified pictures known as overlapping orbitals to describe more complicated molecules. Just to the right we show this model for hydrogen.



CHEMICAL BONDING

BOND LENGTH AND STRENGTH

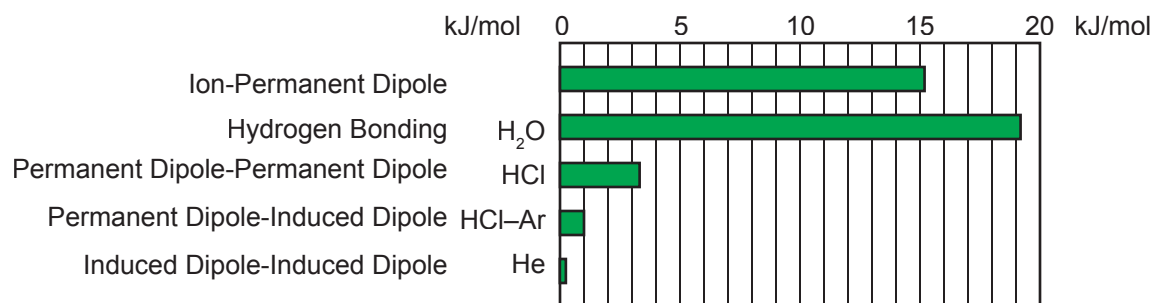
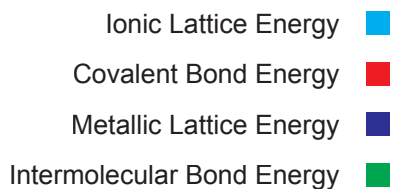
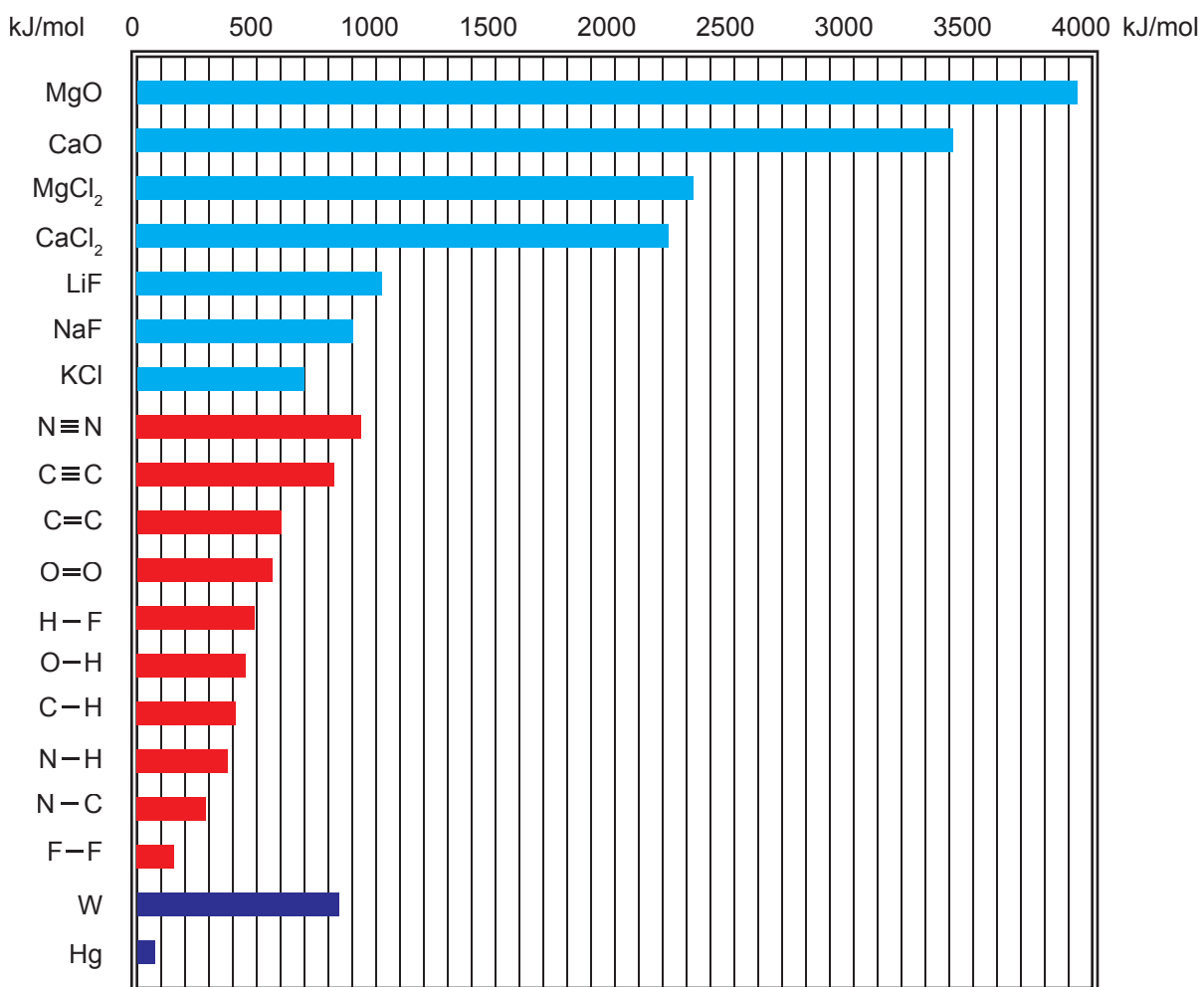


Which are the longest and shortest bonds shown?
Which are the strongest and weakest bonds shown?

In each group of related compounds, what correlation do you observe between bond length and bond strength?
What are some exceptions?

CHEMICAL BONDING

STRONG AND WEAK BONDS



CHEMICAL BONDING

STRONG AND WEAK BONDS

STRONG BONDS

A. Ionic

Much of the strength of ionic bonding comes about when the ions are packed together in crystal lattices, so that each ion is held in an attractive field with several neighbors of the opposite charge. These binding energies can range up to several thousand kilojoules per mole.

B. Covalent

Covalent bonds are also strong, ranging up to 940 kilojoules per mole for triple bond N_2 .

C. Metallic

Metals are also strongly bonded, as you can deduce from their strength and hardness, although the liquid metal mercury is an exception.

WEAK BONDS

Weak bonds, often called intermolecular forces, are several orders of magnitude weaker than strong bonds described above. One of the relatively stronger of the weak bonds is hydrogen bonding with energies ranging from two to ten kilojoules per mole.

D. Ion-Permanent Dipole

These would include salts dissolved in a polar substance, e.g., NaCl dissolved in water.

E. Permanent Dipole - Permanent Dipole

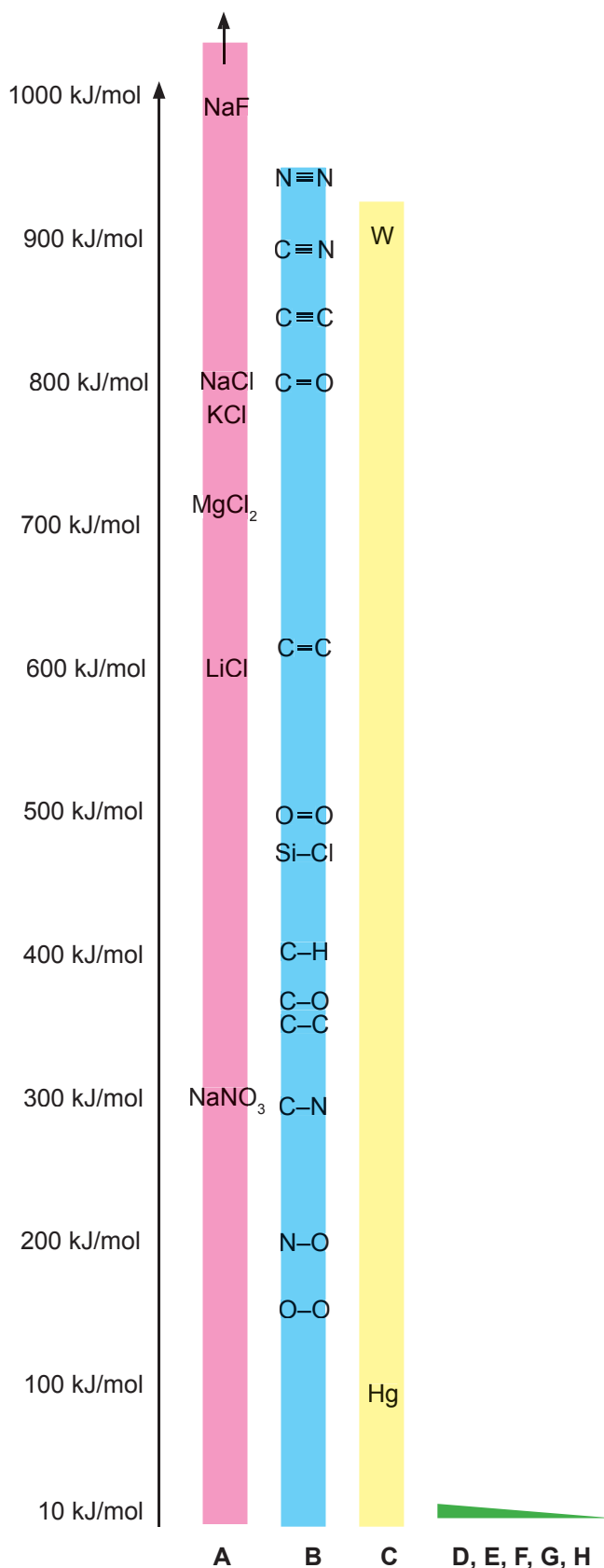
This class of bond includes hydrogen bonding.

F. Ion - Induced Dipole

G. Permanent Dipole - Induced Dipole

H. Induced Dipole - Induced Dipole

These are also known as van der Waals forces or as London dispersion forces. They are quite weak but they always exist between nearby molecules and they are always attractive.



CHEMICAL BONDING

COVALENT TO METALLIC

While we have a simple gradation between ionic and covalent compounds, we are also able to find a path of bonding types which goes from covalent to metallic bonding. This is not a simple gradation but rather detours through the network covalent bonds, some of which are semiconductors.

Our essential procedure in tracing the connections between these types of bonding is to follow the valence electrons.

In covalent bonding the bonding pairs of electrons are held in distinct orbitals, even though their physical location is, as always, given by a continuous probability density.

Several atoms, both like and unlike, can be connected pair-wise together by covalent bonds and large molecules, particularly organic, can be constructed this way. However, we also begin to see phenomena other than pair wise bonding between definite atoms appearing. An example is ozone, O_3 , a linear molecule in which each of the outer atoms is bonded to the central atom equally, but with both of them sharing three bonds between them. In this case the individual electrons cannot be assigned to a definite bond and are said to be delocalized.

There are some types of atoms, such as carbon and silicon, where covalent bonds form between unlimited numbers of the atoms. In the graphite form of carbon three of the bonding electrons of each carbon atom form covalent bonds between neighboring atoms to form a hexagonal planar structure, but the fourth bonding electron sticks out between planes. These bonds overlap and connect the planes together and they are also delocalized, which means that these electrons are free to move around under, say the pressure of an electric field and thus graphite is an electrical conductor. Finally, in metals, all of the valence electrons are held communally by the whole substance and are thus free to conduct electricity or heat.

There are also more extreme cases of delocalization than metals. These include superconductors and the new Bose-Einstein condensates.

Electrons can only be located in space with a probability density, but we can also locate electrons with regard to their situation with respect to other entities.

For example, there are free electrons which are not bound to any atom or molecule but are pushed about by electric and magnetic fields. On earth, they usually do not remain free very long but end up (at least for a while) in one of the following situations.

Describe the location, stability and energy level of an electron in each of the situations listed below.

An electron in an **atomic orbital**.

An electron in a **subshell**.

An electron in a **shell**.

A **valence** electron.

An electron in a filled **shell**.

An electron in an **atom**.

An electron in an **excited state**.

An electron in a **negative ion**.

An electron in a **positive ion**.

An electron in a **molecular orbital**.

A valence electron in a **metal**.

A valence electron in a **superconductor**.

An electron in a **Bose-Einstein condensate**.

CHEMICAL BONDING

ELECTRON DELOCALIZATION

Localized

Delocalized

1	2	3	4	5	6	7	8	9
Ionic CsF NaCl	Polar Covalent H ₂ O CO ₂ CO	Covalent O ₂	Molecular Orbitals O ₃ C ₆ H ₆	Semiconductors Si	Semi-metallic Graphite	Metals Gold	Superconductors K ₃ C ₆₀ at 19K	Bose-Einstein Rb at 10 ⁻⁸ K
Electrons are held by each atom in completed shells.	Bonding electron pairs cluster around the most electronegative atom(s).	Bonding electron pairs are shared equally by both atoms.	Some bonding electrons are held collectively inside the molecule.	A small proportion of the electrons are free to move about the lattice.	In graphite, valence electrons are free to move in two dimensions.	All valence electrons are free to move throughout the lattice.	All the valence electrons are free to move without resistance.	In a Bose-Einstein condensate all of the electrons become part of a single 'atom'.

1 Filled shells are shown in grey. Valence electron clouds are in red. Negative ions are outlined in red. Positive ions are outlined in blue.

2 When two atoms of moderately different electronegativity are bound, the binding electrons are shared unevenly, tending toward the more electronegative atom.

3 In a homonuclear diatomic molecule the binding electron pairs are shared evenly and symmetrically by both atoms.

4 In Benzene six of the bonding electrons are held collectively by the molecule as a whole. In the picture these are represented by the red cloud.

5 In a semiconductor, such as Silicon, a small minority of valence electrons are free to move about the lattice. The free electron is shown as the small red blur at right.

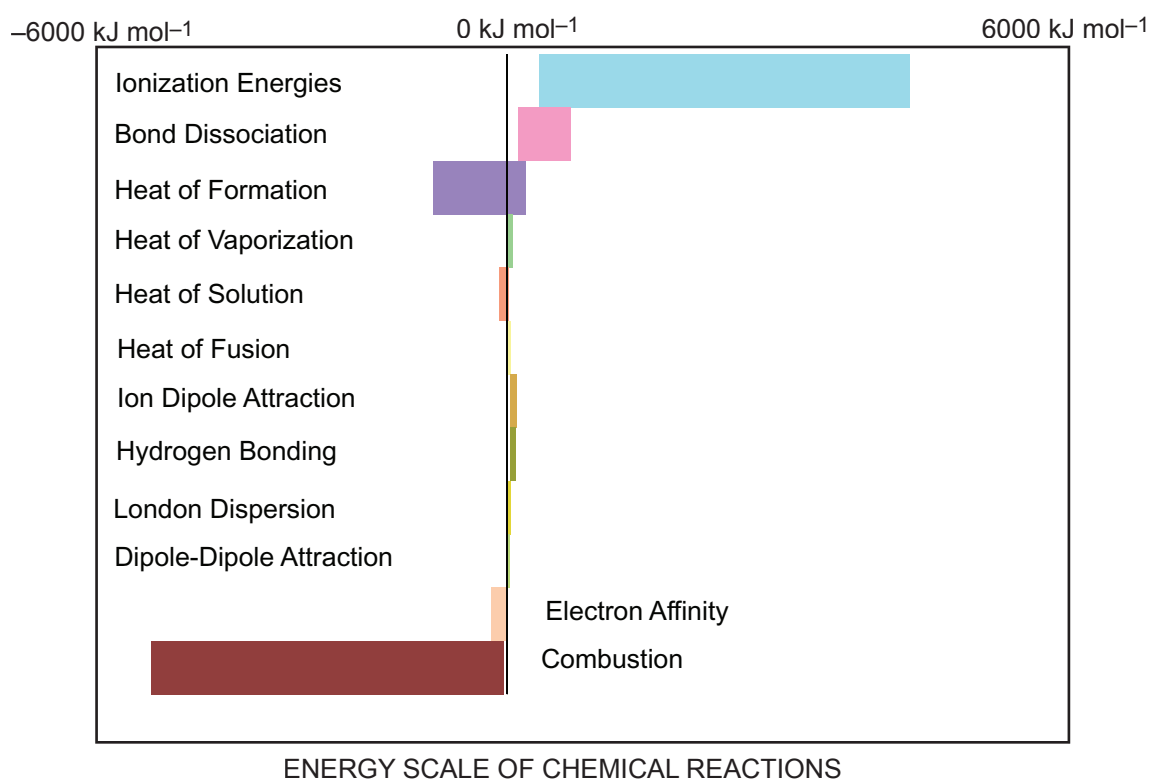
6 In graphite the carbon atoms are bound in hexagons that are arranged in sheets. The sheets are loosely bound to each other and the electrons between the sheets are free to move.

7 In the picture at right, the gray circles represent the core of filled shells while the red cloud is the set of valence or conducting electrons held in common by the metal. Compare and contrast with number nine.

8

9 In the picture at right, the small grey dots represent the separate nuclei. The red cloud represents all (not just the valence) electrons held in common by the substance, as if it were one atom.

CHEMICAL ENERGETICS



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

CHEMICAL ENERGETICS

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CHEMICAL ENERGETICS

SOME EXPERIMENTS

Suppose we place a drop of water in an uncovered petri dish and watch what happens.



Now suppose we vary the experiment in a covered petri dish.



What is this process called?
 What is the reverse process called?
 Where have you observed it in daily life?
 What other effects have you noticed with the first process?

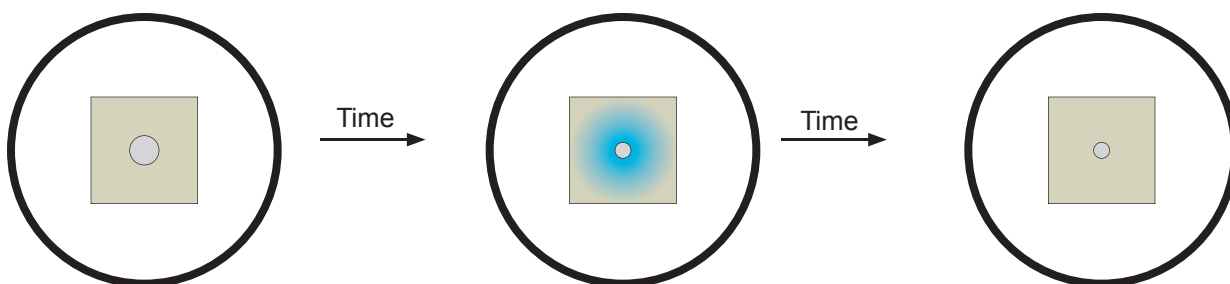
Try these experiments yourself. In the open petrie dish experiment note how long it takes for the water drop to disappear. Try it with different size drops. Try it under different weather conditions.

Now we place a piece of ice on top of the petri dish and observe what happens.



The little circles hanging from the top of the petri dish represent a thin layer of water.

Now suppose we place a square of plastic enclosed liquid crystal inside of the petri dish and then drop the water on. This variety of liquid crystal has the property of changing color when it is cooled.

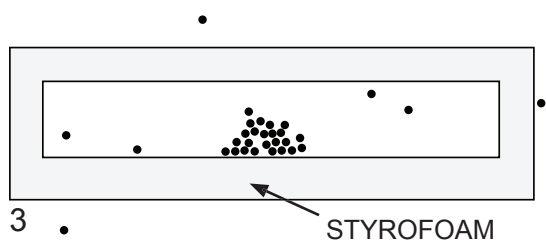
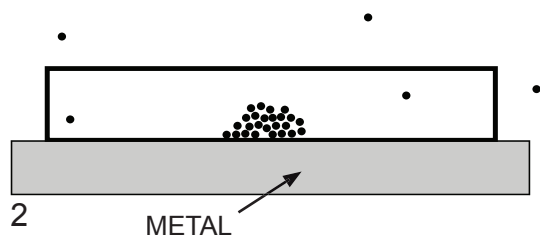
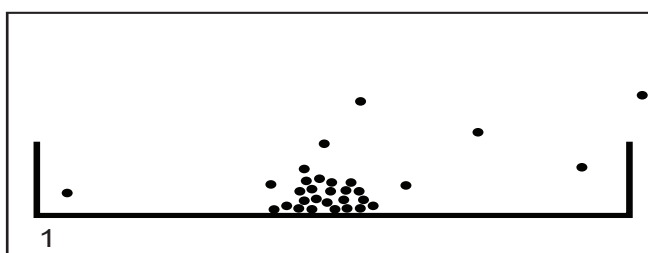


There are several questions we can ask about these experiments. Why do these things happen? How fast do they happen? Can we give a molecular explanation of these events?

CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

In thermochemistry, kinetics and thermodynamics we must always be clear about what it is we are talking about, experimenting with or calculating. So we make an essential distinction between what we call a **system** and everything else, which we call the **surroundings**. In chemistry we distinguish three kinds of systems. These are called **open**, **closed**, and **isolated** systems. An open system can exchange both matter and energy with its surroundings. A breathing person is an open system. A closed system can exchange energy but not matter with its surroundings. An isolated system can exchange neither matter nor energy with its surroundings.



In picture 1, draw a path around an open system which includes the petri dish.
 In picture 2, draw a path around a closed system which includes the petri dish.
 In picture 3, draw a path around an isolated system which includes the petrie dish.

For each of the pictures explain whther the system named is an open, closed or isolated system, explain your answer, giving details about the system, its surroundings, and the interaction, if any, between the system and its surroundings.



AIRPLANE



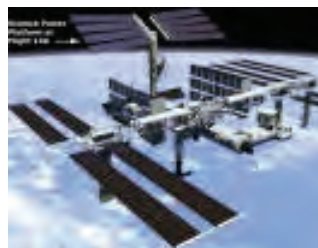
BIOSPHERE



CELLS



EARTH

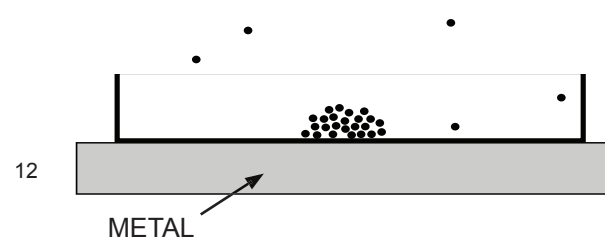
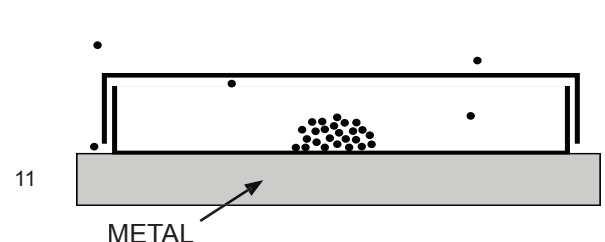
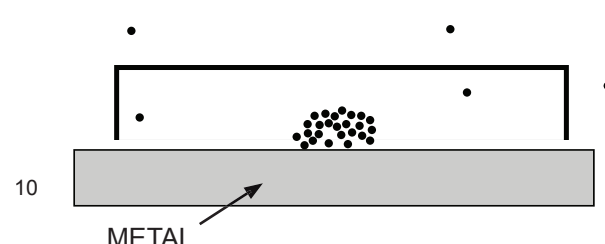
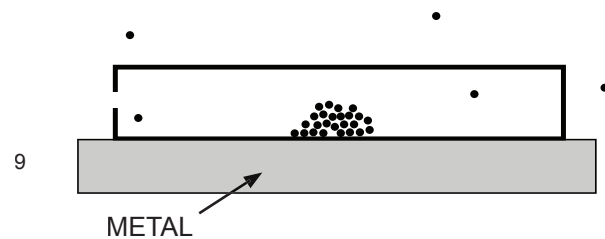
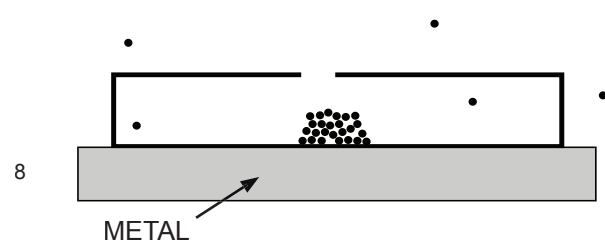
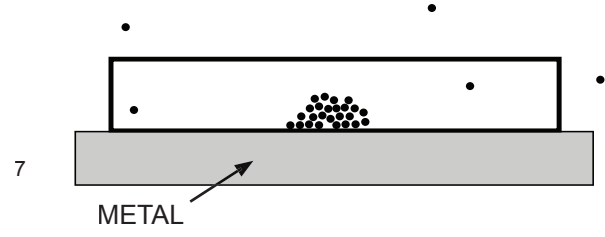
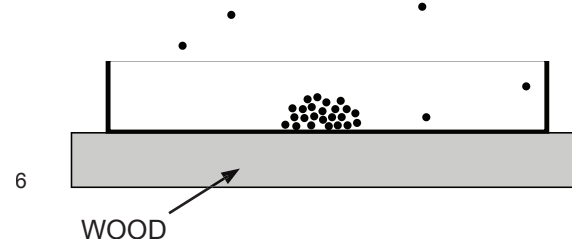
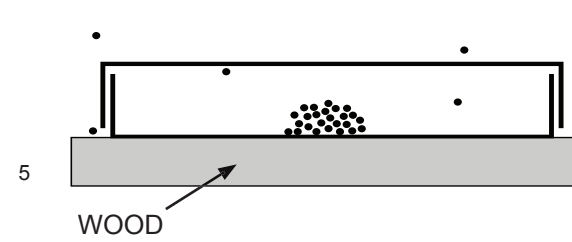
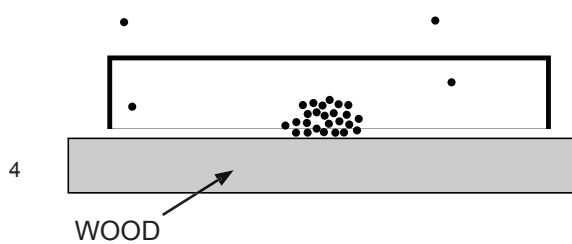
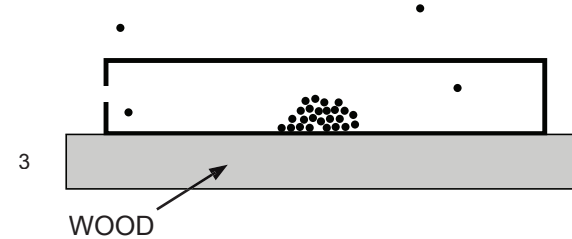
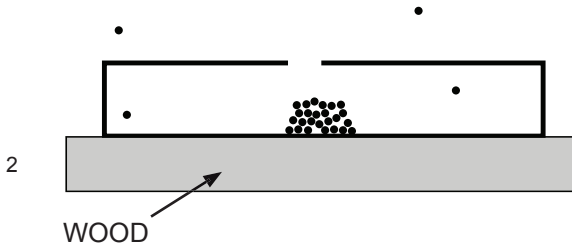
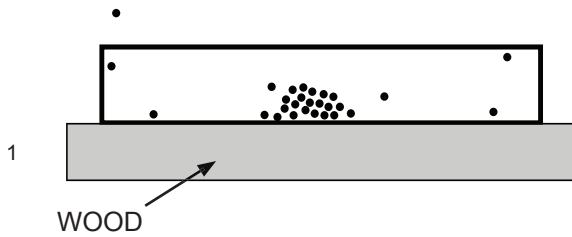


INTERNATIONAL SPACE STATION

CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

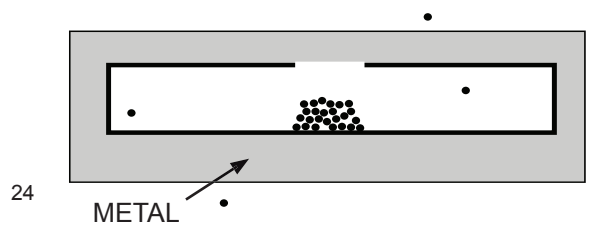
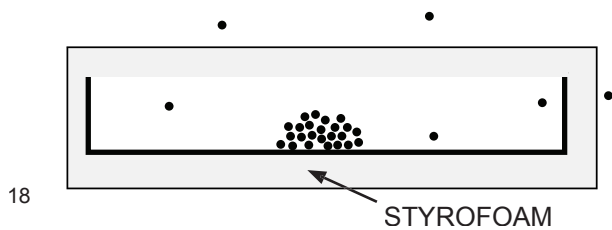
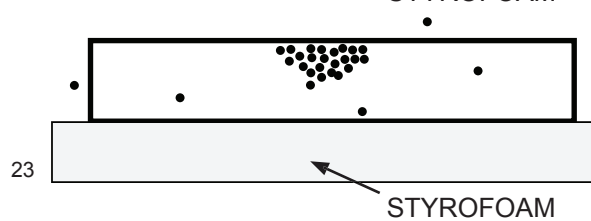
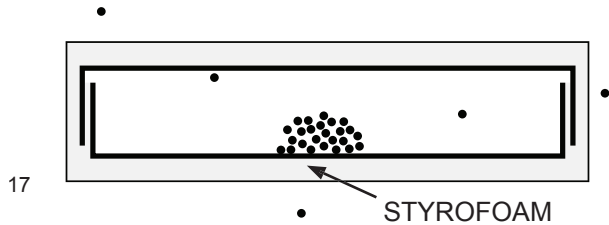
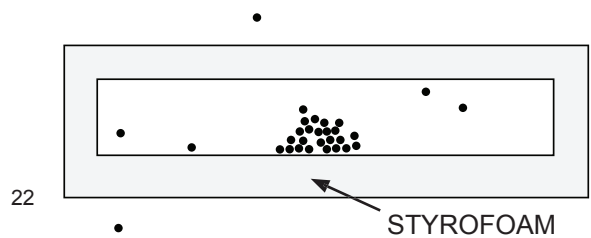
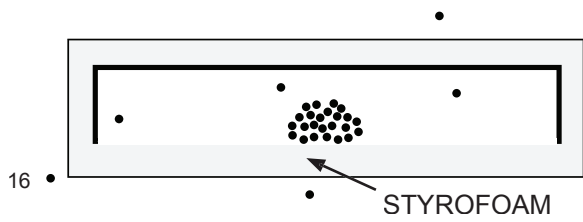
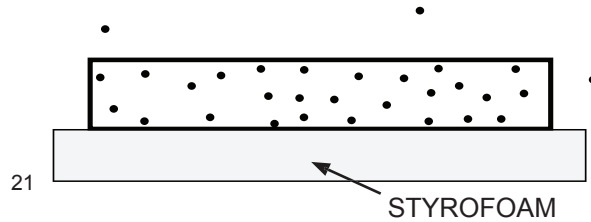
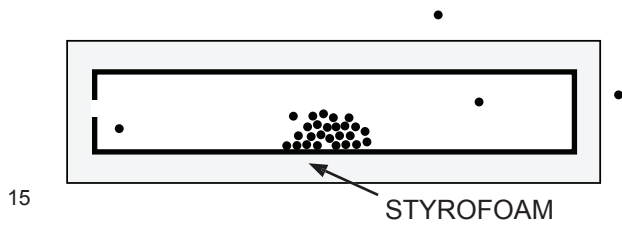
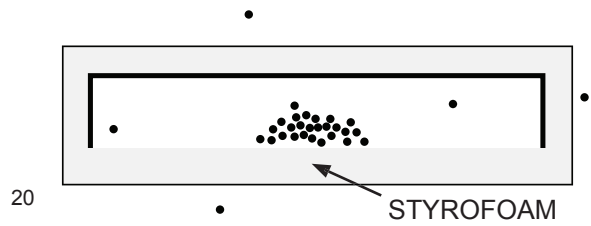
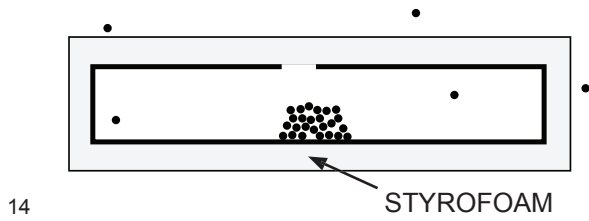
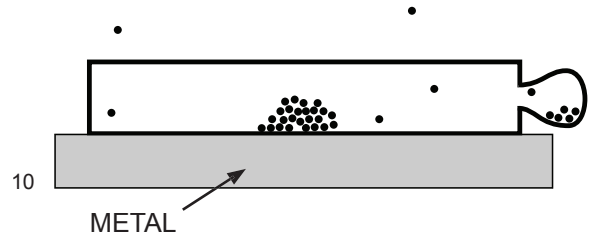
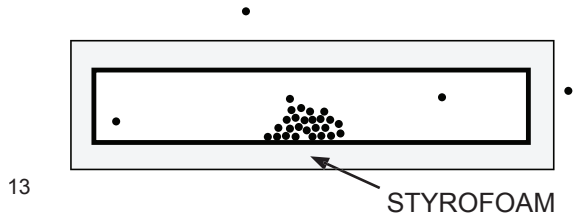
For drawings 1 through 12 define the system in words and draw an outline around the system. Explain whether the system is open, closed or isolated and discuss the reasons for your choice.



CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

For drawings 13 through 24 define the system in words and draw an outline around the system. Explain whether the system is open, closed or isolated and discuss the reasons for your choice.



CHEMICAL ENERGETICS

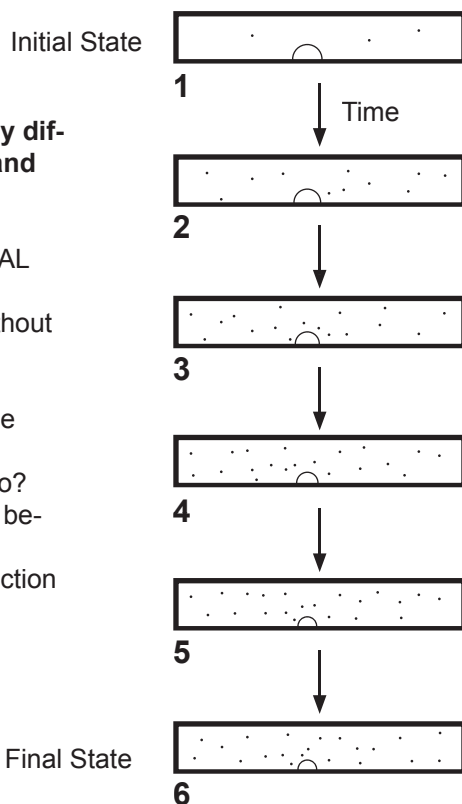
KINETICS AND THERMODYNAMICS

In the experiment shown on this page, a drop of water is placed in a petri dish which is then covered. The black dots represent water molecule in the air. The primary purpose of this page is to clarify the distinction between kinetics and thermodynamics.

THERMODYNAMICS
is concerned with the energy difference between the initial and final states of a reaction.

QUESTIONS OF CHEMICAL THERMODYNAMICS

1. Can the reaction occur without additional energy?
2. How much energy will be released or absorbed when the reaction occurs?
3. How far will the reaction go? How much of the reactant will become product?
4. How can we make the reaction go further?



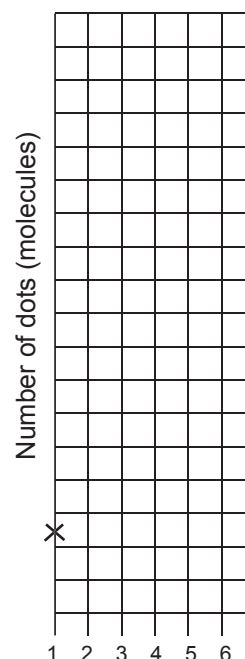
KINETICS
is concerned with the rate of a reaction and the intermediate steps between the initial and final state of a reaction.

QUESTIONS OF CHEMICAL KINETICS

1. What is the rate (speed) of the reaction?
2. How can the rate of the reaction be changed?
3. What is the reaction path, or mechanism, by which the reaction takes place.?

Using the experimental evidence provided by the pictures, explain why the state labelled final state is actually the final state.

If there were a state 7, subsequent to state 6, how would state 7 differ from state 6 and how would it be like state 6?



Using the pictures of the experiment, graph the number of evaporated molecules at each state. (The initial state is done for you.) Describe the rate of the reaction.

CHEMICAL ENERGETICS

ENERGY

Looking into various chemistry texts you will see energy defined as the capacity or ability to do work or that plus the capacity or ability to make heat flow or to cause change. Perhaps energy is too fundamental to give it a good definition. Yet in practice we examine different forms of energy, or energy change, in definite amounts.

The basic SI unit of energy is the Joule, which is defined as a Newton of force moving through a meter of distance. Although many forms of energy, such as chemical energy, may not appear directly as a force moving through a distance, all forms of energy are measured in Joules. A Joule is enough energy to lift your chemistry textbook a couple of centimeters (in earth's gravity). This is not very much energy so chemists usually use kiloJoules, kJ. If you weigh 50 kilograms, it will require about 5 kJ to climb 10 meters of stairs or hillside.

Consider time. There is no such thing as THE TIME. Not only are there different time zones but there are different time systems. For example, computer time is the number of milliseconds since midnight on January 1, 1970. Time is the difference between say, the present instant and the beginning of the system. Differences in time are real.

It is the same with energy, change in energy is real, the difference in energy between two situations is real. When the energy of a situation is given or measured, that always means the difference in energy between that situation and another situation which is arbitrarily set at zero energy. When the change in energy between two situations is measured, it is not necessarily to specify a zero point, but when a situation is said to have some energy, then it is necessary to know what the zero point situation is.

An essential principle of energy is that it is conserved. That is, energy can be neither created nor destroyed but only changed from one form into another. The only exception to this is the transformation between mass and energy according to Einstein's equation

$$E = mc^2$$

but scientists get around this by calling mass another form of energy. Then the principle holds exactly and it is also called The First Law of Thermodynamics.

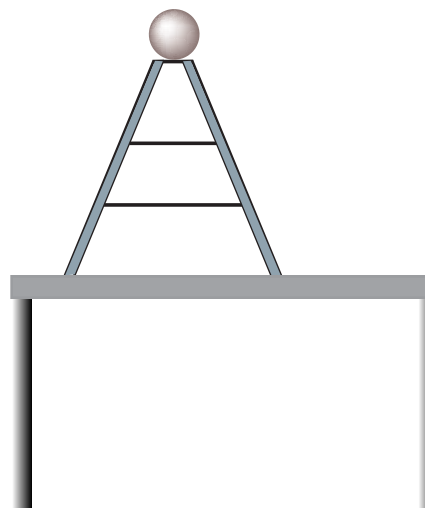
FORMS OF ENERGY:

- Kinetic energy of motion
- Potential energy
- Various forms of chemical energy
- Electrical energy
- Gravitational energy
- Nuclear energy
- Electromagnetic radiation
- Sound
- Heat

What are some other forms of energy?

EXAMPLE

An 8 kg bowling ball resting on a 3 meter high ladder will have a gravitational potential energy above the base of the ladder of 235.2 J. But if the ladder happens to be standing on a 3 meter high platform, the bowling ball will have a gravitational potential energy of 470.4 J above the base of the platform.

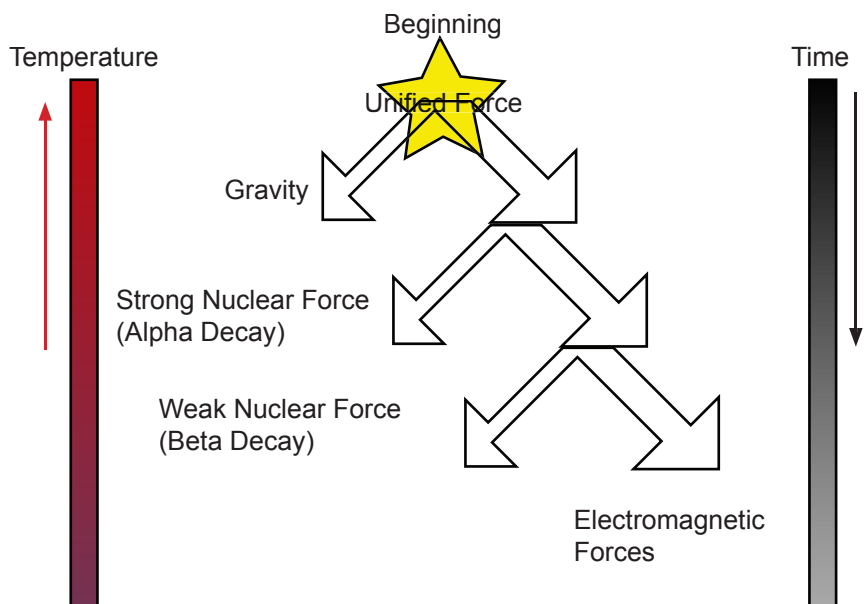


If the bowling ball rolls off of the ladder, into what forms of energy will the gravitational potential energy be changed? Answer this from you own experience, not from theory.

Suppose 10 Joules of light (electromagnetic energy) strikes a surface and 5 Joules of light is reflected from the surface and the rest of the light is absorbed into the surface, becoming heat. How much heat energy is absorbed by the surface?

CHEMICAL ENERGETICS

ENERGY AND FORCE



Energy and force are two different concepts which scientists use to analyze reactions and changes in systems. As there are various forms in which energy appears so there are different forces which arise in nature. In modern terms there are four known forces (although some astronomers have postulated a fifth force to explain certain aspects of the universe). The four forces are the electromagnetic force, the gravitational force, the weak nuclear force and the strong nuclear force. There also exists a theoretical unification of the electromagnetic and weak forces and it is also considered plausible that in the very early stages of the universe all of the forces were combined as one. It is useful to compare the different strengths and qualitative aspects of the different forces.

Gravity is the weakest of the forces but since it is only attractive it can accumulate great strength resulting from large masses.

Electromagnetic forces are about 100 thousand times as strong as gravity and are the forces which control most of our daily lives as well as essentially all of chemistry. There are two charges of which opposites attract and like charges repel, so the normal condition is opposite charges to balance each other.

The weak nuclear force is about 100 times as strong as electromagnetic forces and is responsible for beta decay.

The strong force is what holds fundamental particles like neutrons and protons together.

If gravity is such a weak force, why do we feel so heavy?

The unit of force is the Newton, abbreviated 'N'. By definition, one Newton is the force required to accelerate one kilogram one meter per second per second. According to Newton's third law every force has an equal and opposite force. So since earth's gravity has an acceleration of 9.8 ms^{-1} , the force required to hold up a one kilogram object against gravity is 9.8 N.

A common American unit of force is the pound, abbreviated lb. A pound is approximately equal to 4.45 N. In common usage 'pound' is often used when the mass is what is meant. Pound is the unit of force, or weight, not mass, but the two concepts are related - on Earth!

Many consumer items are marked with their 'weight' from which their mass can be easily derived. For example a weight of one pound, 1 lb, has a mass of 454 gm and a liter, L, of common drinks has a mass of approximately one kg. Read the labels on several packages and calculate the force required to hold them up.

An isolated system consists of an electron and a proton separated by a micron (10^{-6} m). Qualitatively describe the forces and energies involved and how they change over time.

CHEMICAL ENERGETICS

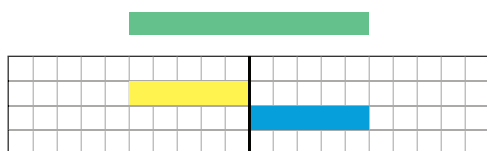
KINETIC AND POTENTIAL ENERGY

Energy comes in a variety of forms, including kinetic and potential energy. What is the difference between these two types of energies?

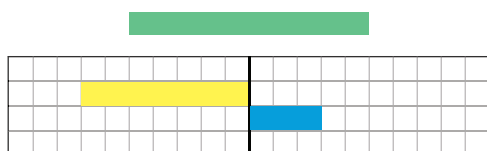
Kinetic energy is the energy due to motion. Potential energy is the energy due to position. The total energy of an object is the sum of its kinetic and potential energies.

When you climb a mountain your gravitational potential energy increases but your kinetic energy remains about the same (unless you fall off). What is the source of this increase in energy?

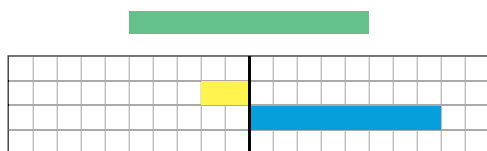
$$\text{Energy}_{\text{total}} = \text{Energy}_{\text{potential}} + \text{Energy}_{\text{kinetic}}$$



1



2



3

Could any of the Chem Logs above represent the energy of the bowling ball resting on top of the ladder? If so, which one and why.

If the bowling ball falls off of the ladder, in what sequence, i.e., first, second and third, might the Chem Logs show the kinetic and potential energies of the falling ball?

KINETIC ENERGY

Kinetic energy of an object is related to its mass and speed through the equation:

$$E_k = \frac{1}{2} mv^2$$

As an example, suppose an 8 kilogram bowling ball is falling at 10 meters per second. We can calculate its kinetic energy:

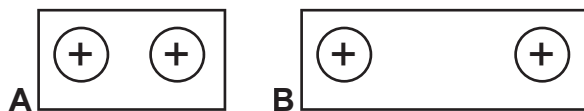
$$E_k = \frac{1}{2} 8 \text{ kg} \times (10 \text{ ms}^{-1})^2 = 400 \text{ J}$$

How much kinetic energy will a 500 kg volkwagon travelling at 20 meters per second have?

POTENTIAL ENERGY

No single equation can be given to determine the potential energy of an object because this energy depends on an arbitrary designation of the zero. However, potential energy can be determined in specific cases.

We looked at gravitational potential energy on the first page of this module but for chemists it is important to understand electrostatic potential energy. There is always electrostatic potential energy between two charged objects. If the objects have the same kind of charge, e.g., both positive, then the potential energy decreases as the distance between the objects increases. If the objects have opposite charges then the potential energy increases as the distance between the objects increases.



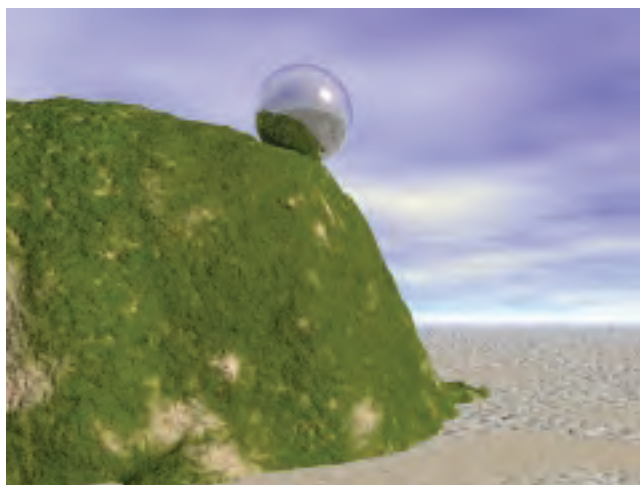
Assuming that the four positive charges above are equal, compare the potential energy of the situation in box A with that of the situation in box B. Which has more potential energy?



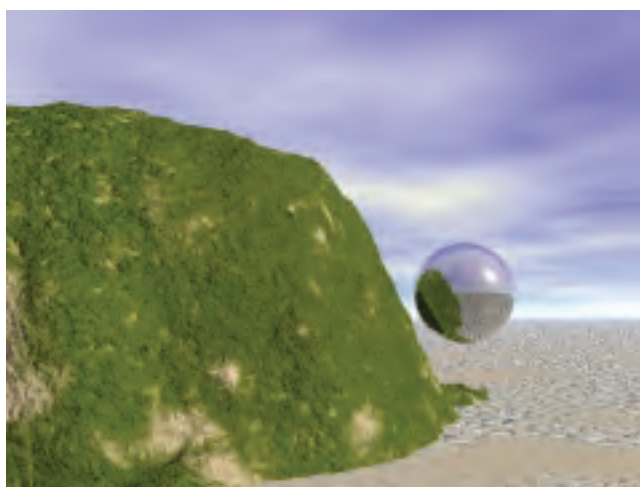
Assuming that the two positive charges above are equal in magnitude and that the two negative charges are equal in magnitude, which situation, A or B, has the greater potential energy?

CHEMICAL ENERGETICS

KINETIC AND POTENTIAL AND THERMAL ENERGY



POTENTIAL ENERGY

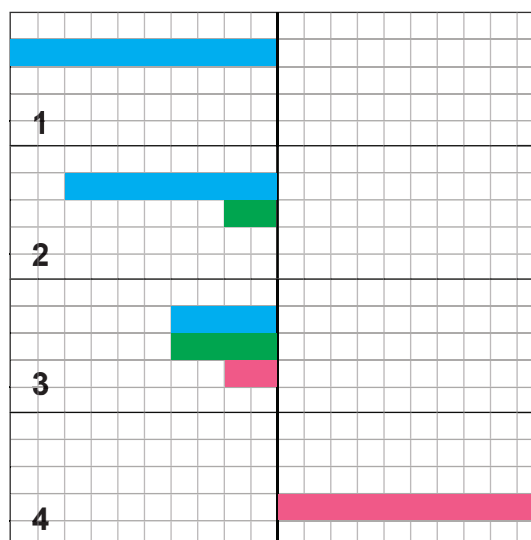


KINETIC ENERGY



THERMAL ENERGY

- Potential Energy
- Kinetic Energy
- Thermal Energy



For each of the four ChemLogs 1 through 4, find the total energy (by counting the colored squares).

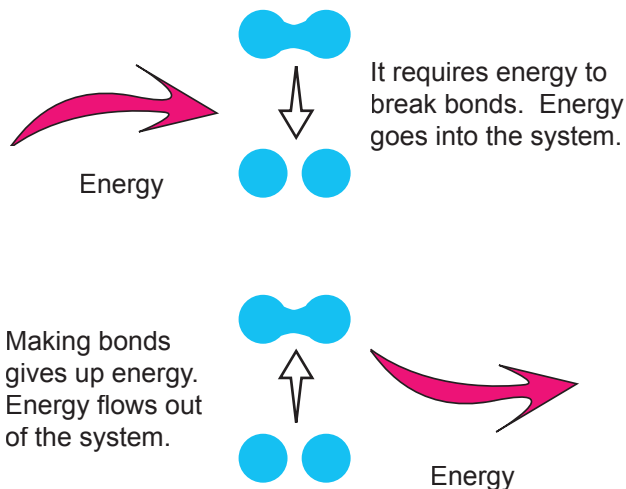
Describe the different forms of energy which occur in the process of hydroelectric power generation.

CHEMICAL ENERGETICS

CHEMICAL ENERGY

Chemical energy is the potential energy stored in the arrangements, or bonding, of atoms in a substance. Changes in chemical energy occur with chemical reactions. Chemical reactions generally involve a change in chemical energy. One important use of chemical energy is help form new materials by providing the energy needed for endothermic reactions.

In other cases there may be energy which is not reused as chemical energy. In an exothermic reaction, this often appears as heat energy but might also include other forms, such as the light absorbed by chlorophyll or the sound of a chemical explosion.



The combustion of methane can be represented by the formula $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$. List the bonds that are broken in this reaction and list the bonds that are formed.

ENERGY SCALES

SOME ONE MOLE INTERACTIONS

Chemical energies are usually expressed in kJ/mol, which is an abbreviation for kiloJoules per mole of substance. Here are some examples which compare chemical energies to other forms of energy.

Ionizing one mole of Argon (20 g) will require as much energy as a 50 kg person climbing two miles.

Dissociating one mole of gas phase dioxygen (32 g) into its constituent atoms will require as much energy as needed to light a 100 watt bulb for 3 hours, six minutes and 45 seconds.

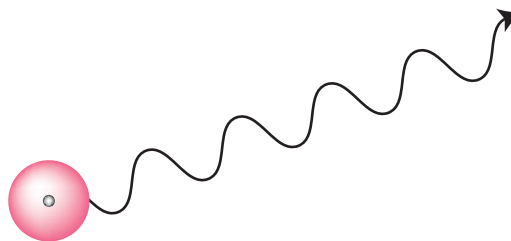
To make one mole of acetylene from its constituent elements would require as much energy as pumping one hundred liters of water up over 230 meters.

It can be seen from the examples that chemical energies are often (not always) quite large.

Describe some applications of chemical energy which are familiar in daily life.



While they are separated there is an electrostatic potential energy between the negatively charged electron (in red) and the positively charged proton (in black).

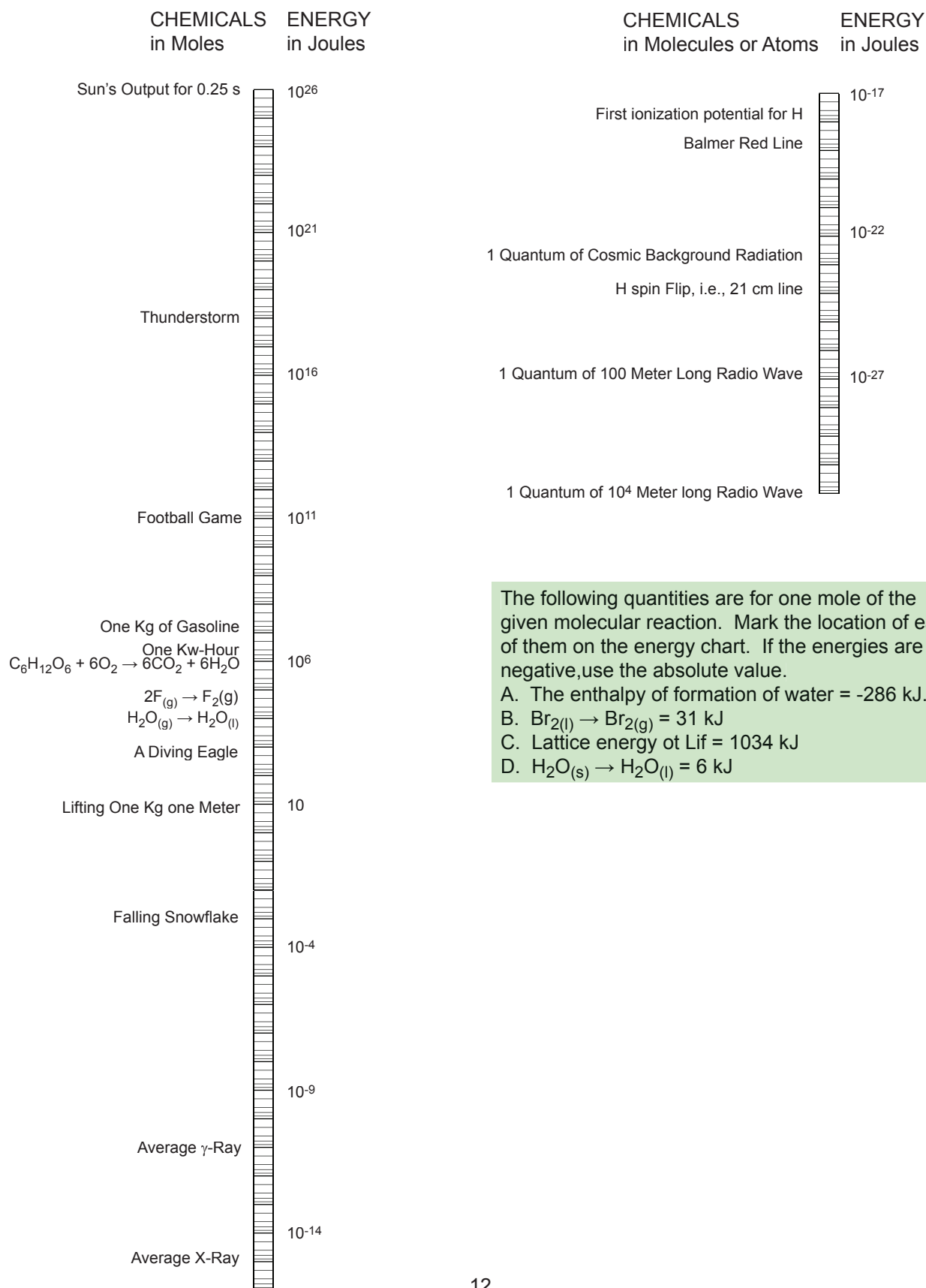


When the electron and proton come together, to produce a hydrogen atom, the electrostatic potential is reduced and that lost energy must still exist. In an isolated atom it is usually carried away by electromagnetic radiation.

Positive and negative charges are usually very closely balanced in nature. Explain why we know this is true and describe what might happen in a situation where they were far out of balance.

CHEMICAL ENERGETICS

ENERGY SCALE



The following quantities are for one mole of the given molecular reaction. Mark the location of each of them on the energy chart. If the energies are negative, use the absolute value.

- The enthalpy of formation of water = -286 kJ.
- $Br_{2(l)} \rightarrow Br_{2(g)} = 31$ kJ
- Lattice energy of $LiF = 1034$ kJ
- $H_2O_{(s)} \rightarrow H_2O_{(l)} = 6$ kJ

CHEMICAL ENERGETICS

SPONTANEOUS VS. NON-SPONTANEOUS REACTIONS

Some chemical reactions will occur spontaneously and some will not. The meaning of spontaneous reaction as we shall use it is “having the potential to proceed naturally without an input of energy from the outside.” We need to consider three questions:

1. Can the reaction occur under any circumstances? Some reactions will not occur under any circumstances.

2. Can the reaction occur spontaneously?

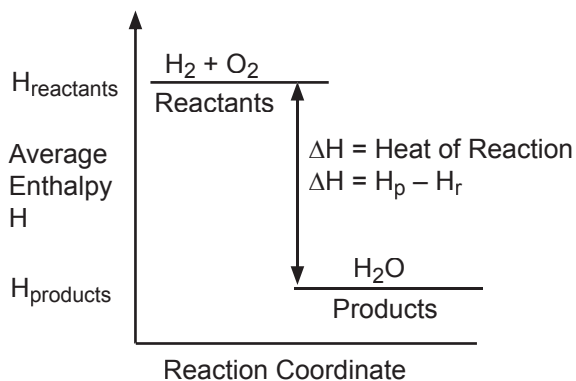
A nonspontaneous reaction is one that does not occur naturally, but it can potentially be made to occur by supplying outside energy.

3. Will the reaction actually occur?

That is, will the reaction occur in a reasonable time?

The average chemical energy or heat content of a chemical system at constant temperature and pressure is called **enthalpy**, represented by the symbol H . The heat evolved or absorbed when a reaction occurs is the difference between the average enthalpy of the products and the reactants and is given the symbol ΔH . This difference in enthalpy is called the **heat of reaction**.

An exothermic reaction such as the reaction between dihydrogen gas and dioxygen gas to form water is accompanied by a decrease in enthalpy and heat is evolved to the surroundings. Thus, the heat of reaction, ΔH , is negative. This indicates that average bond strengths in and between the product molecules (H_2O) are stronger than the average bond strengths in and between the reactant molecules (H_2 and O_2).



Heat of reaction at constant pressure and temperature = Average enthalpy of products – average enthalpy of reactants.

Heat of reaction at constant pressure and temperature = $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

Exothermic Reaction : Heat evolved to surroundings
 ΔH_{system} is –
 Endothermic Reaction : Heat absorbed from surroundings
 ΔH_{system} is +

First Law of Thermodynamics – Law of Conservation of Energy

In all macroscopic chemical and physical changes, energy is neither created nor destroyed but only transformed from one form to another

or

In any process the total energy of the system plus its surroundings remains constant.

The Minimum Potential Energy Principle

Mechanical systems tend spontaneously to a state of minimum potential energy consistent with their surroundings.

The Minimum Chemical Energy Principle

Chemical Reactions tend spontaneously toward a state of minimum chemical energy consistent with its surroundings

or

Exothermic reactions “should” be spontaneous and endothermic reactions ‘should’ be nonspontaneous.

A Tentative Hypothesis—The Minimum Enthalpy Principle

Chemical reaction at constant temperature and pressure tend spontaneously toward a state of minimum enthalpy (H) consistent with their surroundings.

Spontaneous reactions are exothermic: ΔH is –

Nonspontaneous reactions are endothermic: ΔH is +

a. Is the reaction of carbon dioxide (CO_2) and water (H_2O) plus heat to form glucose, a sugar, and dioxygen, exothermic or endothermic?

b. Is ΔH + or –?

c. What is the sign of ΔH for the reverse reaction of glucose and O_2 to form CO_2 and H_2O ?

d. According to the minimum enthalpy principle, which reaction should be thermodynamically spontaneous?

Forward reaction: $CO_2 + H_2O + \text{heat} \rightarrow \text{glucose} + O_2$
or

Reverse reaction: $\text{glucose} + O_2 \rightarrow CO_2 + H_2O + \text{heat}$

e. Which reaction should be nonspontaneous?

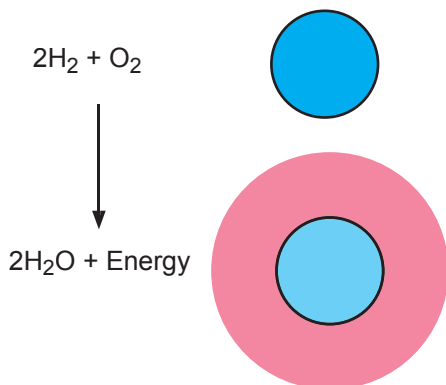
f. If the reaction is thermodynamically spontaneous in one direction, does this mean that this reaction *will* actually occur? Explain.

CHEMICAL ENERGETICS

VIEWS OF THE FIRST LAW

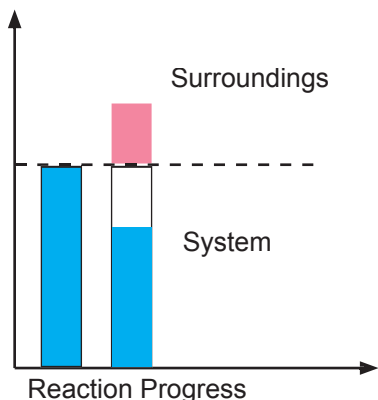
EXOTHERMIC REACTION

- Chemical energy
- Heat energy transferred to the surroundings



The system is the interior of the circle, everything else is the surroundings. The exothermic reaction transforms chemical energy into heat energy. The final result is that the chemical energy of the system is lowered and the lost chemical energy becomes heat energy added to the surroundings.

Another View of the Same Reaction

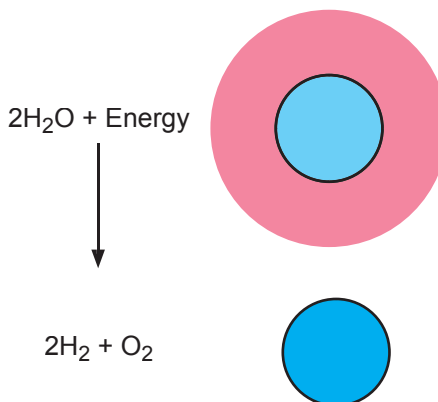


The system is a collection of hydrogen and oxygen atoms which are in H_2 and O_2 molecules before the reaction. After the reaction the system is the same collection of atoms formed into H_2O molecules plus energy. This energy is transferred to the surroundings.

Does the energy transferred from the system to the surroundings in an exothermic reaction always end up as heat energy?

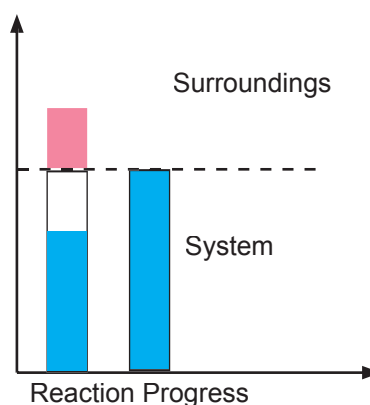
ENDOTHERMIC REACTION

- Chemical energy
- Energy transferred from the surroundings



The system is the interior of the circle, everything else is the surroundings. The endothermic reaction transforms energy from the surroundings into chemical energy in the system. The final result is that the chemical energy of the system is increased and the energy of the surroundings is decreased.

Another View of the Same Reaction



The system is a collection of hydrogen and oxygen atoms which are in H_2O molecules before the reaction. After the reaction the system is the same collection of atoms formed into H_2 and O_2 molecules. The chemical energy of the system has been increased by energy withdrawn from the surroundings.

What other forms of energy, besides heat, can be withdrawn from the surroundings to make an endothermic reaction occur?

CHEMICAL ENERGETICS

ORIGINS OF THE FIRST LAW OF THERMODYNAMICS

In 1798 Count Rumford published an article in the Philosophical Transactions of the Royal Society of London in which he described experiments about boring out brass cannon which showed that heat is not a substance, as previously thought, but a form of motion, or of what we would now call energy. He showed that an inexhaustible amount of heat could be produced with a finite amount of matter, which precluded that heat itself be a substance.

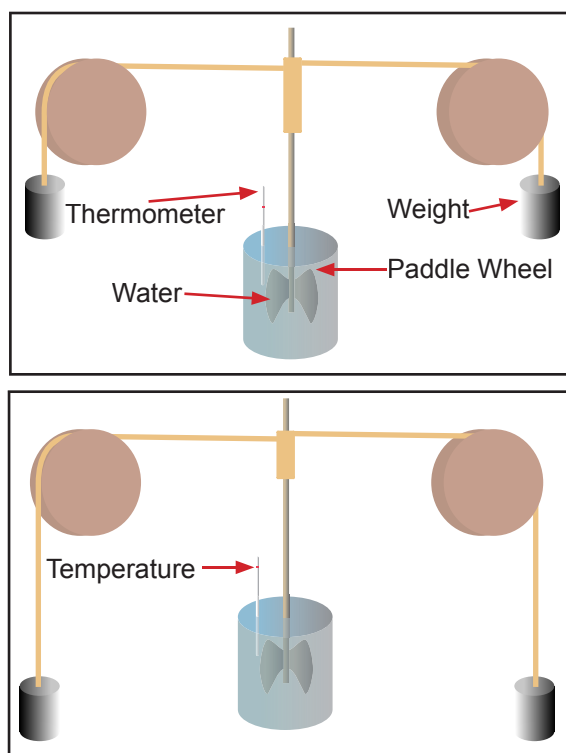
“Being engaged, lately, in superintending the boring of canon, in the workshops of the military arsenal at Munich, I was struck by the very considerable degree of heat which a brass gun acquires, in a short time. By being bored...

*The more I meditated upon these phenomena the more they appeared to me to be curious and interesting, a thorough investigating of them seemed even to bid fair to give a farther insight into the hidden nature of heat; and to enable us to form some reasonable conjectures respecting the existence, or non-existence, of an igneous fluid: a subject on which the opinions of philosophers have, in all ages, been much divided.... And, in reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of heat generated by frictions, in these experiments, appeared evidently to be **inexhaustible**. It is hardly necessary to add that anything which any insulated body, or system of bodies, can continue to furnish **without limitation** cannot possibly be a **material substance**: and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be **MOTION**.*

In the 1840's James Joule conducted a series of experiments measuring the relationship between different forms of energy, in particular electrical, mechanical and heat energy. The pictures below show an experiment in which the potential gravitational energy of the weights turns the paddle wheel as the weights fall, which in turn heats the water by friction. Joule's conclusion was that when energy is changed from one form to another, the amount of energy remains the same.

Now this principle has come to be accepted. It is called conservation of energy or the First Law of Thermodynamics.

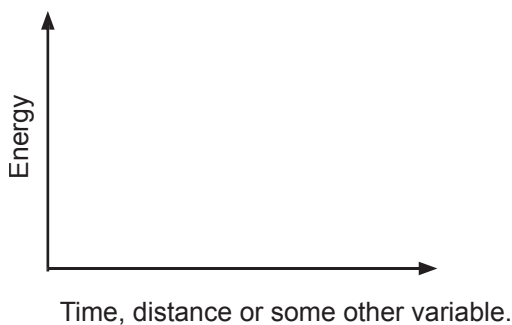
JOULE'S EXPERIMENTAL ARRANGEMENT



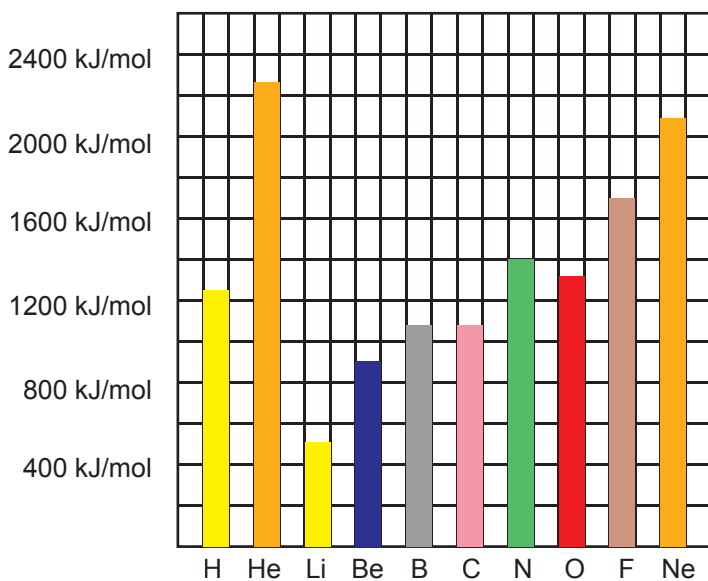
CHEMICAL ENERGETICS

ENERGY DIAGRAMS

It is standard in chemistry to show the energies of systems and energy changes between states by means of diagrams in which the vertical axis represents energy with the upward direction representing higher energy. The horizontal axis can represent changes in some other property or different systems.

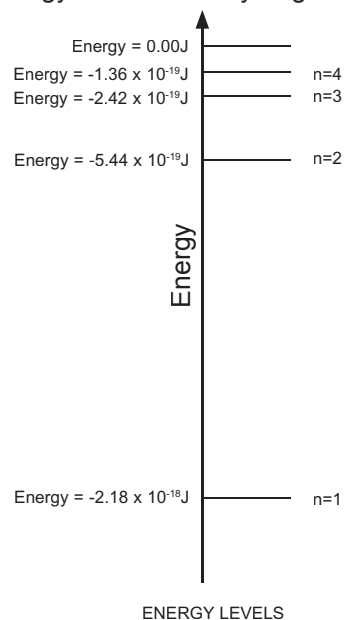


As an example of energy charts comparing different systems we show a chart of the energy required to ionize the first valence electron from the first ten elements. In this chart the vertical energy scale is in kilowatts per mole.



In the ionization energy chart the zero of energy was at the bottom of the chart. Sometimes this is not the case. Charts showing the energy levels of atoms, for example, may have the zero of energy near or at the top of the chart.

Energy levels of the Hydrogen atom.



In this example of the energy levels of the hydrogen atom, there is no real horizontal axis. We just need the space to write in. On the other hand, the other charts on this page do each have a meaningful horizontal axis.



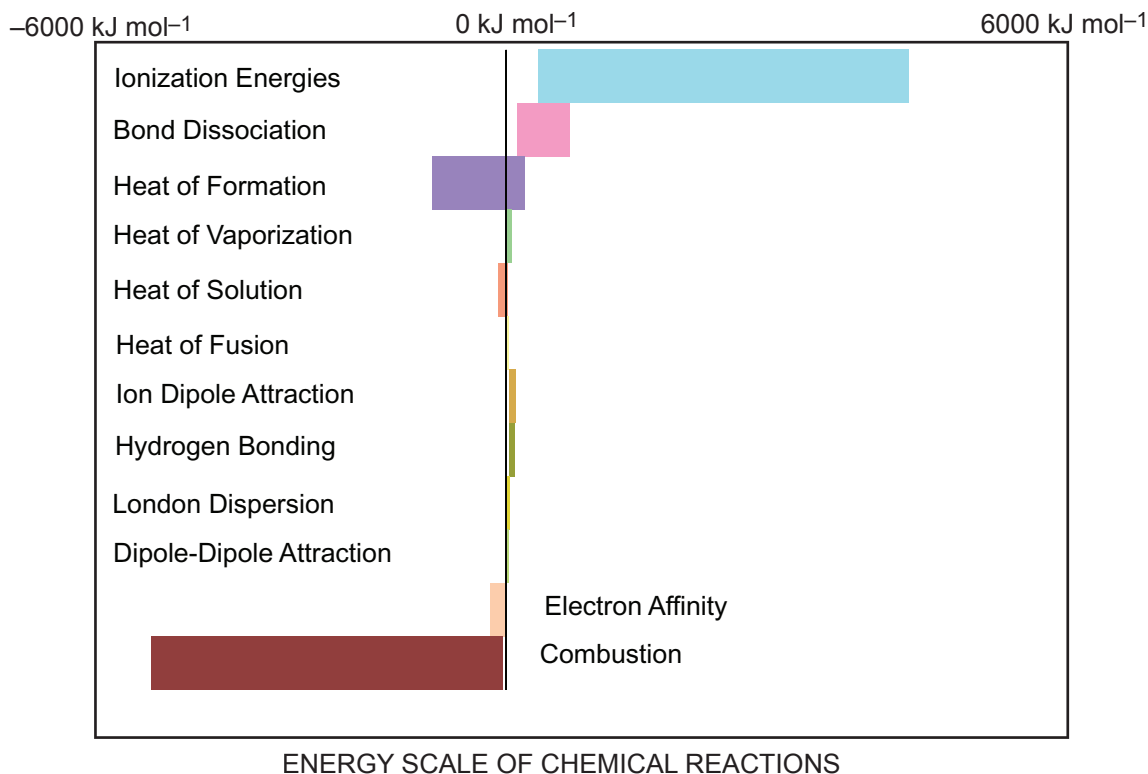
Suppose you are going from your home to chemistry class. In the box above draw a line or curve showing the changes in your gravitational potential energy as you go from home to chemistry class. Draw it from left to right, starting in the middle of the left hand side. Chemistry class is on the right hand side of the box but I don't know how high it is relative to your home.

CHEMICAL ENERGETICS

ENERGY CHEM LOGS

We have examined the common vertical axis representations of energy which you will find in most of your textbooks. However, in Powerful Pictures we have introduced the Chem Log, because sometimes a horizontal bar graph communicates information more intuitively than a vertical presentation.

Look into the media available to you, such as newspapers, magazines, books and the Internet, for examples of horizontal bar graphs. Compare and contrast these examples with Chem Logs.



If you have read our Chem Log tutorial you will know that there are also more sophisticated forms and uses of Chem Log but for our simple version used in this module you need to note that the zero of energy is in the middle and the amount of energy involved varies with the distance from the middle. In the Chem Log above, the left side shows negative, or exothermic reactions, while the right side shows positive, or endothermic, reactions.

Which of these types of chemical reactions are endothermic? Which are exothermic? Which include both endothermic and exothermic possibilities?

Write a list of the types of chemical reactions shown in the Chem Log, ordering it according to the range of energies associated with each type. For example, Heats of Formation occur over a wider range of energies than Bond Dissociation.

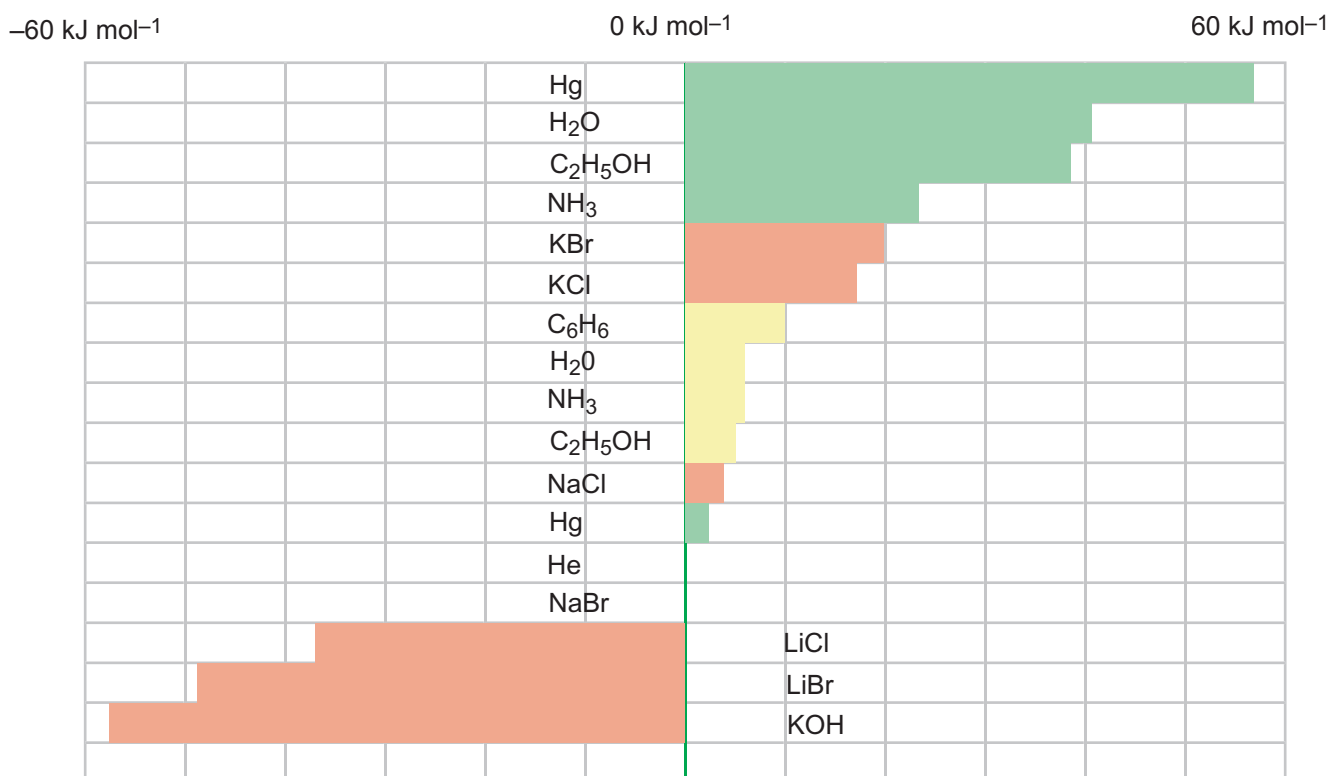
CHEMICAL ENERGETICS

ENTHALPY CHANGES

Enthalpy, H , is a thermodynamic quantity. H is the chemical energy or heat content of a system at constant temperature and pressure. What is important about enthalpy is its change, ΔH , when a chemical process occurs. Provided the process occurs at constant pressure (usually one atmosphere) and the only work done by the system is possibly the production of gas, then ΔH is equal to the heat energy produced or absorbed by the process. When $\Delta H > 0$ the process absorbs heat from its surroundings. When $\Delta H < 0$ the process produces heat.

The chart below shows the enthalpy changes produced by evaporation, melting and dissolving.

- Enthalpy change when a substance goes from the liquid to the gaseous state.
- Enthalpy change when a substance melts.
- Enthalpy change when a substance dissolves into water.



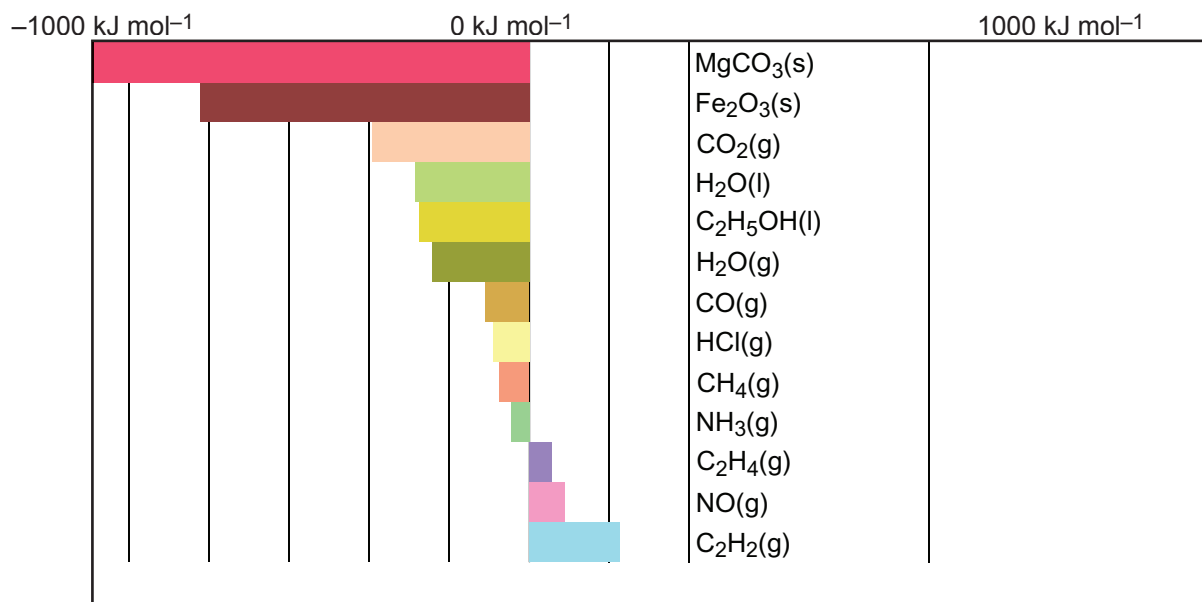
From the chart, would you expect KBr or LiBr to dissolve more readily in water?

Which of the processes shown in the chart are exothermic?

A cold winter day will often become somewhat warmer when snow starts falling. Give an enthalpic explanation of this phenomenon.

CHEMICAL ENERGETICS

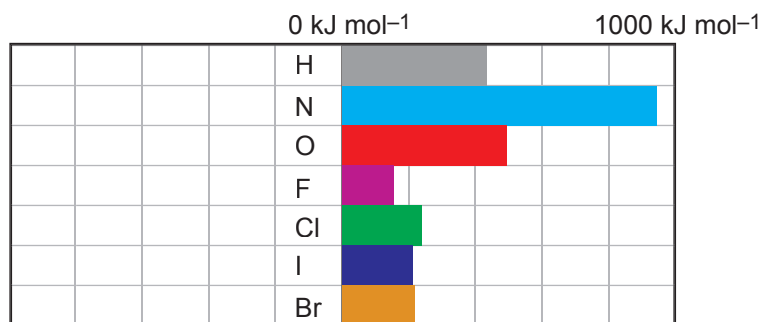
ENTHALPY OF FORMATION



The enthalpy of formation of a substance is the enthalpy change which occurs when a substance is formed from the most stable forms of its component elements. In several cases the most stable form of an element is a diatomic gas which must be decomposed in order to use the atoms in the formation of the substance. The next Chem Log shows the enthalpies of formation for several atomic gases from their more stable diatomic state.

Given its large negative enthalpy of formation, explain why rusting iron usually does not feel warm to the touch (unless it has been left in the sun).

Methane, CH₄(g) is a common fuel, making up a large part of natural gas. Given that we burn methane to produce heat, explain how that can be so when its enthalpy of formation is negative.

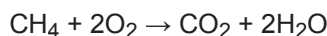


Discuss what effect the bond structures of N₂ and O₂ have in determining the enthalpies of formation of N and O.

CHEMICAL ENERGETICS

ENTHALPIES OF REACTIONS

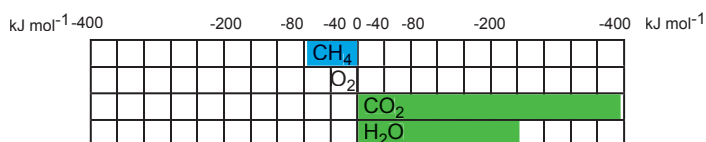
Consider the chemical reaction:



Since we know the enthalpies of formation of each of the reactants and each of the products we can find the enthalpy change in the reaction.

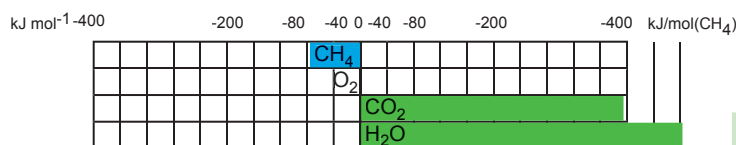
ENTHALPY OF FORMATION

Chemical	H in kJ mol^{-1}
CH_4	-74.8
O_2	0
CO_2	-393.5
H_2O	-241.8



ENTHALPIES OF FORMATION

The stoichiometry of the reaction requires two moles of water be formed, so we double the enthalpy of the water.



ENTHALPIES OF THE REACTION

In order to find the enthalpy change, ΔH , of the reaction we first sum the enthalpies of the products.



TOTAL ENTHALPY OF THE PRODUCTS

Then we subtract the enthalpy of the reactants.



DIFFERENCE OF ENTHALPIES

Which gives us the enthalpy change of the reaction.



ENTHALPY CHANGE OF THE REACTION

Tell whether the reaction is endothermic or exothermic and explain why.

Explain why the enthalpy of formation of O_2 is zero.

Find the total enthalpy of the products on the chart called TOTAL ENTHALPY OF THE PRODUCTS.

Find the enthalpy change of the reaction on the chart called ENTHALPY CHANGE OF THE REACTION.

The scale on the bottom four charts is labeled $\text{kJ/mol}(\text{CH}_4)$. This means kiloJoules per mole of CH_4 . Explain why it is labeled that way instead of kJ mol^{-1} and state an alternative label.

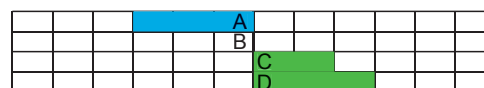
For the given products, what would have been the total enthalpy of the reactants for the reaction to be in equilibrium?

The charts below apply to a reaction in the type $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$

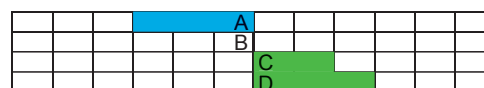
In the charts, draw in an enthalpy of reactant B that would be required in order for the reaction to

- Proceed to the left
- Be at equilibrium
- Proceed to the right.

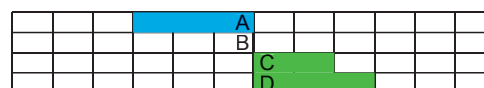
Assume that all the enthalpies are negative and that the enthalpy of B is NOT zero.



a. Proceed to the left.



b. Equilibrium



c. Proceed to the right.

CHEMICAL ENERGETICS

HESS'S LAW

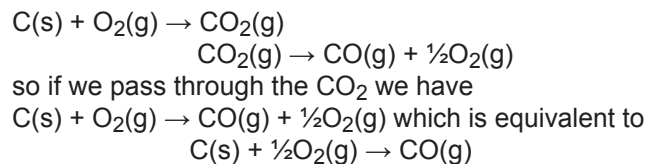
Hess's Law states that the enthalpy change in a given process is equal to the sum of the enthalpy changes of the several processes that, when added, yield the process of interest.

Because enthalpy, H, is a state function, enthalpy change, ΔH , between two states only depends upon the difference in enthalpy between the states and not upon how one state was changed into the other one. So we can use Hess's Law to determine ΔH for a reaction, R, if we can find a set of reactions which combine to give an equivalent reaction to R, even if these are NOT the actual processes by which R happens.

Suppose we want to find ΔH for the combustion of carbon to give carbon monoxide:

- a. $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H = ?$
 given that we know ΔH for the reactions
 b. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5 \text{ kJ}$
 c. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0 \text{ kJ}$

Here is the plot. Reaction b gives the enthalpy for combusting carbon into carbon dioxide. If we reverse reaction c we can get rid of the carbon dioxide and obtain carbon monoxide, which is what we are looking for.

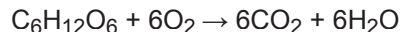


To get the ΔH of that reaction we subtract the ΔH of reaction c from the ΔH of reaction b.

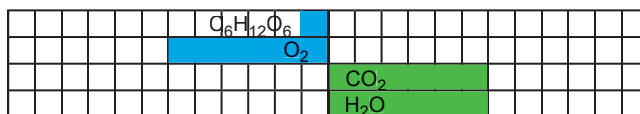
$$\begin{array}{r} \Delta H(\text{Reaction b}) \quad -393.5 \text{ kJ} \\ -\Delta H(\text{Reaction c}) \quad -(-282.0 \text{ kJ}) \\ \hline \Delta H(\text{Reaction a}) \quad -111.5 \text{ kJ} \end{array}$$

State functions depend only upon the difference between two states and not upon the path between them. Suppose you climb a mountain. Which of the following quantities is a state function and which is not?
 The change in altitude between the bottom and top of the mountain?
 The distance traveled while climbing the mountain?

Consider the oxidation of glucose, which is a primary source of energy in our bodies, where it is also called respiration. The chemical formula is:



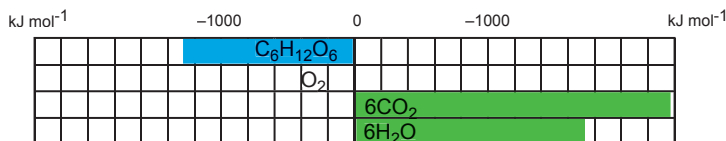
We can express this reaction by a ChemLog:



STOICHIOMETRY

We can now look at the enthalpy change involved in the reaction. We begin with the enthalpies of formation, ΔH_f
 $\Delta H_f(C_6H_{12}O_6) = -1273 \text{ kJ mol}^{-1}$
 $\Delta H_f(O) = 0 \text{ kJ mol}^{-1}$
 $\Delta H_f(CO_2) = -393.5 \text{ kJ mol}^{-1}$
 $\Delta H_f(H_2O) = -285.8 \text{ kJ mol}^{-1}$

We can express the enthalpies as a chem log

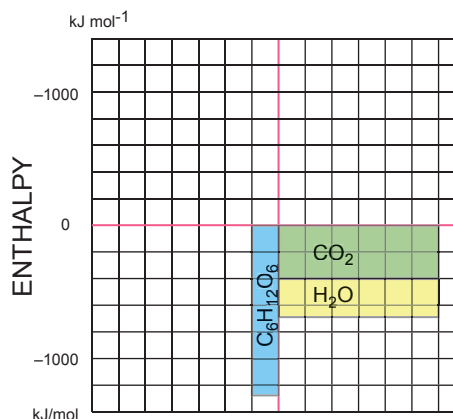


ENTHALPY

Now we introduce another variety of ChemLog where the height of the bar is the enthalpy in kJ mol^{-1} . Positive enthalpies appear above the horizontal axis and negative enthalpies appear below that axis.

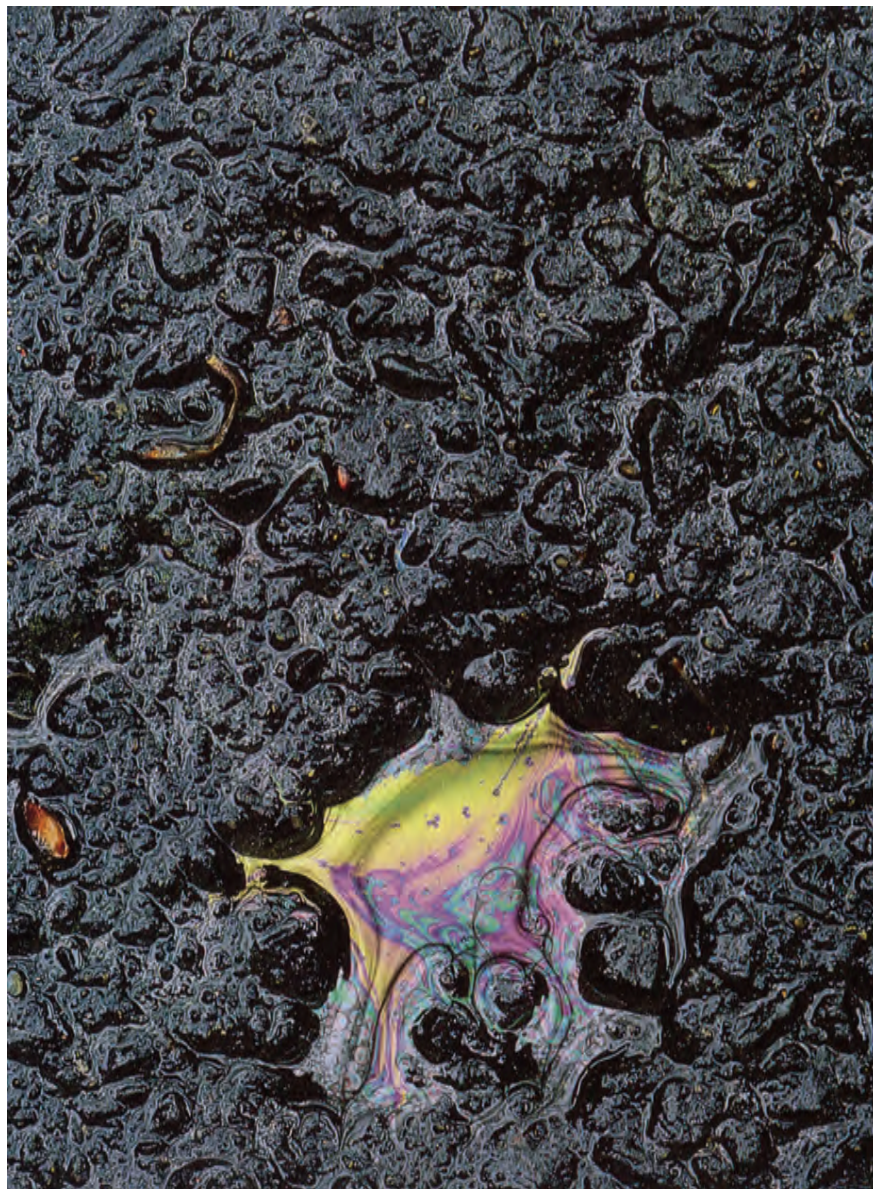
As we have done before the width of the bar is determined by the number of moles of the substance in the reaction: Reactants to the left of the vertical axis and products to the right of that axis.

The value of this kind of ChemLog is that the area of a bar is proportional to its enthalpy.



STOICHIOMETRY

DO MOLECULES EXIST AND HOW SMALL ARE THEY?



by **Dr. Stephen Thompson**
Mr. Joe Staley
Ms. Mary Peacock

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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

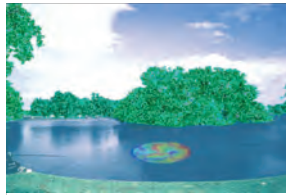
BENJAMIN FRANKLIN STILLS THE WAVES



1



2



3



4

Throughout his life Benjamin Franklin was interested in the calming effect of oil on turbulent water. In 1774, he described a series of experiments in which he poured oil on a pond in England. He observed that a teaspoon of olive oil poured on the surface spread to about one half of an acre. In an article in *Philosophical Transactions* 64, 1774, 445-460, he also reported, as seen in the excerpt given here:

Franklin searched for a scientific explanation of these phenomena because he was interested in the practical problem of saving the lives of sailors shipwrecked at sea in violent storms. He didn't realize that this simple experiment could actually be used to determine the size of olive oil molecules! Before determining their size, let's explore why olive oil molecules spread on water. This alone was fascinating to Franklin because on other surfaces, olive oil doesn't spread. How can this be?



5

In 1989, when the Exxon Valdez grounded at Prince William Sound and spilled 10.8 million gallons of oil into the sea, the clean-up process was expensive and difficult because of the simple fact that oil spreads on water. Several methods to clean Prince William Sound were employed, including the use of a boom, as seen in the following picture. The boom can be pulled across the surface to collect the oil but is usually employed more as a guard to protect an area.

[450]

After this, I contrived to take with me, whenever I went into the country, a little oil in the upper hollow joint of my bamboo cane, with which I might repeat the experiment as opportunity should offer; and I found it constantly to succeed.

In these experiments, one circumstance struck me with particular surprize. This was the sudden, wide, and forcible spreading of a drop of oil on the face of the water, which I do not know that any body has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking-glass that lies horizontally; the drop remains in its place, spreading very little. But when put on water it spreads instantly many feet round, becoming so thin as to produce the prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance. It seems as if a mutual repulsion between its particles took place as soon as it touched the water, and a repulsion so strong as to act on other bodies swimming on the surface, as straws, leaves, chips, &c. forcing them to recede every way from the drop, as from a center, leaving a large clear space. The quantity of this force, and the distance to which it will operate, I have not yet ascertained; but I think it a curious enquiry, and I wish to understand whence it arises.

Notice the color variation in the water. Describe the contaminated water. Are Franklin's observations similar to yours? Why or why not?

When oil is spilled on water, does it float on top, sink to the bottom, or get dispersed throughout the water?

What other methods have been used to clean up oil spills.
What new methods can you suggest?

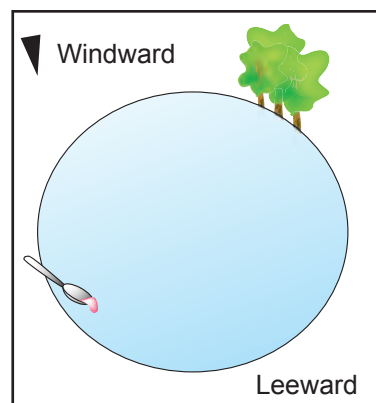
Read Benjamin Franklin's original discussion, which is included with your course resources.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ON CLAPHAM POND-1

Benjamin Franklin was interested in the effect of pouring oil upon troubled waters. As a practical man he thought that the effect might help prevent ships from sinking and sailors from drowning. The following quotes are from the 1774 Philosophical Transactions of the Royal Society.

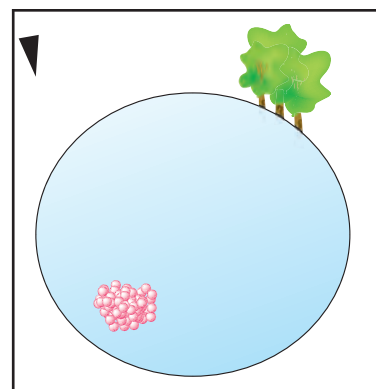
“At length being in CLAPHAM where there is, on the common, a large pond, which I observed to be one day very rough with wind, I fetched out a cruet of oil, and dropt a little of it on the water.”



6

“I saw it spread itself with surprising swiftness upon the surface; but the effect of smoothing the waves was not produced...”

Why not?

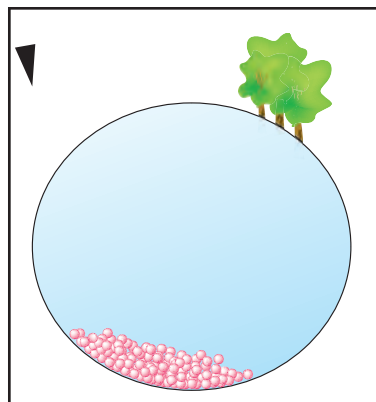


7

“...for I had applied it first upon the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore.”

What would you have done next after getting this result?

Why do you suppose the wind pushed the oil upon the shore when the wind does not push the water upon the shore. Or does it?



8

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ON CLAPHAM POND-2

Visit a small or medium sized pond on a windy day. Observe the character of the waves both on the leeward and the windward sides. Repeat Franklin's experiments on both sides of the pond and describe your results.

"I then went to the windward side, where they began to form..."

Olive oil is attracted to the water. How does this experiment support this statement?

Olive oil is attracted to itself. How does this experiment support this statement?

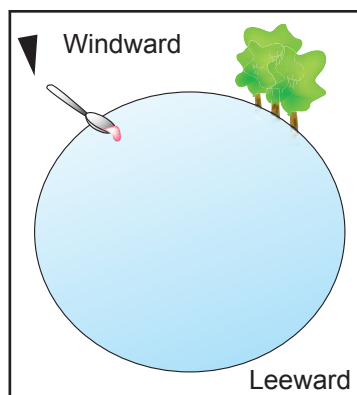
"...and there the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square..."

What do you think would happen if the olive oil molecules were smaller than water molecules?

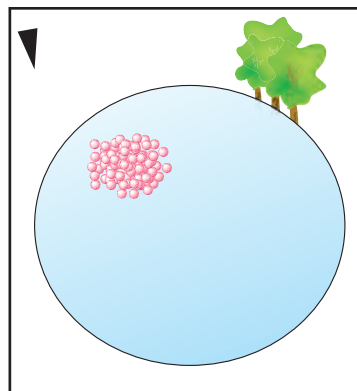
"...which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass."

You might suppose that the oil spread because it was blown by the wind. Do you think that there might have been another reason why the oil spread?

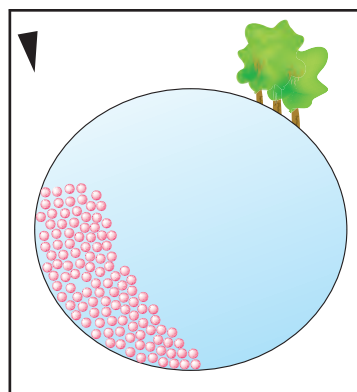
What do you think Franklin would have found if he had returned to look at the pond the next day? Why, from a molecular point of view do you think that?



9



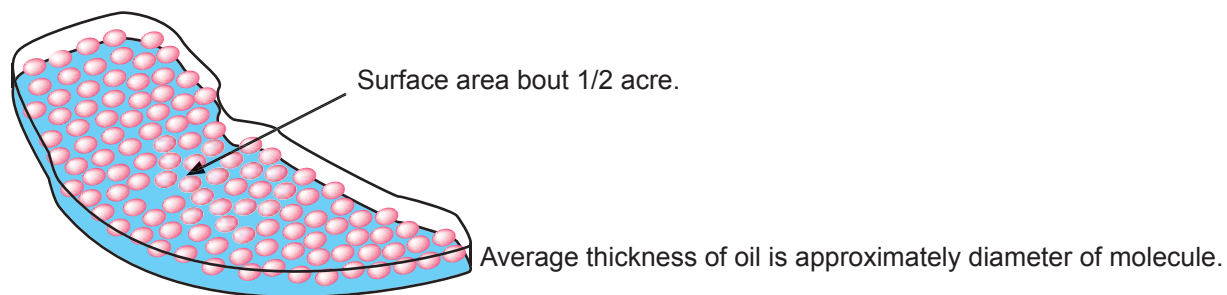
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

SURFACE AREA CALCULATION



12

One acre = 43,560 square feet = 4,840 square yards = 4047 square meters.

It is reasonable to approximate “perhaps half an acre” as 2000 square meters.
Call the surface area A
 $A = 2000 \text{ m}^2$
Call the diameter of the oil layer D .
Call the volume of the oil V .
From geometry, $V = AD$
But eighteenth century teaspoons in museums hold approximately two cubic centimeters, so we know that $V = 2 \text{ cm}^3$
Now we can put our facts together and see that $2 \text{ cm}^3 = 2000 \text{ m}^2 \times D$
You can finish the calculation.

Benjamin Franklin could have done this calculation but he did not. Why do you think that he did not? What implications would it have had for the development of science if he had?

A few years ago Professor Stephen Thompson of Colorado State University attempted to repeat Franklin’s experiment by dropping olive oil onto City Park lake in Fort Collins. It did not work. Why not?

We are assuming that the oil, after spreading to half an acre, was one molecular layer thick. Of what significance for our assumption is the fact that after spreading to half an acre the oil STOPPED spreading.

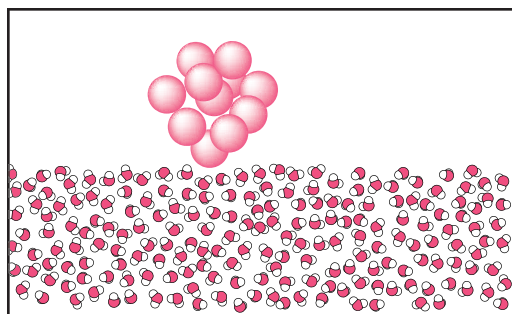
Calculate the number of molecules in Dr. Franklin’s teaspoonful.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

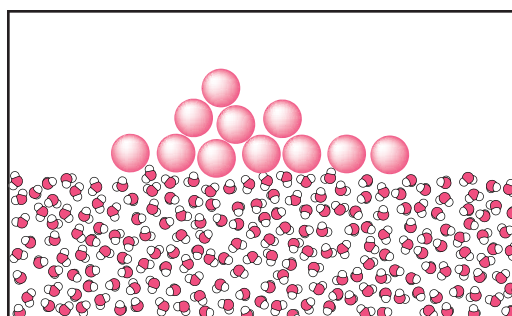
OIL ON WATER

If you look closely at the pictures on the right you will notice that the positions and/or orientations of (some of) the water molecules have changed. Did you try the experiment of placing a drop of oil on ice? Did the oil spread? Can you explain why the motion of the water molecules is necessary for the oil to spread? Could the spreading of the oil be simply due to the random motion of the water molecules? Could it be due to the weight of the oil pushing itself flat across the water?

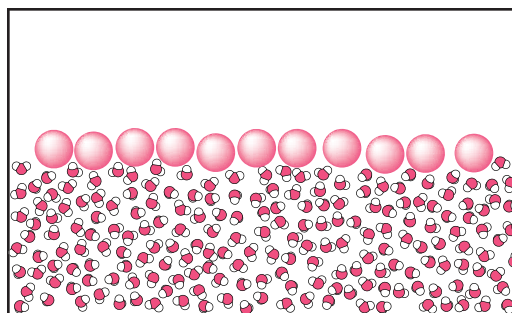
Did you try the experiment of placing a drop of mineral oil on water? Did it spread? How does that fact fit with the explanation of spreading as due to random molecular motion or to the weight of the oil?



13



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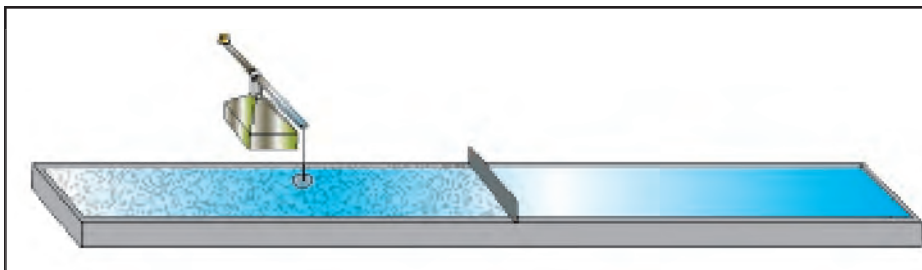
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AGNES POCKLES

In 1891 the famous scientist Lord Rayleigh (who won the 1906 Nobel Prize for the discovery of Argon) received a letter from an unknown German lady, Agnes Pockles. An English translation of the letter was published in Nature on March 12, 1891.

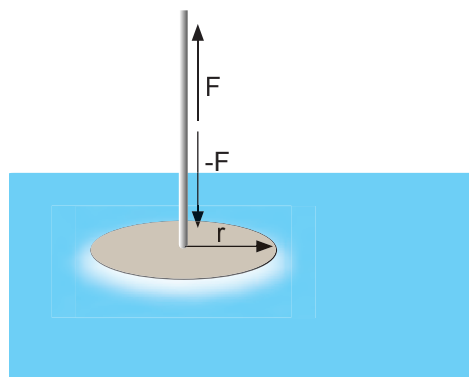
Pockles found experimentally that the surface tension of a saturated solution of sodium chloride was 15.4% greater than the surface tension of pure water. Can you give a molecular explanation for that fact?



16

Agnes Pockles experimental apparatus for measuring surface tension.

The picture on the right shows Pockles' method of measuring surface tension. From this method, discuss why the units of surface tension are Newtons per meter. Devise another method of measuring surface tension.



17

Among Pockles' results were the following:

“...that the surface layer of water can take up more of soluble substances than the internal liquid...”

and similarly

“...in which a thin disk of camphor, so hung that it is half immersed in the cleanest possible water surface, is cut through in the course of a few hours.”

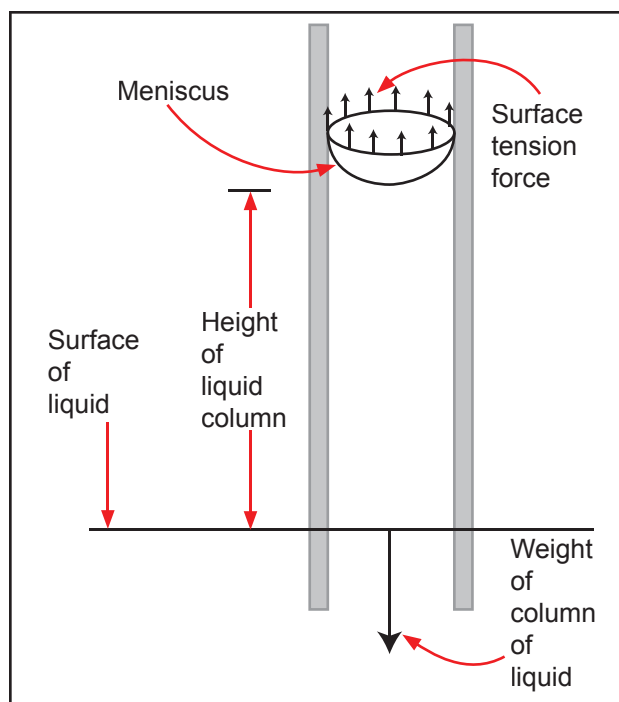
Explain what you can deduce about the molecular nature of water surfaces from these observations?

Read Ms. Pockles letter to Lord Raleigh, as translated and published in Nature, which is included in your course resources. Explain what you consider to have been her most significant or interesting results.

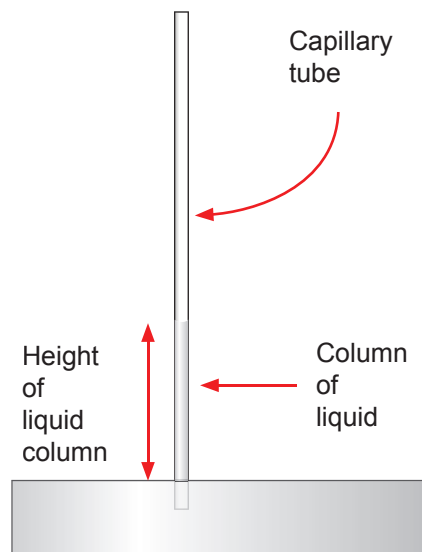
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MEASURING SURFACE TENSION BY THE CAPILLARY METHOD

The Pockles method of measuring surface tension is rather difficult to use but here is a simpler method, although it still requires careful technique.



18



19

Using the capillary method, measure the surface tension of different fluids, including distilled water, soapy water, tap water, an aqueous salt solution and ethanol. (The density of 95% by volume ethanol is 0.82g cm^{-3} .)

Why is careful attention to cleanliness essential for this measurement? When the liquid used is water, should the capillary tube material be hydrophilic or hydrophobic and what would happen if it were the opposite?

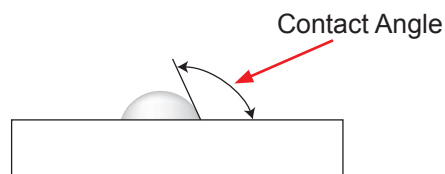
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

CONTACT ANGLES

We can often surmise the interaction between a liquid and a solid by observing the contact angle between a droplet of the liquid placed on the surface of the solid.

What can you determine about the relative hydrophilicity of the four surfaces illustrated in the drawings to the right? Assume that the droplet is made of water.

Place droplets of water on various surfaces, including both clean and dusty glass, different plastics and metals. Observe and draw the contact angles and discuss the hydrophobicity or hydrophilicity of the substances. Repeat the experiment with other liquids such as alcohol and various vegetable and mineral oils.



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

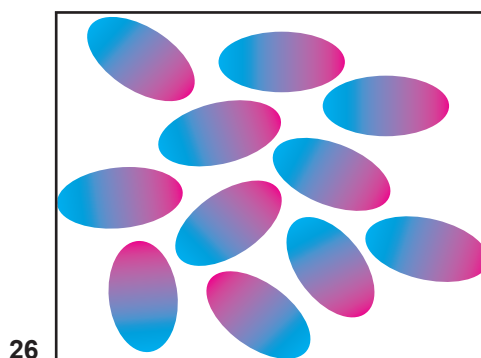
INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the structure of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?
Why is it more important in liquids than in gases?
Can homonuclear diatomic molecules such as H_2 , O_2 and N_2 have dipole-dipole forces?



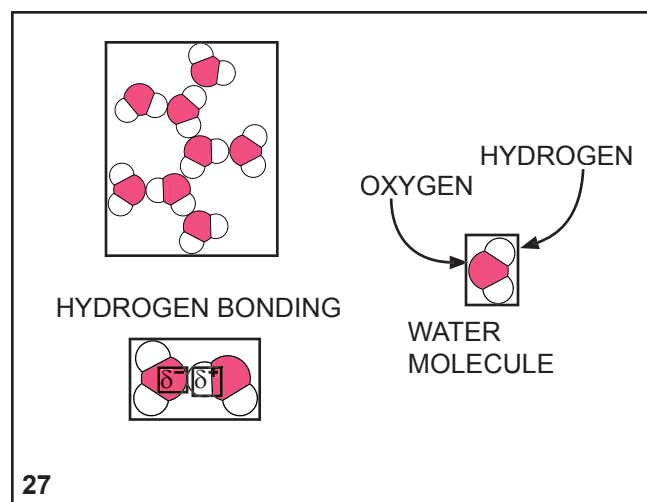
26

DIPOLE DIPOLE INTERACTION

HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom.

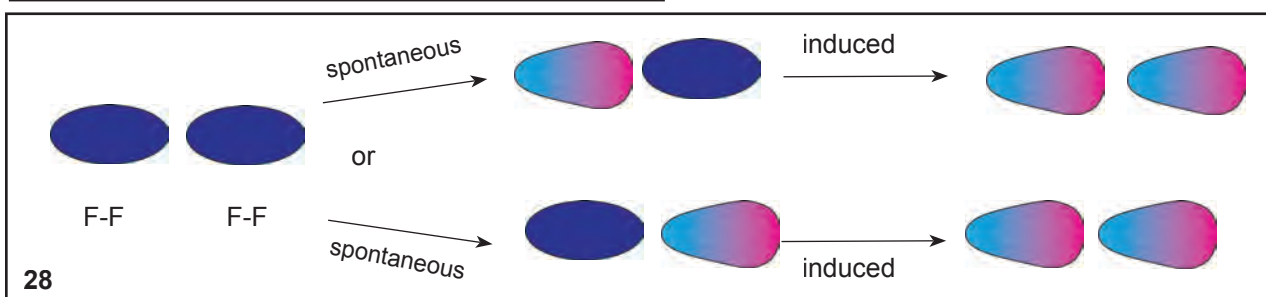
Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.



27

LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecule so that the two molecules have opposite charges on their near sides and attract each other.



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

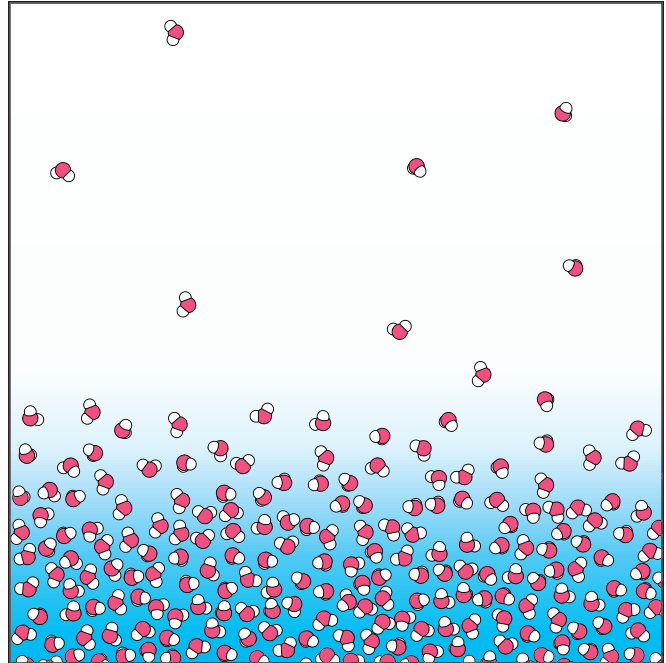
SURFACE TENSION

In the drawing on the right, circle a water molecule in the bulk of the water, a water molecule in the air and a water molecule in the surface layer of the water.

We know that it takes energy to evaporate water and that water molecules in air have a higher energy than water molecules in the liquid. What about water molecules in the surface layer?

What happens, in terms of energy, when we move more molecules from the bulk into the surface by stretching the surface layer?
What does this imply about the shape of a water/air interface, i.e. a surface?

The surface tension of water is 7.2×10^{-3} Newtons per meter. Multiply this by one square meter. What is the resulting unit? What kind of thing is that? (e.g. force, energy, viscosity,...?)



29

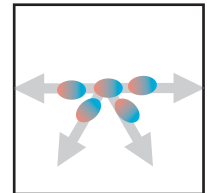
DISPELLING THE MYTHS

Some people may think of surface tension as implying some sort of skin or film on the surface, but we know that is almost the opposite of the truth.

A more sophisticated myth, because it is in the chemistry and physics textbooks, is that surface tension arises because, while a molecule in the bulk of the liquid is pulled equally in all directions by its neighboring molecules, a molecule on the surface is not pulled in the upward direction. This is a true statement about forces but its result is to keep the surface a surface and has nothing to do with surface tension.

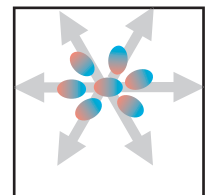
With the model of surface tension presented here it is possible to deduce whether surface tension would increase or decrease with increasing temperature, say from 300 K to 310K. Which is it?

In what direction is the resultant force on the surface molecule?



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Forces on a surface molecule.



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Forces on a bulk molecule.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AMPHIPHILIC OIL ON WATER

What are the three types of inter-molecular forces involved in this system? (Hint: water-water (hydrogen bonding) is one.)

By referencing these three forces, how does palmitic acid spread into a monolayer? How do the relative strengths of these three forces compare to each other?

Does the surface tension of the water increase or decrease at the palmitic acid/water interface?

Using a similar molecular force description, why doesn't motor oil spread into a monolayer on water?

Draw a picture of what a "puddle" of motor oil on water might look like.

Draw a molecular picture of what the interface of the motor oil/water puddle might look like.

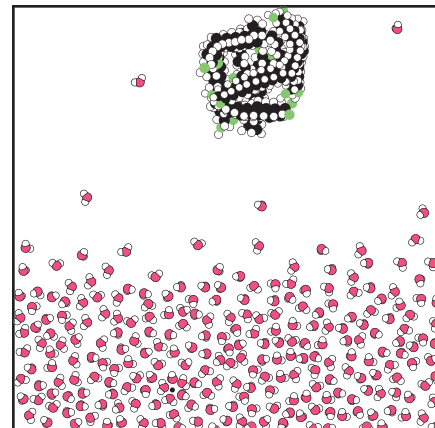
Why does the palmitic acid form a monolayer? Why don't individual palmitic acid molecules "break off" from the edges? (Or water penetrate the interior of the mono-layer, separating portions of it?)

Why is the constant molecular motion of the water surface necessary for the oil to spread? Incidentally, this is why oil will not spread to form a mono-layer on a glass surface.

Devise an experiment to show whether the time required for the oil to spread is dependent on the temperature of the water. What is your hypothesis?

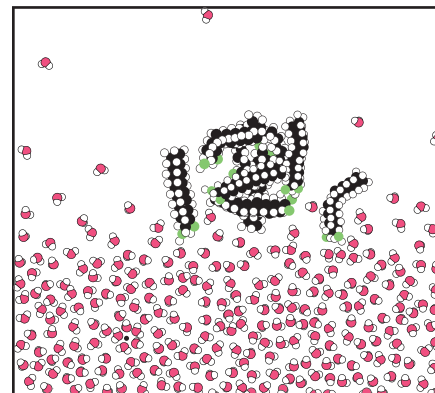
Perform the experiment. Report your results.

Why are there individual water molecules "floating" in the air above the surface?



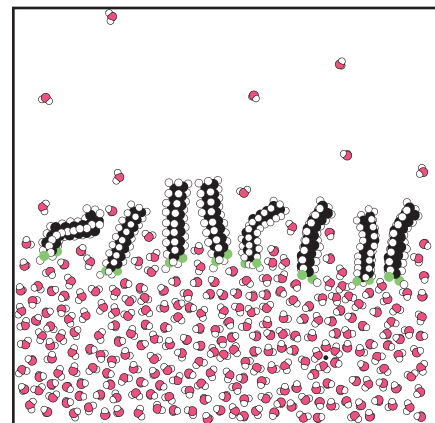
34

A small drop of palmitic acid falling towards a water surface.



35

The palmitic acid reaches the surface.



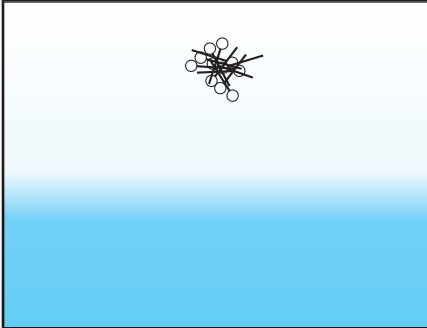
36

The palmitic acid spread into a monolayer.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

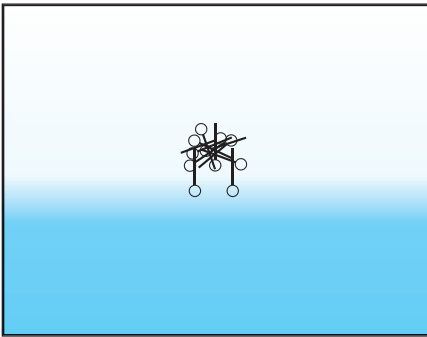
AMPHIPHILIC OIL ON WATER

37

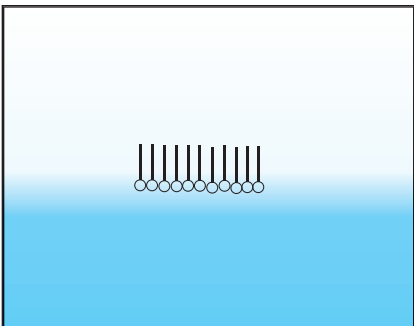


Using a simplified form such as the ones shown here - and it might be easier to put in the water with a blue marker- draw the sequence of molecular events if a drop of mineral oil were placed on water. Remember to modify the oil molecules to show that they are nonpolar.

38



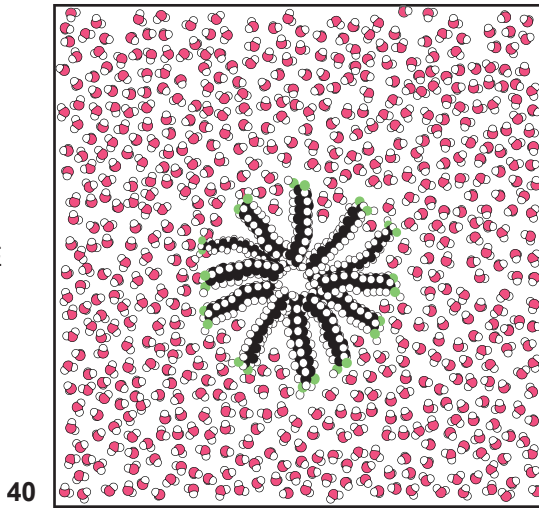
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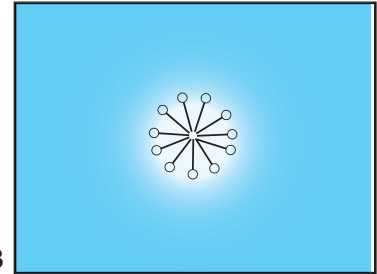
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AMPHIPHILIC OIL AND WATER

MICELLE

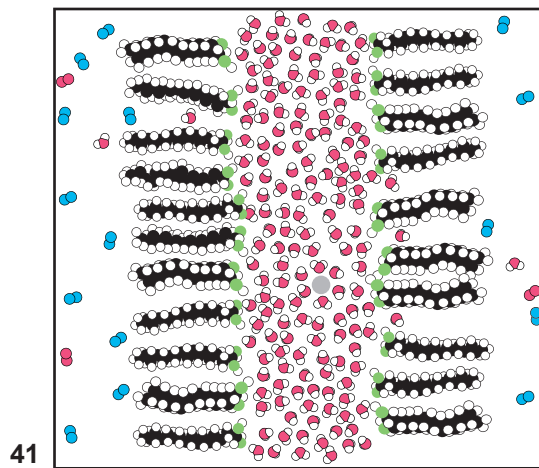


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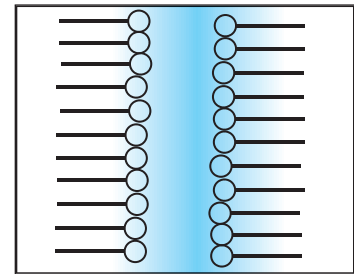


Investigate and describe occurrences of micelles, bilayers and vesicles. Give a molecular explanation for their occurrence and properties.

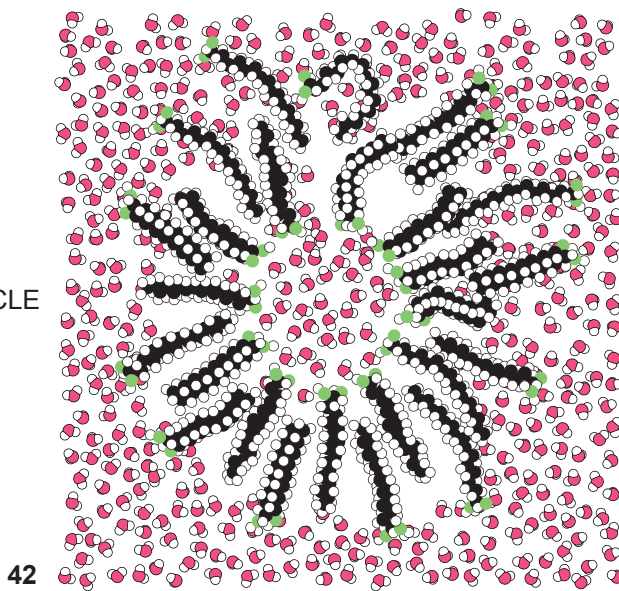
BILAYER



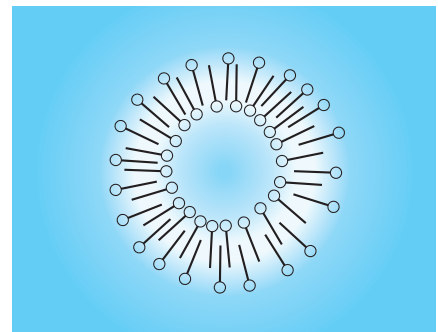
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VESICLE



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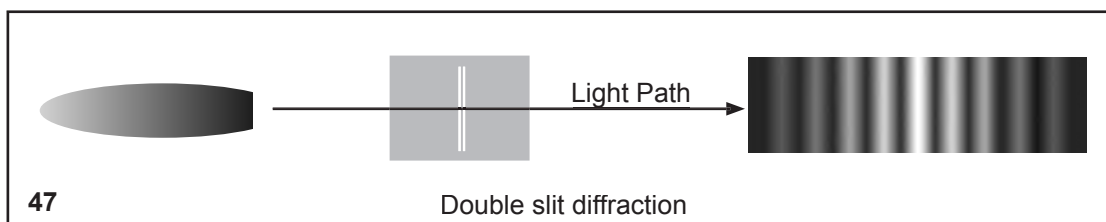
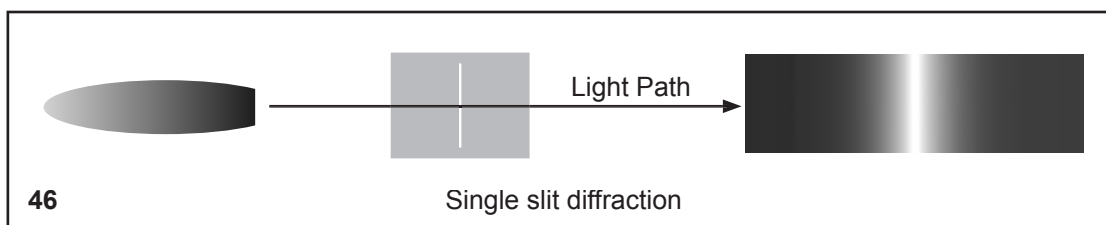
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MODERN MOLECULAR IMAGING

We began investigating molecules through the simple technology of placing oil on water and we have seen Ms. Pockles device. But this is the 21st century and we can now look at molecules directly. Among the modern methods of seeing molecules we will look at x-ray diffraction, atomic force microscopy and the scanning tunneling microscope.

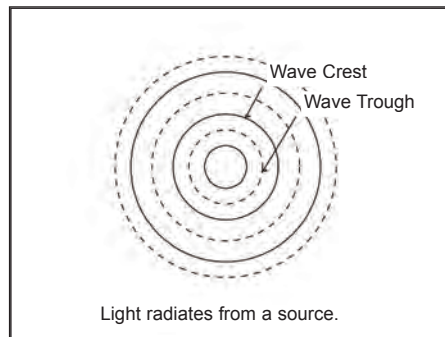
DIFFRACTION

Hold a sharp edge object, such as a pencil, at various distances away from a flat white surface in direct sunlight. From observing the shadows produced, what can you deduce about the nature of light?

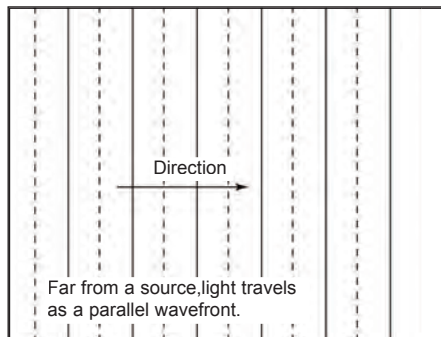


DO MOLECULES EXIST AND HOW SMALL ARE THEY?

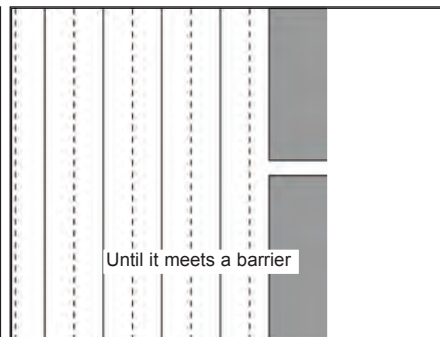
DIFFRACTION



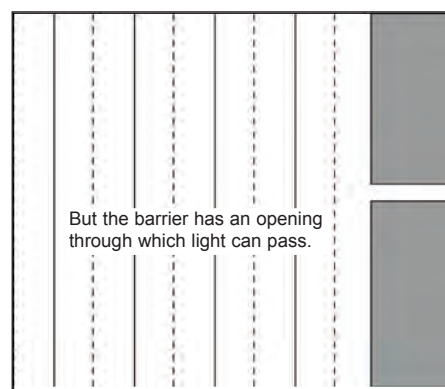
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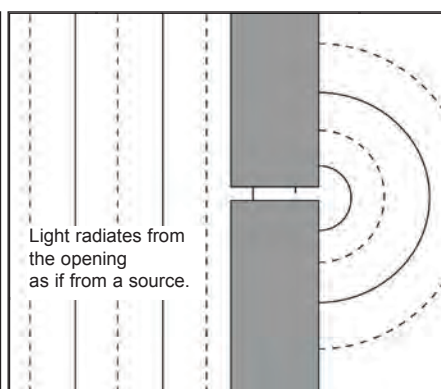
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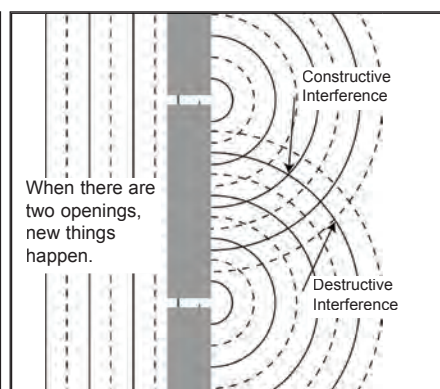
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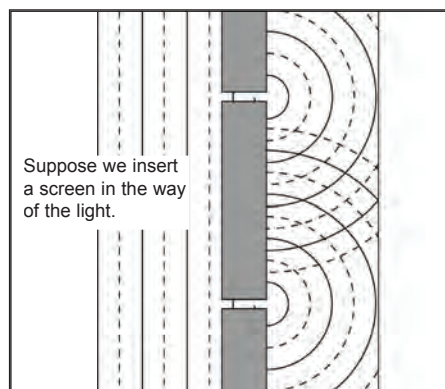
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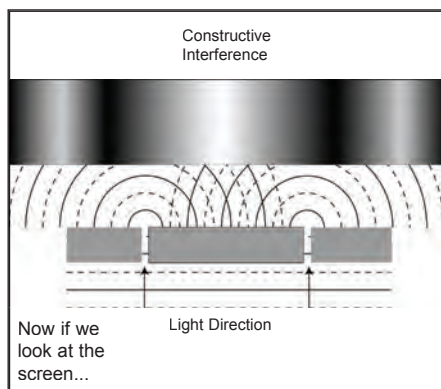
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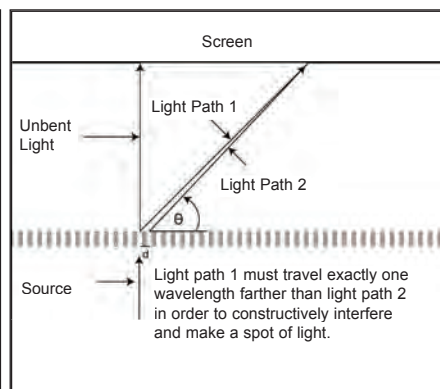
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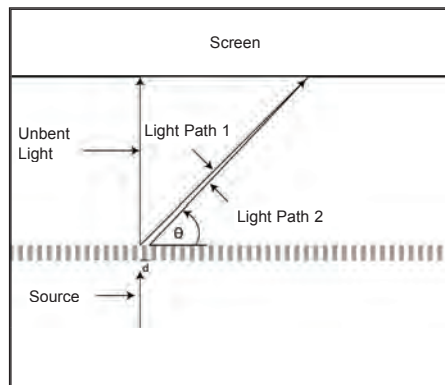
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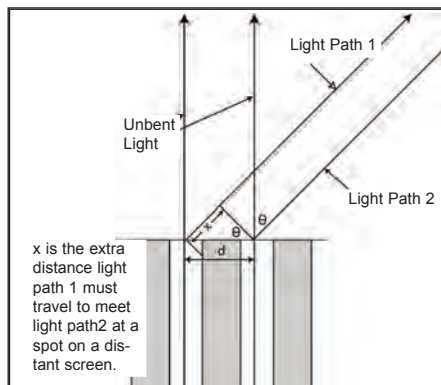
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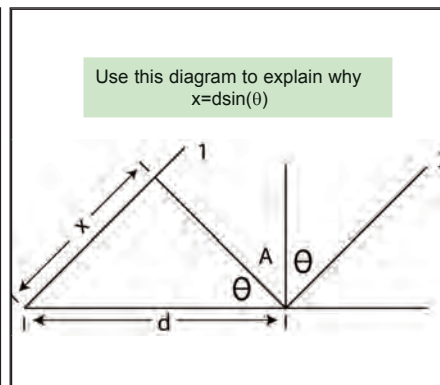
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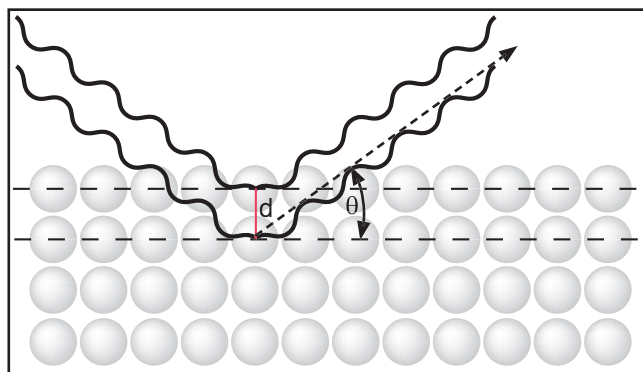
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

X-RAY DIFFRACTION

There are several methods of X-ray diffraction but they all depend upon the wavelength of X-rays being the same order of magnitude, or smaller, than atomic sizes or the spacing between atoms.

Also, X-rays are reflected from the electron clouds of atoms and molecules, rather than from the nuclei.



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In the picture above two x-rays arrive and are reflected from the substance at the same angle θ . When the angle is just right, the bottom wave will travel exactly one wavelength farther than to top wave and so the two waves will be in phase and interfere constructively, giving a dot on a screen. The relationship which connects the angle of reflection, the wavelength, λ , of the x-rays and the distance, d , between atomic (or molecular) planes is given by Bragg's Law.

$$n\lambda = 2d\sin(\theta)$$

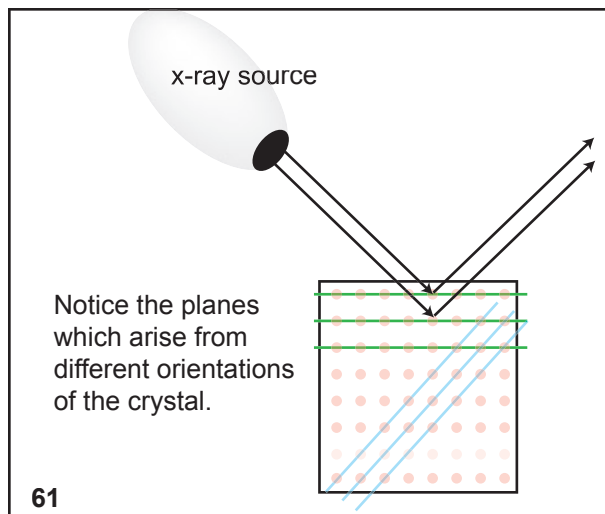
where n is a small positive integer.

When we are trying to find the separation d , which is effectively the atomic or molecular size, we solve the equation for d and then substitute experimentally determined values for λ and θ .

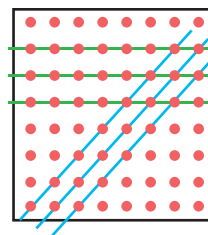
$$d = \frac{n\lambda}{2\sin(\theta)}$$

Compare the process of using x-ray diffraction for deducing crystal structure to the process of using a diffraction grating for spectroscopy. In what ways are the processes alike and in what ways do they differ?

Why can visible light waves not be used to measure atomic sizes?



61



62

Find some other planes in the pattern shown.

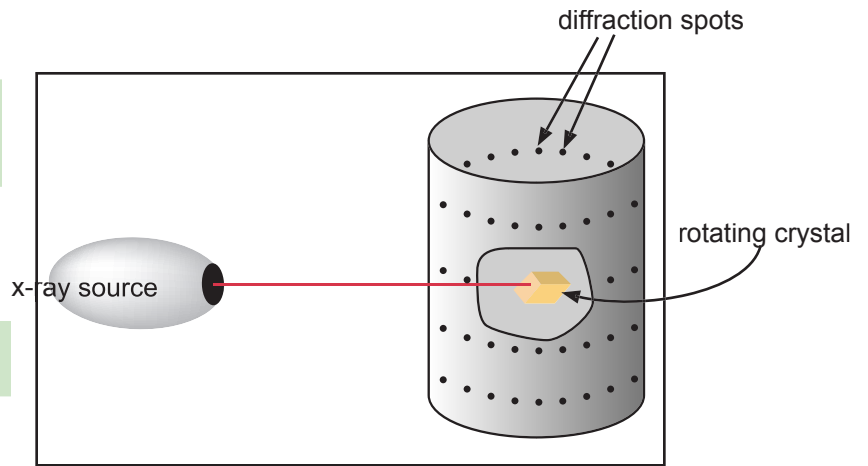
Suppose you could see at one meter wavelength. Describe, preferably by drawing, what the world would look like.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

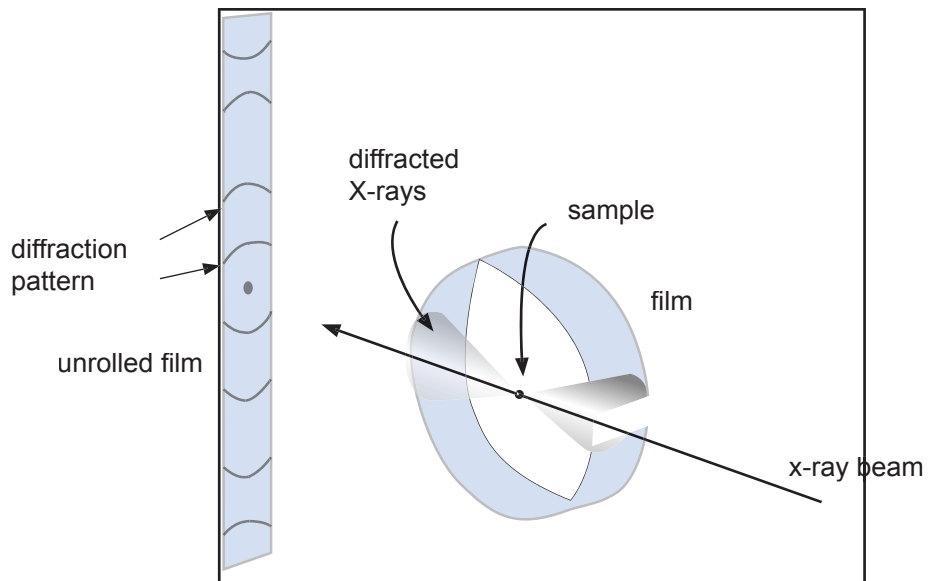
X-RAY DIFFRACTION

Explain why it is necessary to use a single crystal in the rotating crystal method?

How would you use x-ray diffraction to distinguish between glass and quartz?



63 Rotating Crystal Method



64 Powder Diffraction

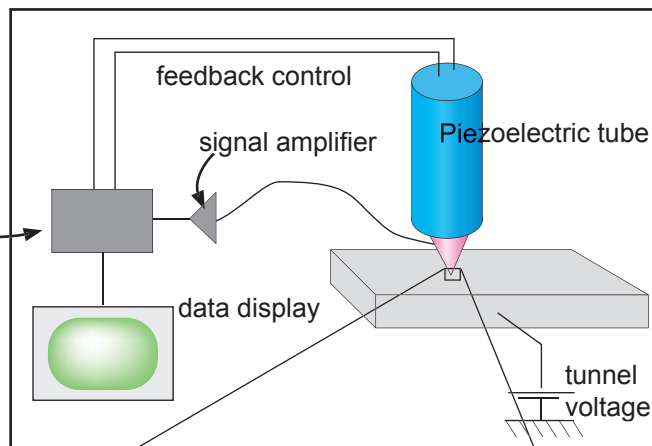
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

THE SCANNING TUNNELING MICROSCOPE

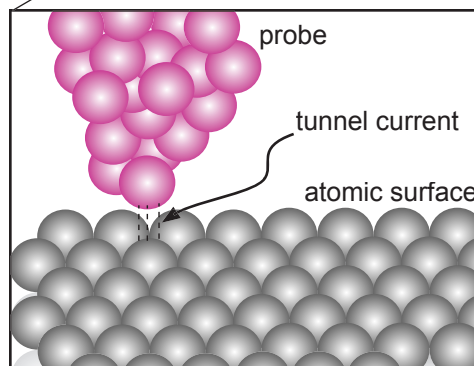
The scanning tunneling microscope (STM) measures the minute current between the atomic surface and the tip of a very fine probe. Because the current is very sensitive to the distance between the probe and the surface, the STM can recognize the bumps on the surface caused by single atoms.

What limitations to the use of STM are implied by the necessity of using a tunneling current?

distance control
and scanning unit



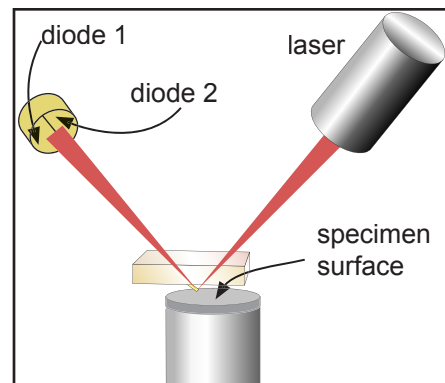
The piezoelectric effect in some materials provides a transduction between electric currents and mechanical vibrations. Quartz exhibits the piezoelectric effect.



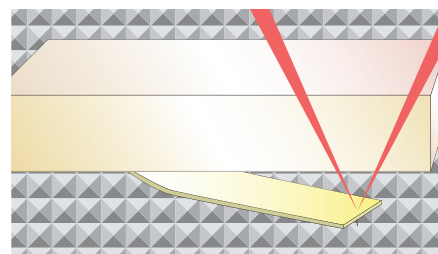
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ATOMIC FORCE MICROSCOPY

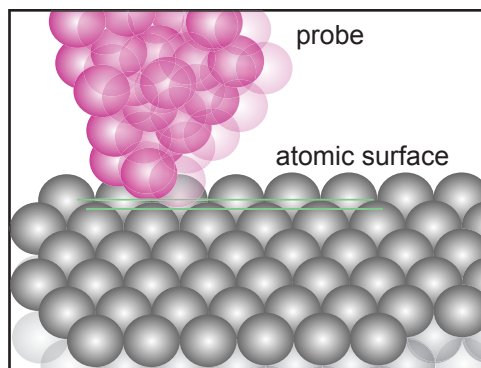
Atomic Force Microscopy relies upon direct contact, or near contact, between a finely pointed probe and an atomic surface. As the probe is moved across the surface, or vice-versa, the probe is pushed or pulled up and down by the variations in height between the top of an atom and the interstices between atoms. This motion is transmitted to a cantilever beam. The effect can be magnified several thousand times by a laser beam reflected off of the cantilever and measured by the relative strength of reception between two adjacent light measuring diodes.



67

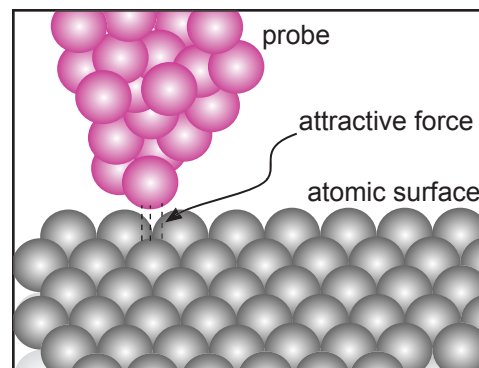


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Contact Mode

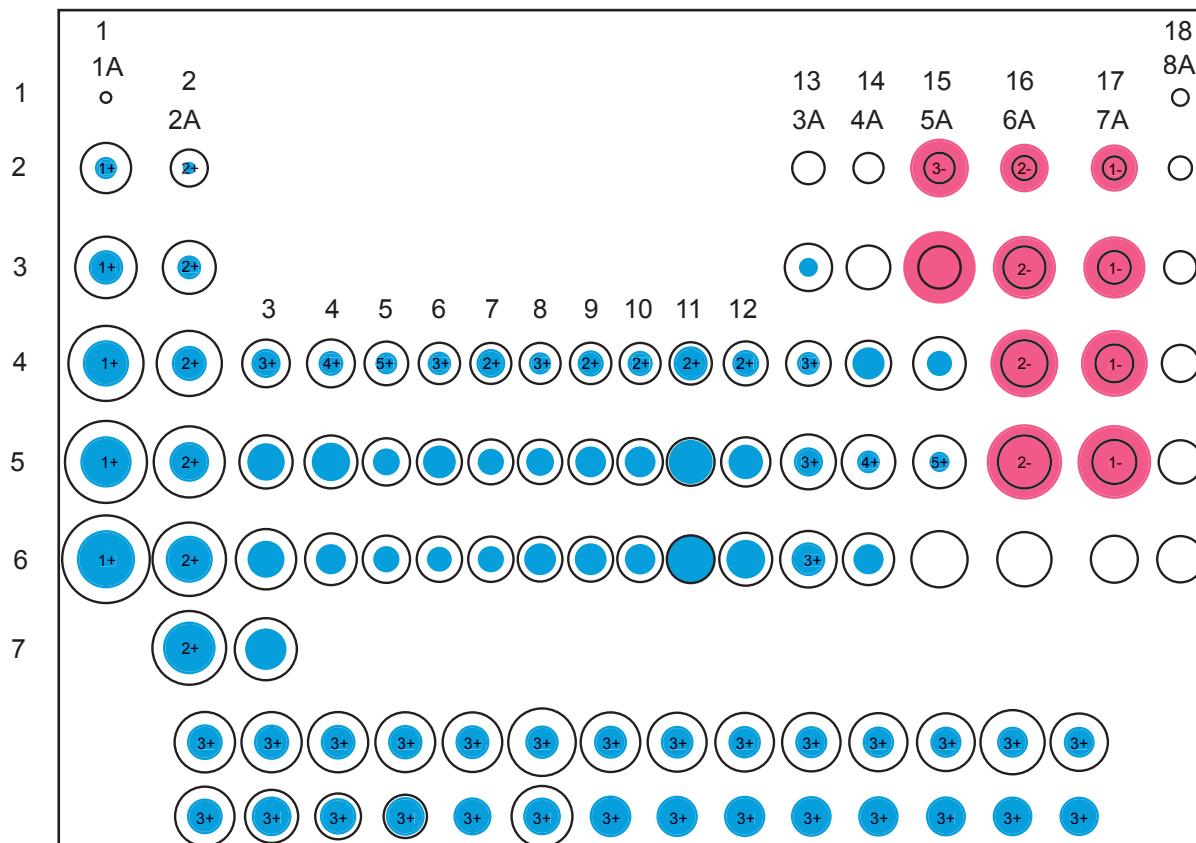





70

Attractive Mode

There is a link on our website to another site which offers explanations of several other forms of modern molecular study techniques. Visit at least one of these sites, study the material and write an explanation of the process. Preferably draw it.

CHEMICAL BONDING



 Neutral Atom
 Positive Ion
 Negative Ion

by
 DR. STEPHEN THOMPSON
 MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

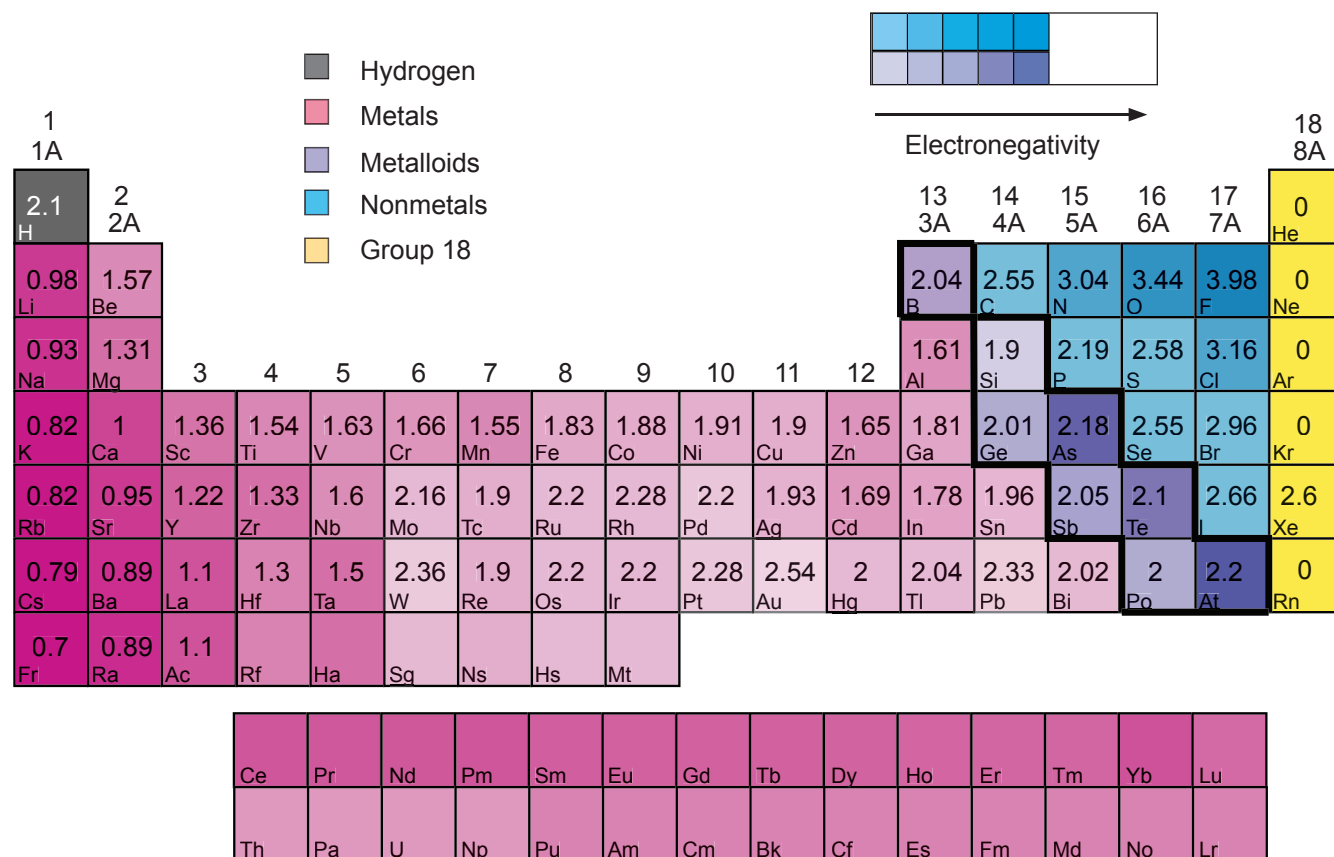
CHEMICAL BONDING

CONTENTS

2	Electronegativity
3	Road Map
4	Types Of Bonding
5	Properties Controlled By Chemical Bond
6	Polar Bonds
7	Metallic Bonding
8	Intermolecular Forces
9	Ions: Counting Electrons And Protons
10	Ionic And Atomic Radii
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12	Lithium Fluoride
13	Crystal Packing
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15	Crystal Packing
16	Covalent H ₂
17	Quantization
18	Bond Length And Strength
19	Strong And Weak Bonds
20	Strong And Weak Bonds
21	Covalent To Metallic
22	Electron Delocalization

CHEMICAL BONDING

ELECTRONEGATIVITY



Electronegativity is the ability of an atom to attract shared electrons to itself. It is largely the difference between the electronegativities of two atoms which determines what kind of bond is formed between them.

What is the most electronegative element?

What is the least electronegative element (aside from the noble gases)?

What is the range of electronegativity for the metals? Metalloids? Nonmetals?

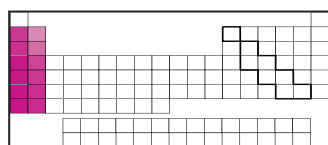
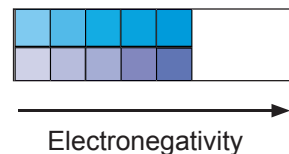
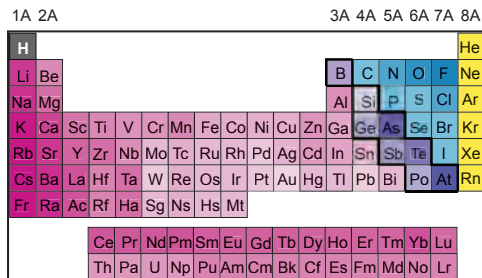
Why is the electronegativity of the noble gases listed as zero?

For an electron shared between hydrogen and chlorine, would you expect the electron to be closer to the hydrogen or the chlorine?

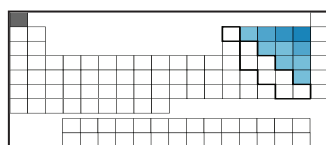
CHEMICAL BONDING

ROAD MAP

- Hydrogen
- Metals
- Metalloids
- Nonmetals
- Group 18



Groups 1 and 2 Metals

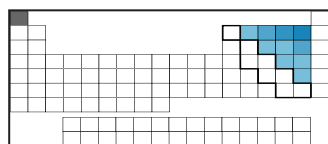


NonMetals and H

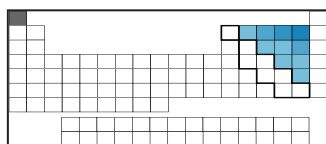
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Ionic Bonding



NonMetals and H

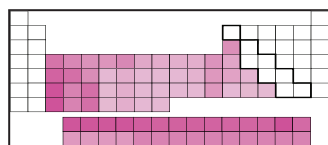


NonMetals and H

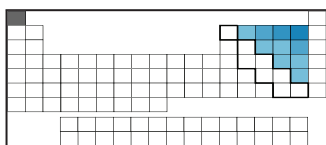
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Covalent Bonding



Other Metals

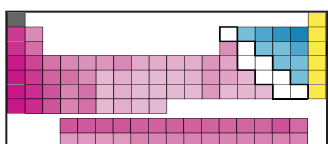


NonMetals and H

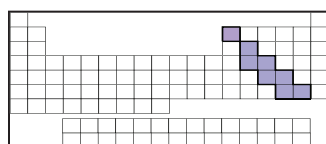
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Polar Bonding



Non Metalloids

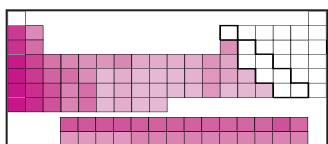


Metalloids

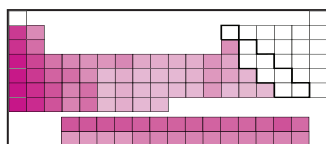
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Polar Bonding



Metals



Metals

+

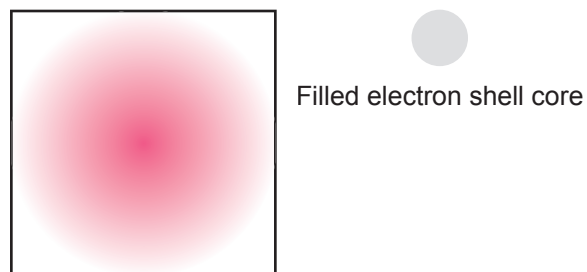


Metallic Bonding

CHEMICAL BONDING

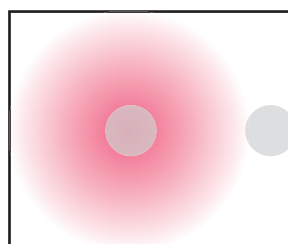
TYPES OF BONDING

The different types of chemical bonding are determined by how the valence electrons are shared among the bonded atoms.



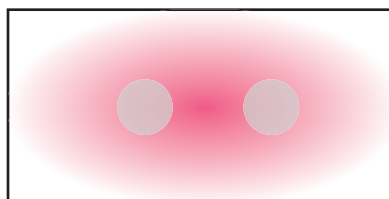
Valence Electron Cloud

In **IONIC BONDING** the valence electrons are completely transferred from one atom to the other atom. Ionic bonds occur between metals and nonmetals when there is a large difference in electronegativity.



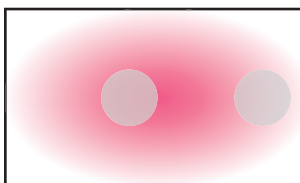
Ionic Bonding

In **COVALENT BONDING** the valence electrons are shared as pairs between the bonded atoms. Pure covalent bonding only occurs when two nonmetal atoms of the same kind bind to each other. When two different nonmetal atoms are bonded or a nonmetal and a metal are bonded, then the bond is a mixture of covalent and ionic bonding called polar covalent bonding.



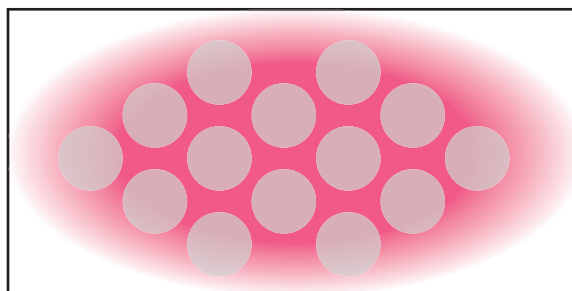
Covalent Bonding

In **POLAR BONDING** the electrons are shared but NOT equally. Many compounds have the characteristics of BOTH ionic and covalent bonding. Electronegativity differences determine the balance of character.



Polar Bonding

In **METALLIC BONDING** the valence electrons are shared among all of the atoms of the substance. Metallic bonding occurs when metals bond to either themselves or mixed with other metals in alloys.



Metallic Bonding

Using the periodic table of electronegativities from the last page, write down examples of atom pairs which you would expect to form covalent bonds, polar covalent bonds and ionic bonds.

CHEMICAL BONDING

PROPERTIES CONTROLLED BY CHEMICAL BOND

Chemical bonding determines the physical properties of substances. These properties are listed below for covalent, ionic and metallic bonding.

Covalent

Gas, liquid, or a soft solid.

Low melting point and low boiling point.

Insoluble in H₂O

Soluble in nonpolar solvents.

Nonconductor of heat and electricity.

Nonlustrous

Using the list of properties on the left, try to assign as many of the common substances in your environment to one of the types of bonding.

List and describe some substances which do not seem to fit into any of the three types of bonding.

Ionic

Crystalline solid.

Very high melting point.

Soluble in H₂O.

Insoluble in nonpolar solvents.

Nonconductor of heat and electricity.

Conducts electricity in aqueous solutions.

Examples: NaCl, CaCO₃

Metallic

Malleable solid.

High melting point and boiling point.

Insoluble in H₂O.

Insoluble in nonpolar solvents.

Conducts heat and electricity.

Lustrous

Examples: gold, copper

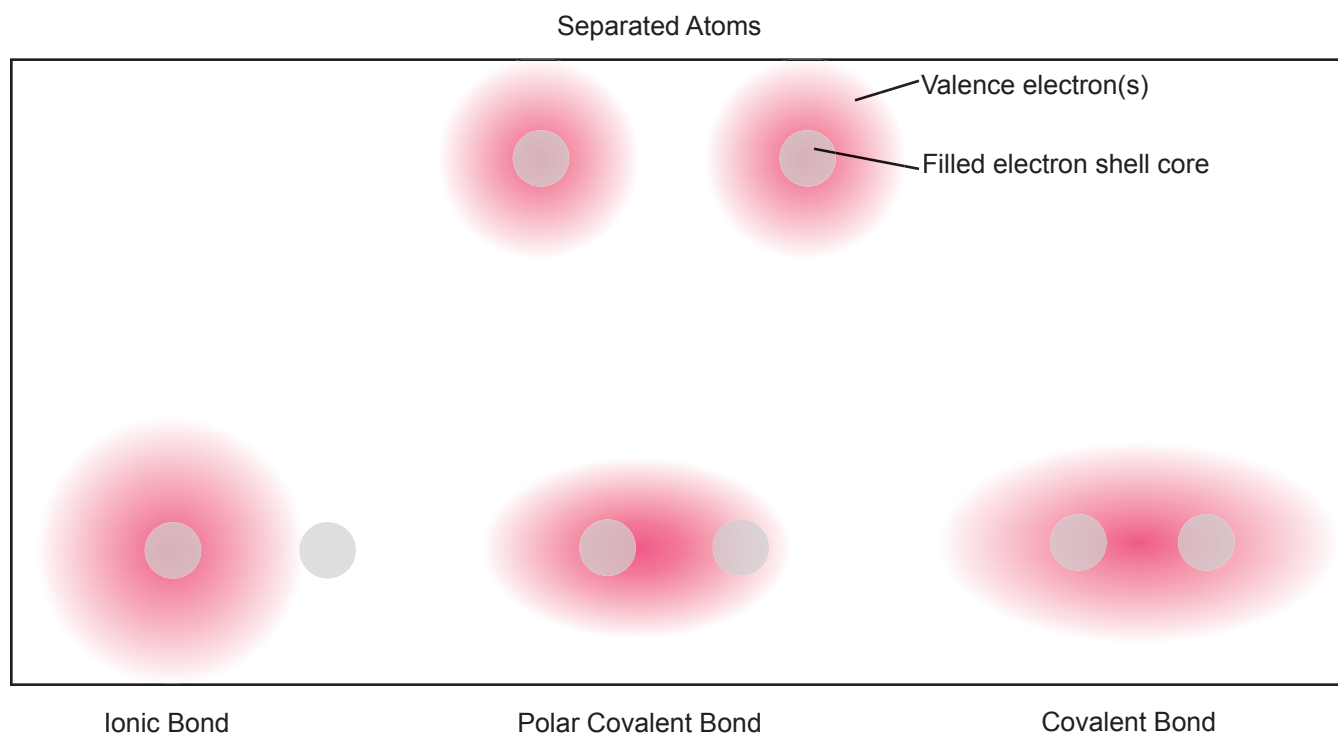
CHEMICAL BONDING

POLAR BONDS

Ionic and covalent bonds are two ideal types.

Many bonds share characteristics of both ionic and covalent bonding. They are called polar covalent bonds and they tend to occur between atoms of moderately different electronegativities.

In polar covalent bonds the electrons belong predominantly to one type of atom while they are still partially shared by the other type, as illustrated in the following pictures of the valence electron densities.



In the picture above, the separated atoms look alike. If, in fact, they are the same kind of atom, which of the three bonds shown is possible? Why only that one? What other type of bonding is possible between identical atoms?

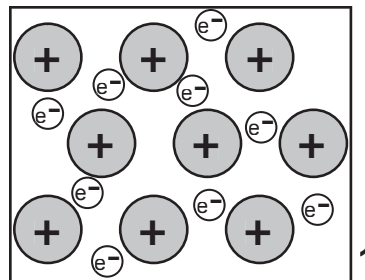
Using the chart of electronegativities, arrange the following compounds in an order from most ionic to most covalent:
 Al_2O_3 , CaCl_2 , NaF , O_2 , NaCl ,

CHEMICAL BONDING

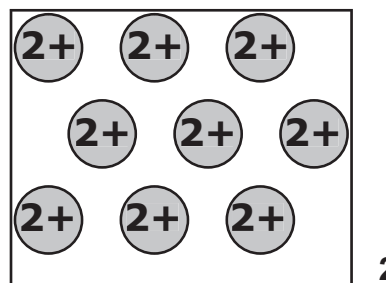
METALLIC BONDING

'ELECTRON SEA' MODEL FOR METALS

Metals are formed from elements on the left hand side of the periodic table. Having generally low electronegativity they tend to lose their valence electrons easily. When we have a macroscopic collection of the same or similar type of metallic atoms, the valence electrons are detached from the atoms but not held by any of the other atoms. In other words, these valence electrons are free from any particular atom and are only held collectively by the entire assemblage of atoms. In a metal the ion cores are held more or less at fixed places in an ordered, or crystal, lattice. The valence electrons are free to move about under applied stimulation, such as electric fields or heat.



Picture 1 presents a regular arrangement of the ion cores for a metal with a single valence electron per atom as well as a snapshot of the location of the freely moving valence electrons.



Picture 2 shows a collection of ion cores for a metal with two valence electrons. Draw in the valence electrons. (Little circles are good enough.)
HINT: Metals are neutral in charge.

What is the origin of electrical and thermal conductivity in sodium metal?

Why do metals exhibit a wide range of melting points and hardness?

CHEMICAL BONDING

INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the stability of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

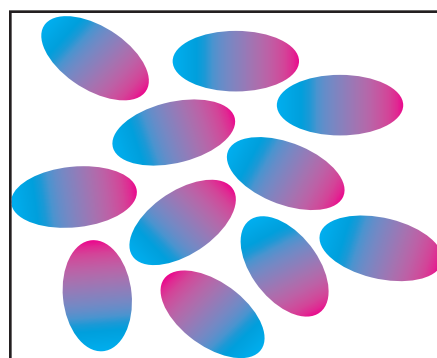
DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?

Why is it more important in liquids than in gases?

Can homonuclear diatomic molecules such as H_2 , O_2 and N_2 have dipole-dipole forces?

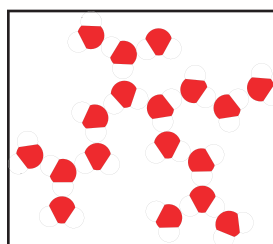


DIPOLE-DIPOLE INTERACTION

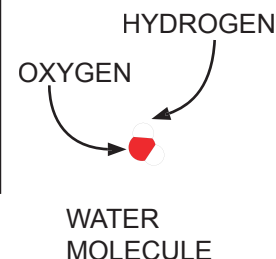
HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom.

Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.



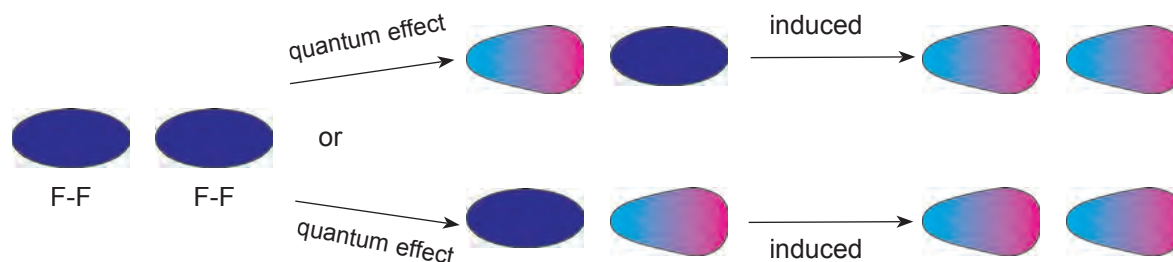
HYDROGEN BONDING



WATER MOLECULE

LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecule so that the two molecules have opposite charges on their near sides and attract each other.



CHEMICAL BONDING

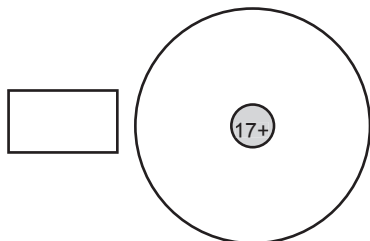
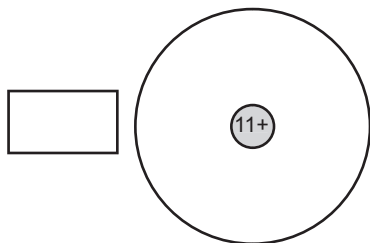
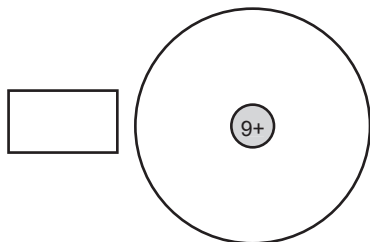
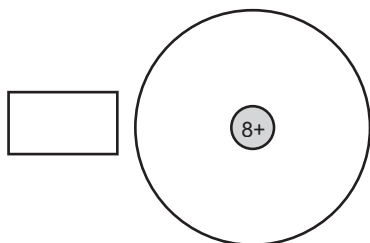
IONS: COUNTING ELECTRONS AND PROTONS

NEUTRAL ATOMS

Neutral atoms have the same number of electrons as protons. In the picture below, the nuclear charge is represented by the gray circle marked 3+, for the 3 protons in the nucleus of lithium. Electrons are marked as horizontal dashes, one for each electron.

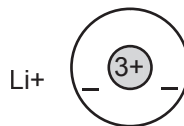


In the pictures below, draw in the number of electrons required to make the atom neutral and write the element symbol in the box to the left of the atom.

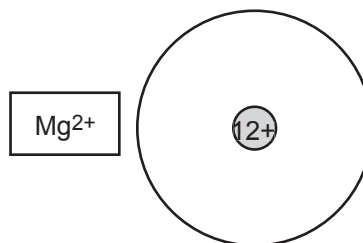
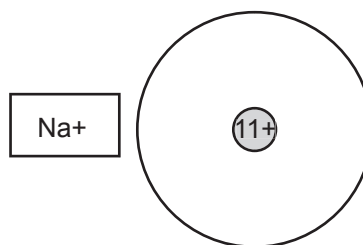


POSITIVE IONS

Positive ions have more protons than electrons. Since the number of protons an atom has is fixed in ordinary chemical reactions, positive ions are produced by removing electrons from the atoms.



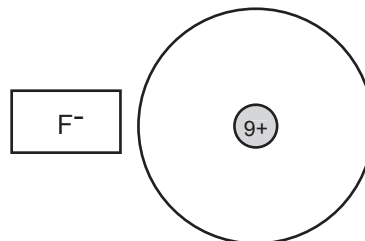
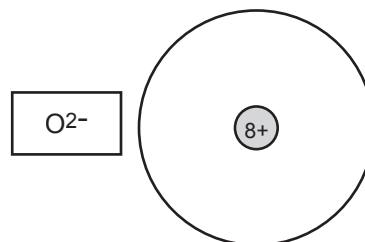
In the pictures below draw in the number of electrons needed to make the ion named in the box.



NEGATIVE IONS

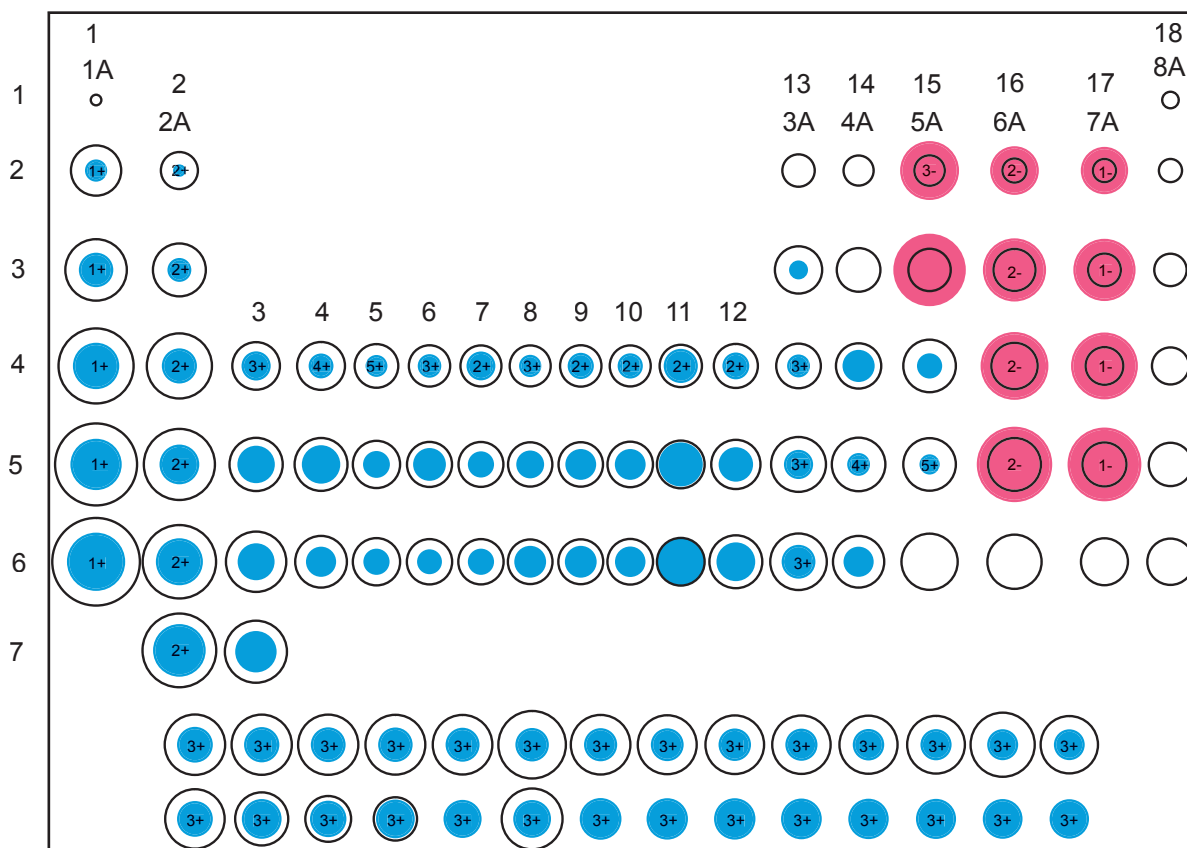
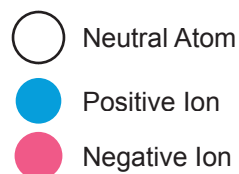
Negative ions have more electrons than protons. Since the number of protons is unchanged from the neutral atom, negative ions are formed by the addition of electrons.

In the pictures below draw in the number of electrons needed to make the ion named in the box.



CHEMICAL BONDING

ATOMIC AND IONIC RADII



In this version of the periodic table the relative sizes of both neutral atoms and of their most common ions are shown, as well as the charges on their ions. The atoms are shown as black outline circles and the ionic diameters are colored blue for positive ions and red for negative ions.

Why are the positive ions smaller than their neutral atoms while the negative ions are larger than the neutral atoms?

Why do both ions and atoms tend to grow larger as we go down the periodic table?

What is the smallest atom? What atom has the smallest ion (too small to show on the table)? Find the largest atom and identify it on a standard periodic table.

What kind of ions do atoms with large electronegativities tend to form?

What makes the atoms and ions in the middle of periods 4, 5 and 6 so small? What makes the samarium atom so large?

Identify the two kinds of atom which appear about the same size as their ion and explain why this is so.

Why are the antimony and beryllium ions so small? Differentiate between the causes.

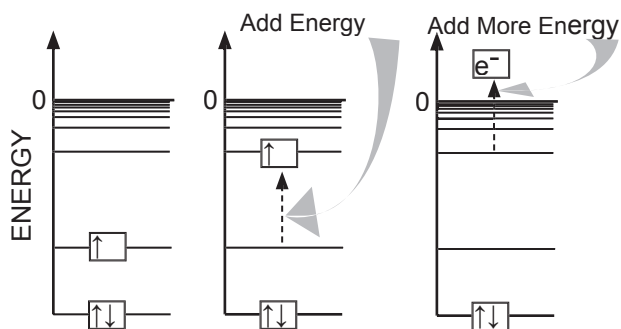
Why are the Lanthanide ions of such similar size?

How might you use the chart of atomic and ionic radii to explain the strengths of ionic bonding between various ions?

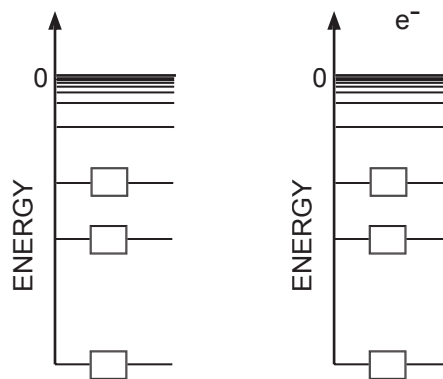
Compare the ionic and atomic radii table above with the chart of electronegativities and attempt to explain as many aspects of the sizes of atoms and ions in terms of electronegativity as possible.

CHEMICAL BONDING

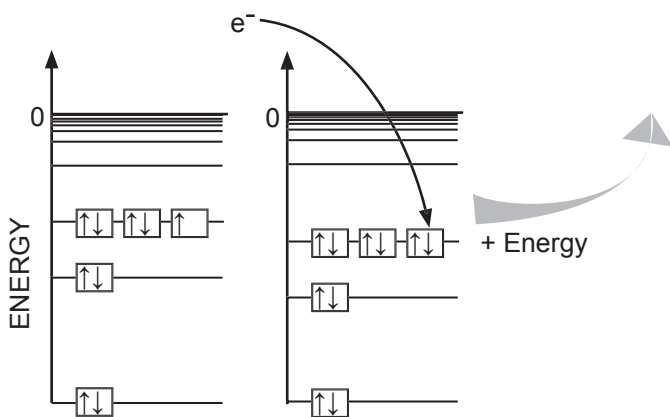
IONS AND ENERGY



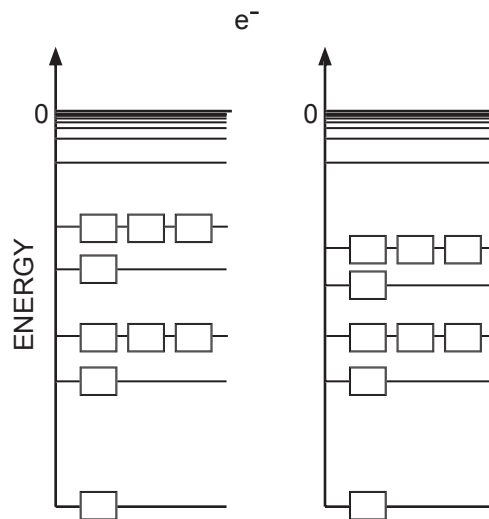
The diagrams above show the ground state of the lithium atom, followed by an excited state, followed by the lithium ion with the free electron. What is the charge of the lithium ion in the right hand drawing?



In the diagrams above, draw in the electrons as arrows which occupy the ground state orbitals of the sodium atom in the left hand picture. In the right hand picture draw in the orbitals and electrons of the sodium ion.



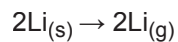
The diagrams above show the ionization of fluorine. What is the charge of the fluoride ion?



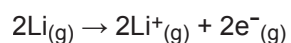
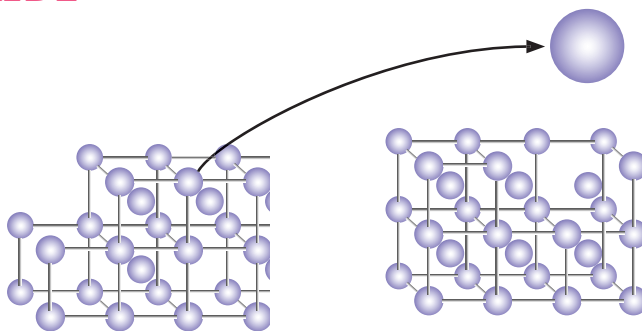
In the diagrams above, draw in the electrons (arrows) for the chlorine atom on the left and for the chloride ion on the right. What is the charge of the chloride ion?

CHEMICAL BONDING

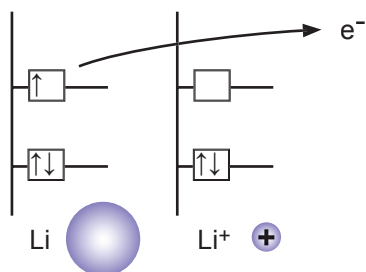
LITHIUM FLUORIDE



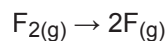
It requires 155 kJ/mol to separate lithium atoms from their body centered cubic crystal structure.



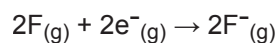
It requires 520 kJ/mol to ionize lithium atoms.



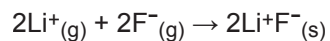
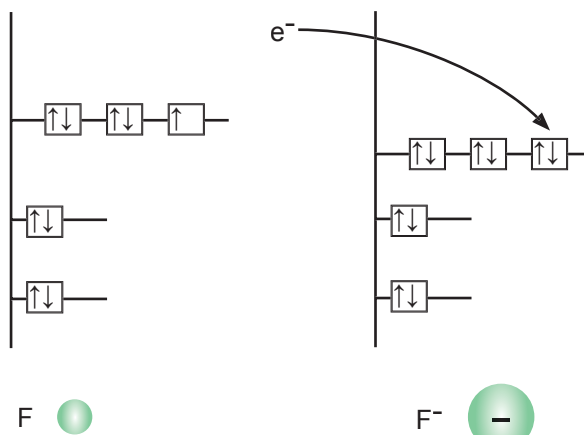
Add the energies which are associated with the process of making lithium fluoride crystal, lithium crystal, and difluoride molecules. Is the net reaction endothermic or exothermic?



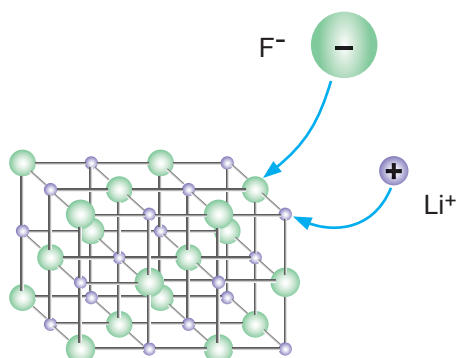
It requires 80 kJ/mol to dissociate the difluoride molecule.



Ionization of the fluorine atom gives off 328 kJ/mol of energy.

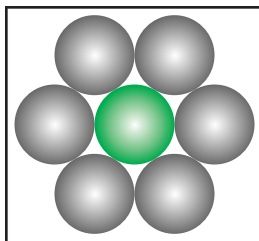


Combining the lithium and fluoride ions into their crystal gives off 1030 kJ/mol of energy.



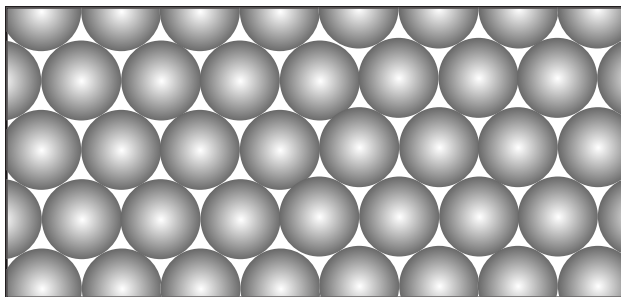
CHEMICAL BONDING

CRYSTAL PACKING



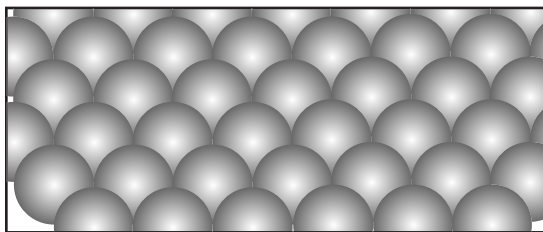
The picture at left shows seven spheres packed as close together as possible in the plane. This is called close packing. How many gray spheres touch the green sphere?

1

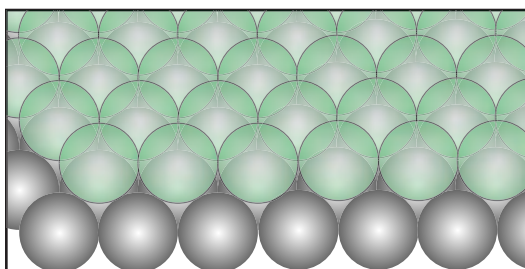


2

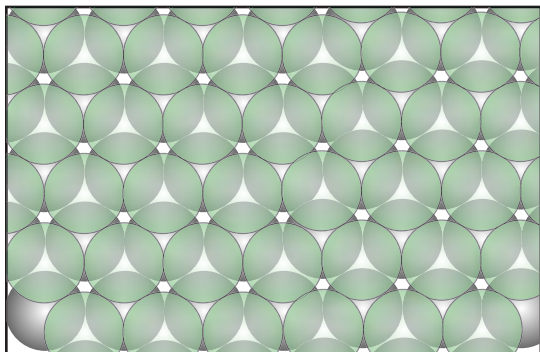
The picture above shows how close packing can fill, or *tile*, the plane. Notice the little triangles (with curved sides) that lie in between the spheres. Some of them point up and some of them point down. Compare the number of each kind of triangle.



3



4



5



Using circles, sketch in the box above another way to tile the plane.

Picture 3 is simply picture 2 looked at through an angle.

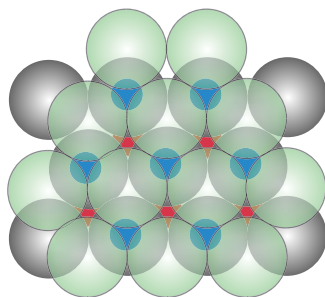
Picture 4 shows the spheres of picture 3 topped by another plane of spheres set to fit as closely as possible into the lower plane. For clarity, the second plane is semitransparent green with a black outline.

Picture 5 shows the same planes of atoms as in picture 4 but viewed from above. What proportion of the triangular spaces between the spheres of the lower (grey) plane are occupied by the second (green) plane of spheres?

CHEMICAL BONDING

CRYSTAL PACKING

Picture 6 shows the same two layers as picture 5 but two different sets of spaces between the green spheres of layer 2 are marked either red or blue. We can construct a third layer by placing spheres either in the blue spaces or the red spaces.



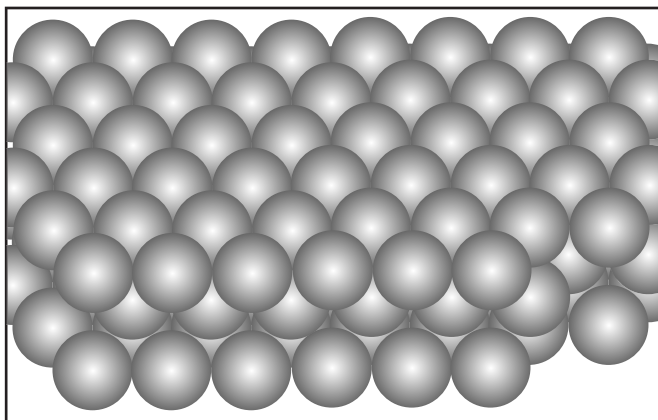
6

Notice that the blue spaces lie directly above the grey spheres of layer 1. If we use these spaces for layer 3 then we get a two level repeating structure. If we name layer 1 A and Name layer 2 B then we can describe the structure as ABABAB....

This is called hexagonal close packing or hcp for short.

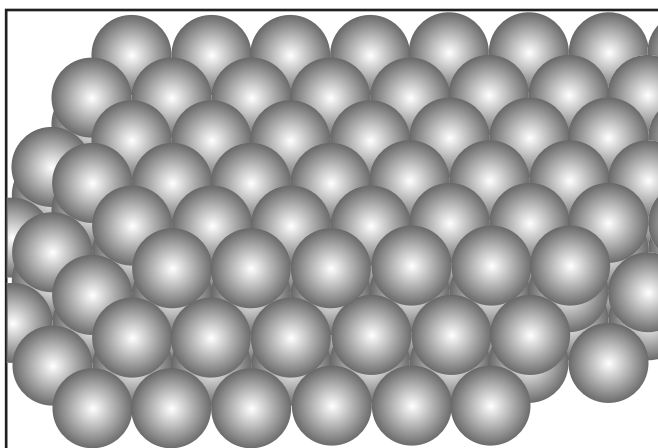
Alternatively we can place the third layer of spheres in the red spaces. Then the third layer is differently located than either of the first two and is named C. We can describe this structure as ABCABC....

It is called cubic close packing or ccp.



7

hcp



8

ccp

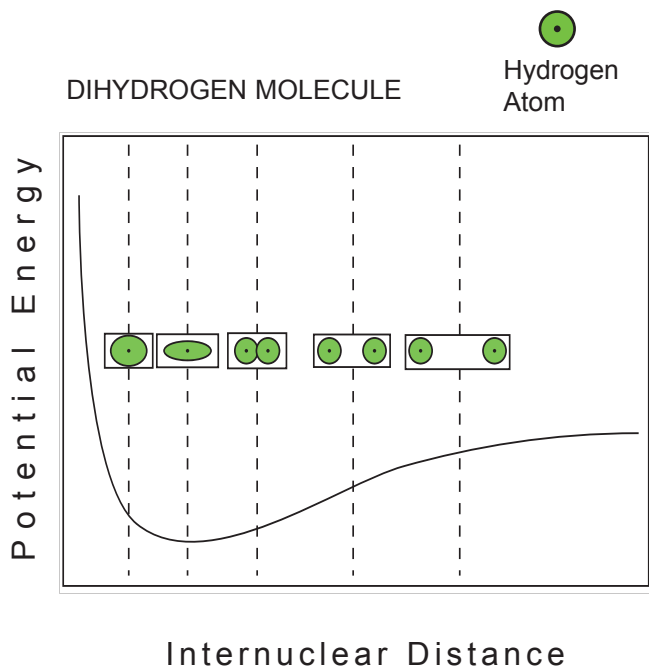
Why can we not use both the red and the blue spaces for placing the layer 3 spheres?

Using colored pencils, pens or crayons, draw circles representing the hcp structure in the box above.

Using colored pencils, pens or crayons, draw circles representing the ccp structure in the box above.

CHEMICAL BONDING

COVALENT H₂



Confining electrons makes them 'dance'. This is part of quantum theory. The tighter electrons are squeezed the harder they dance. Dancing electrons have kinetic energy. But electrons will slow down if they can. When they have more room they can slow down, which means they have less kinetic energy.

In a hydrogen molecule the electrons can move through the space of two atoms instead of one, which means that they have more room and thus can dance slower and have less kinetic energy. (Picture 1)

There are also electric attractions and repulsions between the particles in the molecule. Picture 2 shows the repulsions of like charges as colored arrows and the attractions of opposite charges as black arrows.

The additive combination of the electric and kinetic energy effects gives the covalent bond for hydrogen.

Suppose you have two well separated hydrogen atoms and begin moving them closer together. From the picture above you can see that the energy of the system will decline as they are being moved together until at some distance the system will have a minimum energy.

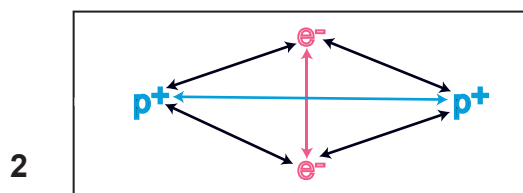
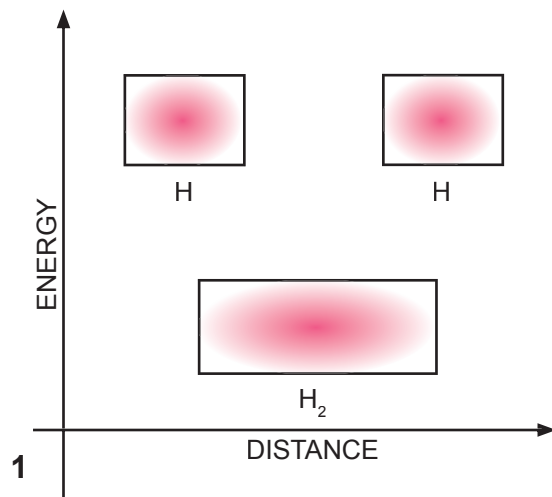
What causes the energy to rise as the atoms are moved closer than the minimum energy?

A dihydrogen molecule consists of two hydrogen nuclei (protons) held a fixed distance apart and surrounded by a probability density cloud of two electrons.

As you can see from the picture above, the separation is that at which the system is in the state of lowest energy. But what are the factors which cause this to be a low energy state?

There are primarily two factors. They are quantum and electrostatic effects.

Quantum theory produces two effects, lowered energy and discrete energy levels.

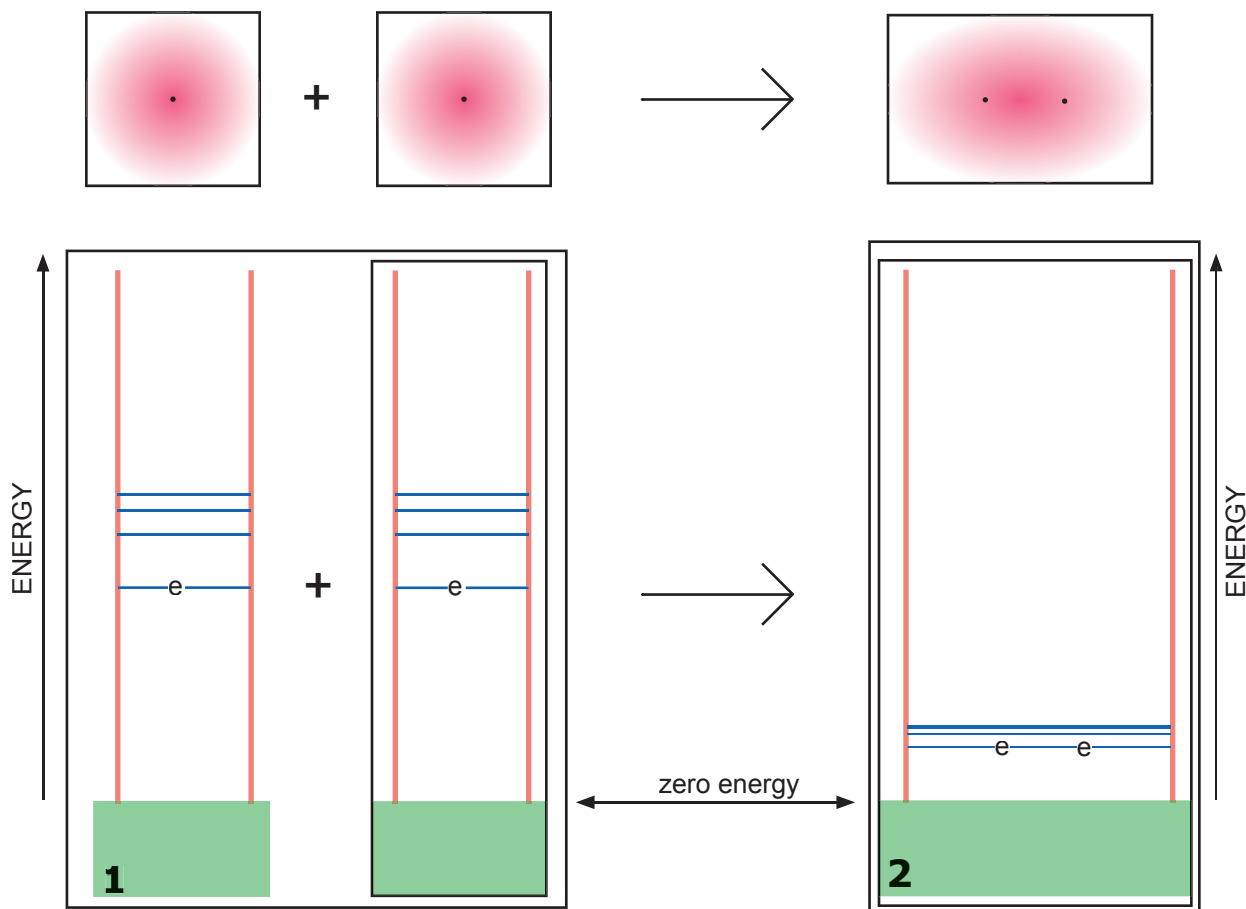


CHEMICAL BONDING

QUANTIZATION

Just below we show two hydrogen atoms and their combination as H_2 on the right.

The red electron cloud represents the probable location of the electrons. Notice that the space for electrons is larger in the H_2 molecule than it is in the separated hydrogen atoms.



One of the basic principles of quantum mechanics is that whenever anything is confined in a finite space, it can only occupy one of a discrete set of energy levels. It is also the case that when the space is made larger the energy states are lower.

In picture 1 the blue lines represent the energy states available for a particle confined between the orange walls.

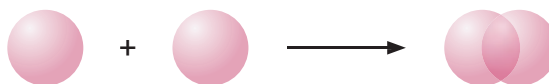
In picture 2 the blue lines show how the energy states are lower when the particles are given more space.

Which picture, number 1 or number 2, has the lowest total energy?

If picture 1 represents the energy states of two separate hydrogen atoms, then what could picture 2 represent?

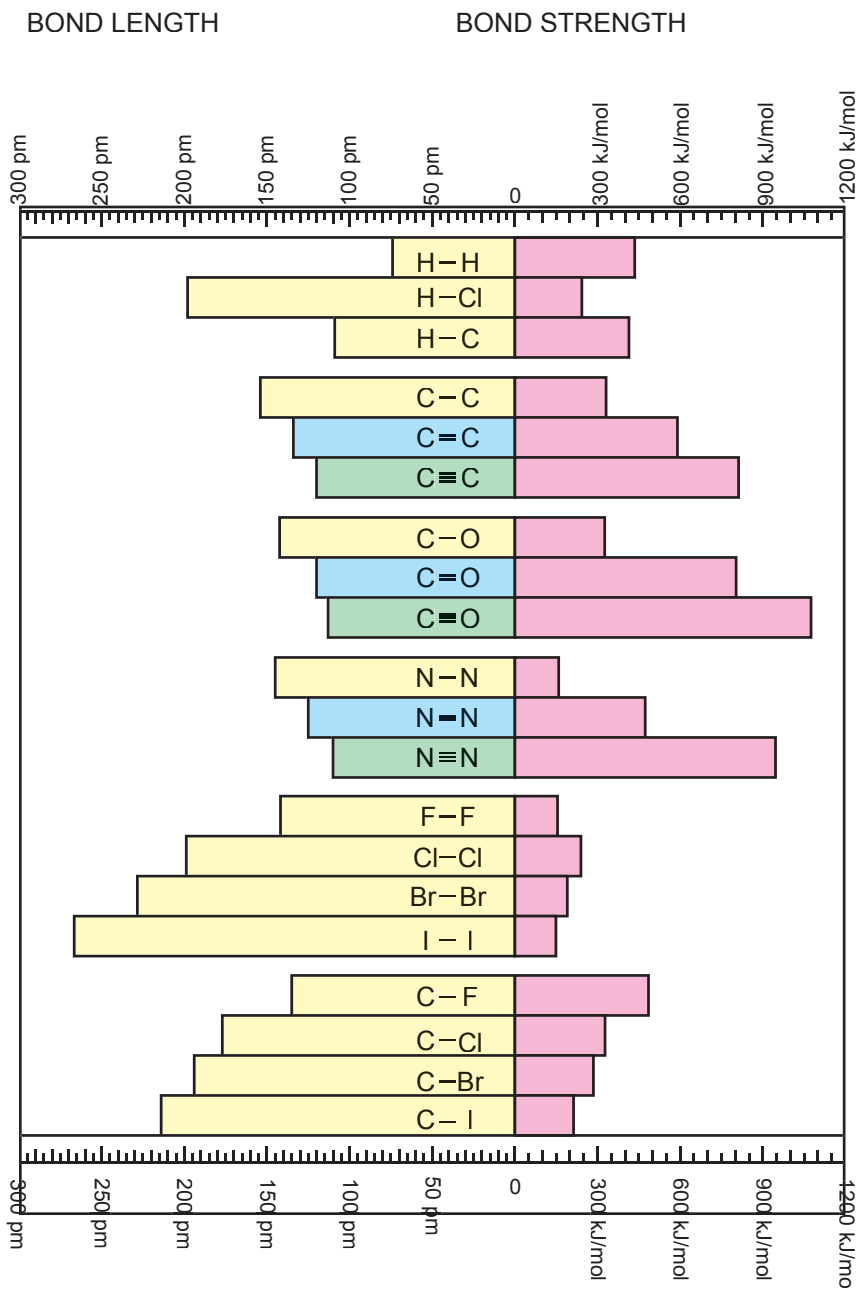
These pictures do not necessarily show that if you move two hydrogen atoms close together they will bond to form a hydrogen molecule but they do show that the hydrogen molecule will be at a lower energy state than the combined energies of the separate atoms and that you would need to add energy to the molecule to get the atoms separated and that therefore the molecule will hold together until you add that energy.

Now that we know why covalent bonding occurs we will use simplified pictures known as overlapping orbitals to describe more complicated molecules. Just to the right we show this model for hydrogen.



CHEMICAL BONDING

BOND LENGTH AND STRENGTH

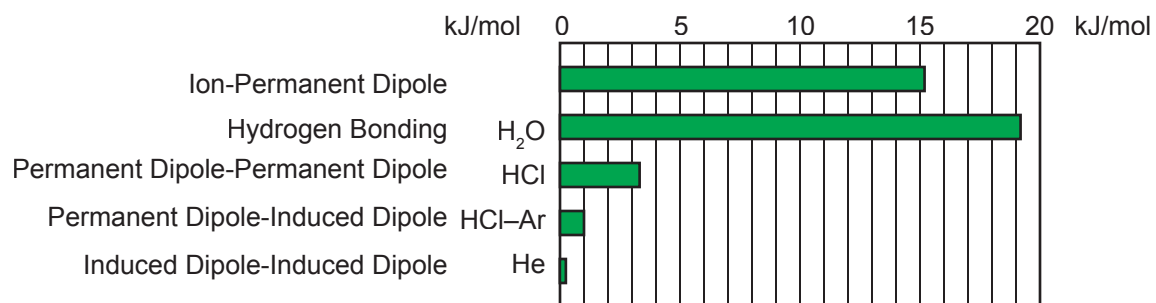
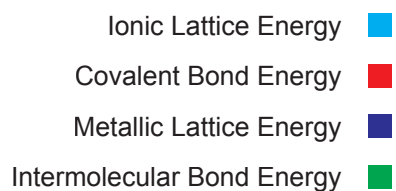
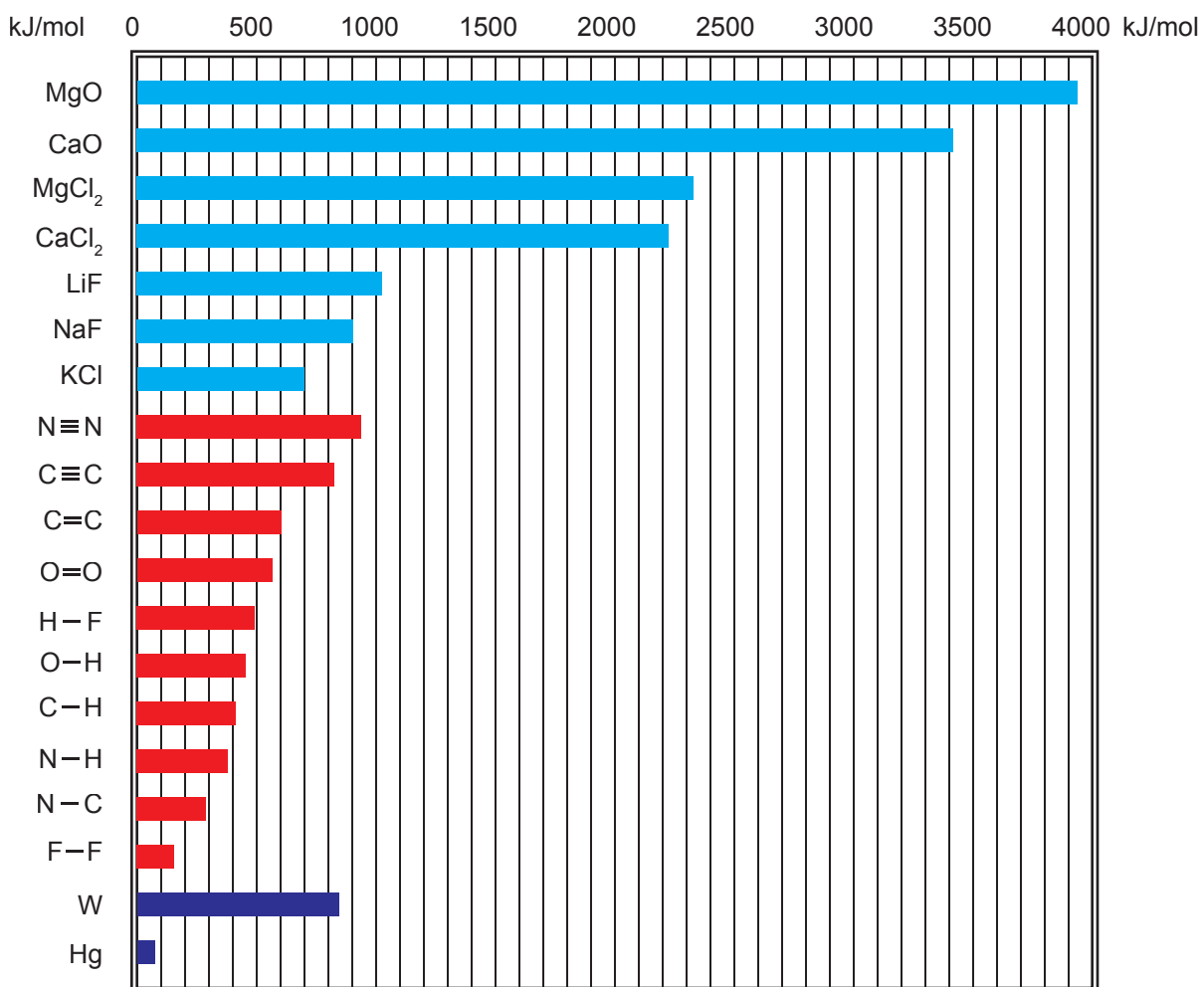


Which are the longest and shortest bonds shown?
Which are the strongest and weakest bonds shown?

In each group of related compounds, what correlation do you observe between bond length and bond strength?
What are some exceptions?

CHEMICAL BONDING

STRONG AND WEAK BONDS



CHEMICAL BONDING

STRONG AND WEAK BONDS

STRONG BONDS

A. Ionic

Much of the strength of ionic bonding comes about when the ions are packed together in crystal lattices, so that each ion is held in an attractive field with several neighbors of the opposite charge. These binding energies can range up to several thousand kilojoules per mole.

B. Covalent

Covalent bonds are also strong, ranging up to 940 kilojoules per mole for triple bond N_2 .

C. Metallic

Metals are also strongly bonded, as you can deduce from their strength and hardness, although the liquid metal mercury is an exception.

WEAK BONDS

Weak bonds, often called intermolecular forces, are several orders of magnitude weaker than strong bonds described above. One of the relatively stronger of the weak bonds is hydrogen bonding with energies ranging from two to ten kilojoules per mole.

D. Ion-Permanent Dipole

These would include salts dissolved in a polar substance, e.g., NaCl dissolved in water.

E. Permanent Dipole - Permanent Dipole

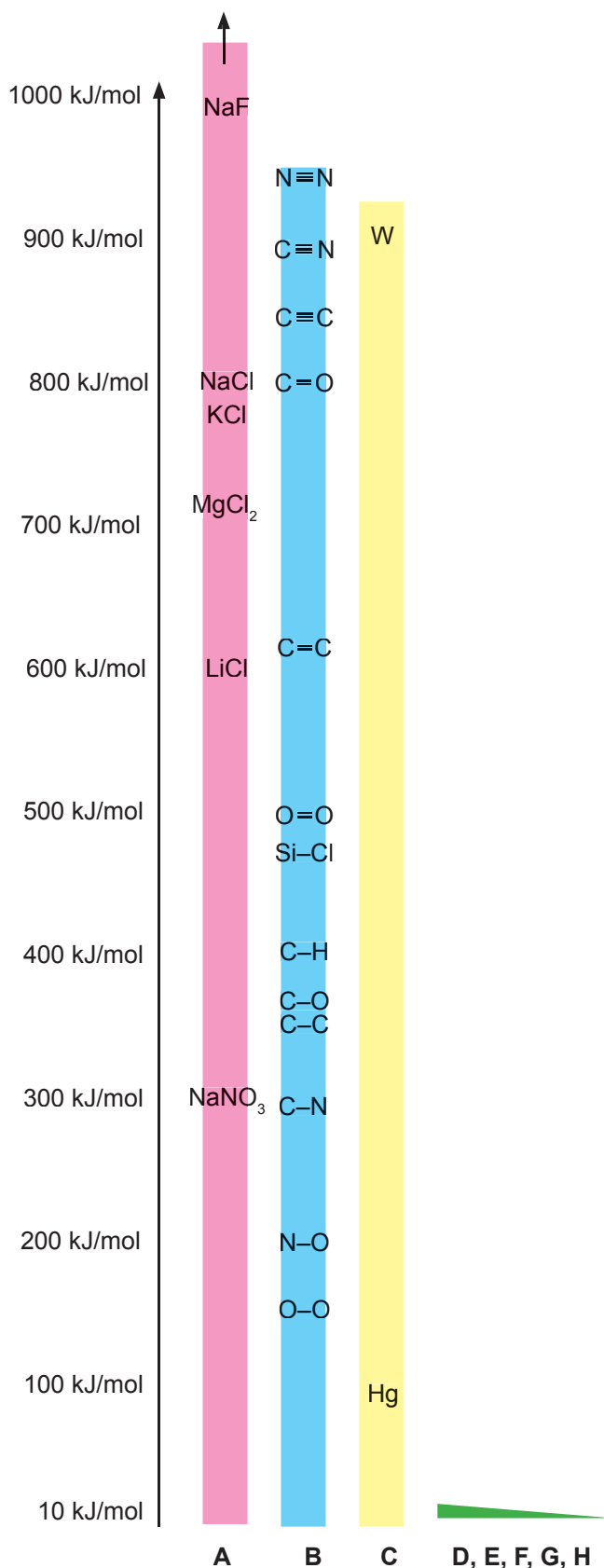
This class of bond includes hydrogen bonding.

F. Ion - Induced Dipole

G. Permanent Dipole - Induced Dipole

H. Induced Dipole - Induced Dipole

These are also known as van der Waals forces or as London dispersion forces. They are quite weak but they always exist between nearby molecules and they are always attractive.



CHEMICAL BONDING

COVALENT TO METALLIC

While we have a simple gradation between ionic and covalent compounds, we are also able to find a path of bonding types which goes from covalent to metallic bonding. This is not a simple gradation but rather detours through the network covalent bonds, some of which are semiconductors.

Our essential procedure in tracing the connections between these types of bonding is to follow the valence electrons.

In covalent bonding the bonding pairs of electrons are held in distinct orbitals, even though their physical location is, as always, given by a continuous probability density.

Several atoms, both like and unlike, can be connected pair-wise together by covalent bonds and large molecules, particularly organic, can be constructed this way. However, we also begin to see phenomena other than pair wise bonding between definite atoms appearing. An example is ozone, O_3 , a linear molecule in which each of the outer atoms is bonded to the central atom equally, but with both of them sharing three bonds between them. In this case the individual electrons cannot be assigned to a definite bond and are said to be delocalized.

There are some types of atoms, such as carbon and silicon, where covalent bonds form between unlimited numbers of the atoms. In the graphite form of carbon three of the bonding electrons of each carbon atom form covalent bonds between neighboring atoms to form a hexagonal planar structure, but the fourth bonding electron sticks out between planes. These bonds overlap and connect the planes together and they are also delocalized, which means that these electrons are free to move around under, say the pressure of an electric field and thus graphite is an electrical conductor. Finally, in metals, all of the valence electrons are held communally by the whole substance and are thus free to conduct electricity or heat.

There are also more extreme cases of delocalization than metals. These include superconductors and the new Bose-Einstein condensates.

Electrons can only be located in space with a probability density, but we can also locate electrons with regard to their situation with respect to other entities.

For example, there are free electrons which are not bound to any atom or molecule but are pushed about by electric and magnetic fields. On earth, they usually do not remain free very long but end up (at least for a while) in one of the following situations.

Describe the location, stability and energy level of an electron in each of the situations listed below.

An electron in an **atomic orbital**.

An electron in a **subshell**.

An electron in a **shell**.

A **valence** electron.

An electron in a filled **shell**.

An electron in an **atom**.

An electron in an **excited state**.

An electron in a **negative ion**.

An electron in a **positive ion**.

An electron in a **molecular orbital**.

A valence electron in a **metal**.

A valence electron in a **superconductor**.

An electron in a **Bose-Einstein condensate**.

CHEMICAL BONDING

ELECTRON DELOCALIZATION

Localized

Delocalized

1	2	3	4	5	6	7	8	9
Ionic CsF NaCl	Polar Covalent H ₂ O CO ₂ CO	Covalent O ₂	Molecular Orbitals O ₃ C ₆ H ₆	Semiconductors Si	Semi-metallic Graphite	Metals Gold	Superconductors K ₃ C ₆₀ at 19K	Bose-Einstein Rb at 10 ⁻⁸ K
Electrons are held by each atom in completed shells.	Bonding electron pairs cluster around the most electronegative atom(s).	Bonding electron pairs are shared equally by both atoms.	Some bonding electrons are held collectively inside the molecule.	A small proportion of the electrons are free to move about the lattice.	In graphite, valence electrons are free to move in two dimensions.	All valence electrons are free to move throughout the lattice.	All the valence electrons are free to move without resistance.	In a Bose-Einstein condensate all of the electrons become part of a single 'atom'.

1 Filled shells are shown in grey. Valence electron clouds are in red. Negative ions are outlined in red. Positive ions are outlined in blue.

2 When two atoms of moderately different electronegativity are bound, the binding electrons are shared unevenly, tending toward the more electronegative atom.

3 In a homonuclear diatomic molecule the binding electron pairs are shared evenly and symmetrically by both atoms.

4 In Benzene six of the bonding electrons are held collectively by the molecule as a whole. In the picture these are represented by the red cloud.

5 In a semiconductor, such as Silicon, a small minority of valence electrons are free to move about the lattice. The free electron is shown as the small red blur at right.

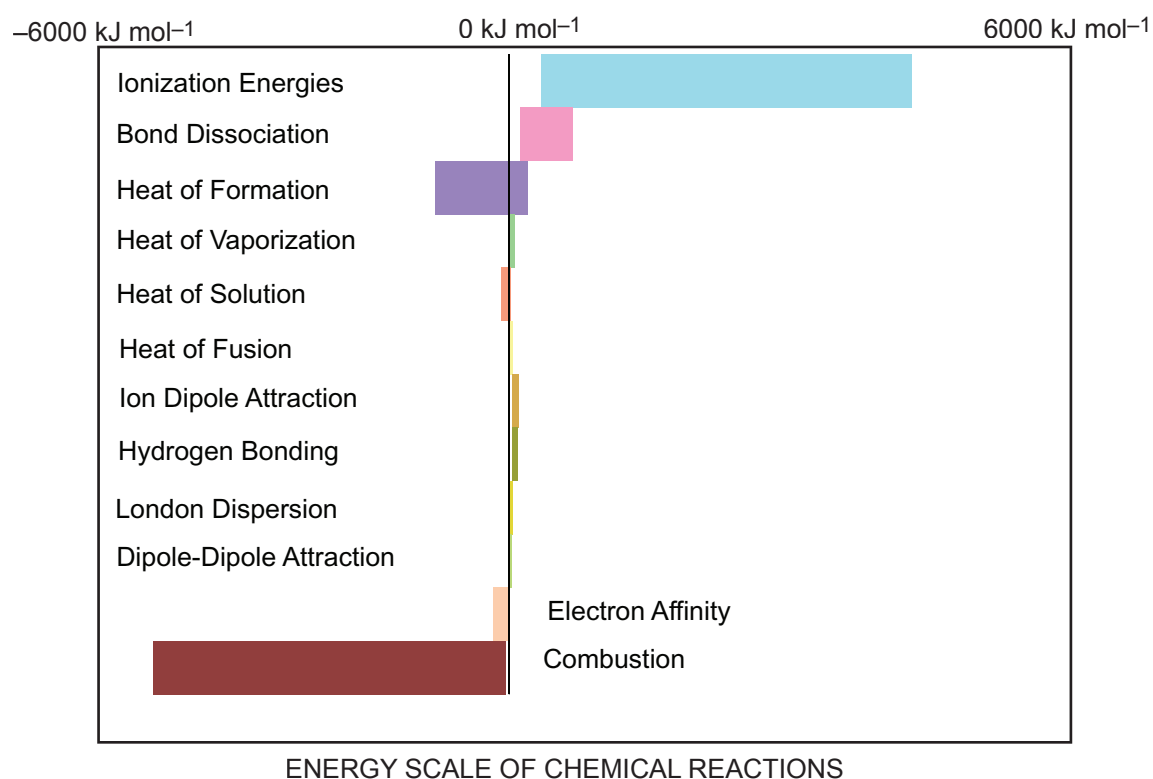
6 In graphite the carbon atoms are bound in hexagons that are arranged in sheets. The sheets are loosely bound to each other and the electrons between the sheets are free to move.

7 In the picture at right, the gray circles represent the core of filled shells while the red cloud is the set of valence or conducting electrons held in common by the metal. Compare and contrast with number nine.

8

9 In the picture at right, the small grey dots represent the separate nuclei. The red cloud represents all (not just the valence) electrons held in common by the substance, as if it were one atom.

CHEMICAL ENERGETICS



by
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MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

CHEMICAL ENERGETICS

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CHEMICAL ENERGETICS

SOME EXPERIMENTS

Suppose we place a drop of water in an uncovered petri dish and watch what happens.



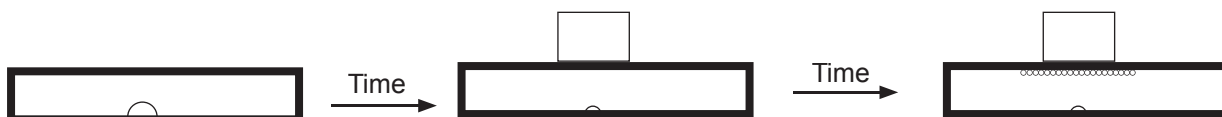
Now suppose we vary the experiment in a covered petri dish.



What is this process called?
 What is the reverse process called?
 Where have you observed it in daily life?
 What other effects have you noticed with the first process?

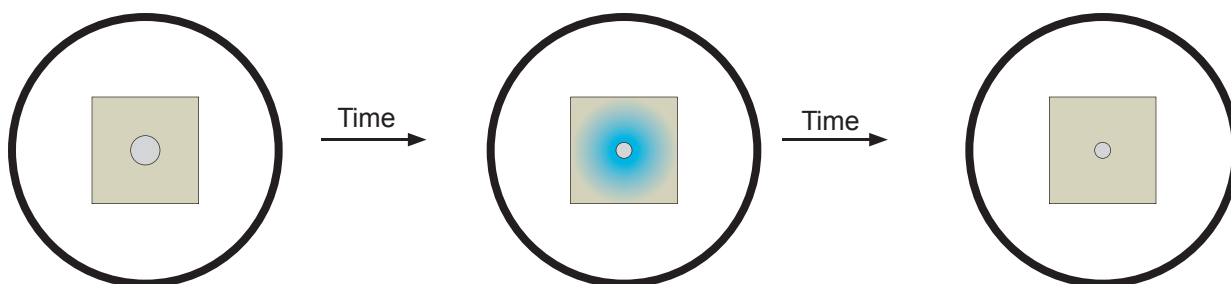
Try these experiments yourself. In the open petri dish experiment note how long it takes for the water drop to disappear. Try it with different size drops. Try it under different weather conditions.

Now we place a piece of ice on top of the petri dish and observe what happens.



The little circles hanging from the top of the petri dish represent a thin layer of water.

Now suppose we place a square of plastic enclosed liquid crystal inside of the petri dish and then drop the water on. This variety of liquid crystal has the property of changing color when it is cooled.

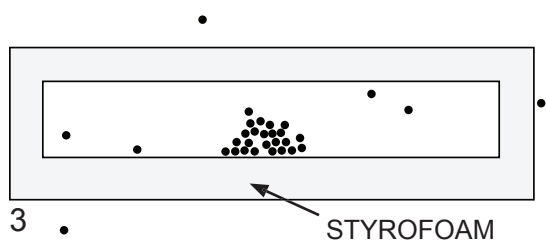
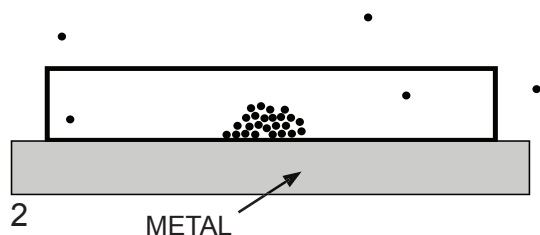
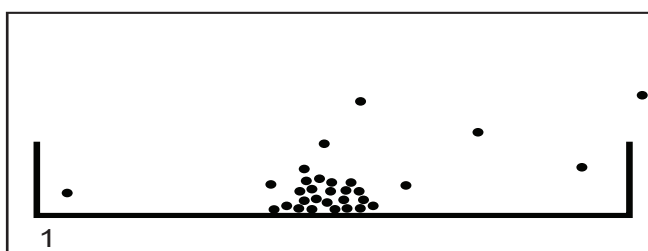


There are several questions we can ask about these experiments. Why do these things happen? How fast do they happen? Can we give a molecular explanation of these events?

CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

In thermochemistry, kinetics and thermodynamics we must always be clear about what it is we are talking about, experimenting with or calculating. So we make an essential distinction between what we call a **system** and everything else, which we call the **surroundings**. In chemistry we distinguish three kinds of systems. These are called **open**, **closed**, and **isolated** systems. An open system can exchange both matter and energy with its surroundings. A breathing person is an open system. A closed system can exchange energy but not matter with its surroundings. An isolated system can exchange neither matter nor energy with its surroundings.



In picture 1, draw a path around an open system which includes the petri dish.
 In picture 2, draw a path around a closed system which includes the petri dish.
 In picture 3, draw a path around an isolated system which includes the petrie dish.

For each of the pictures explain whther the system named is an open, closed or isolated system, explain your answer, giving details about the system, its surroundings, and the interaction, if any, between the system and its surroundings.



AIRPLANE



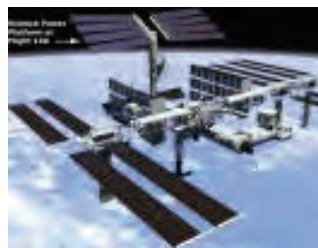
BIOSPHERE



CELLS



EARTH

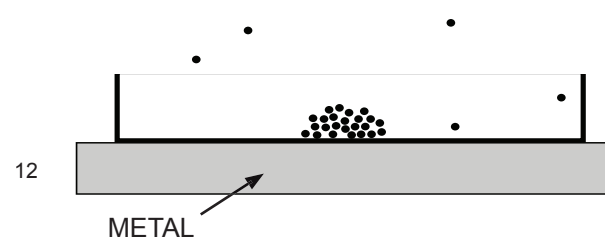
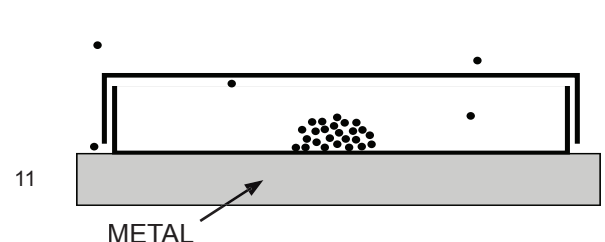
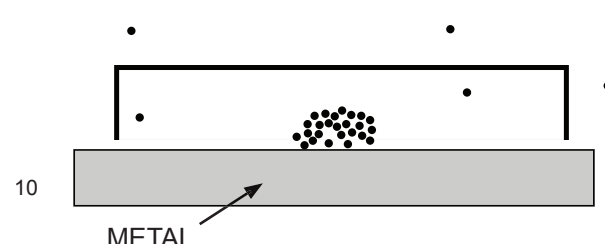
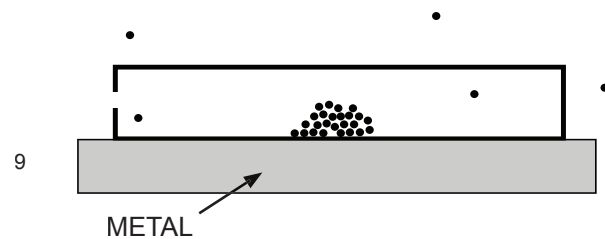
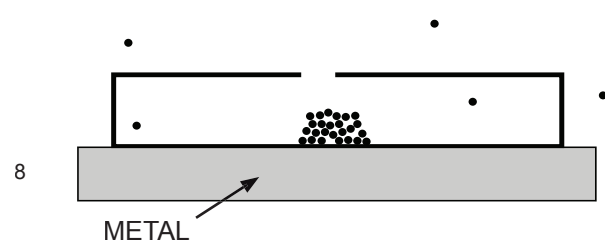
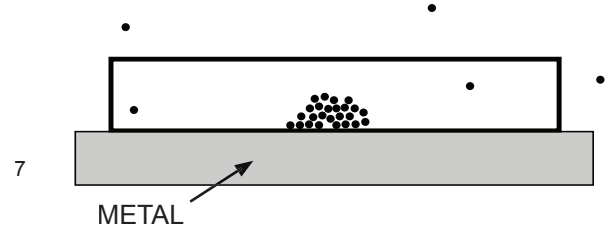
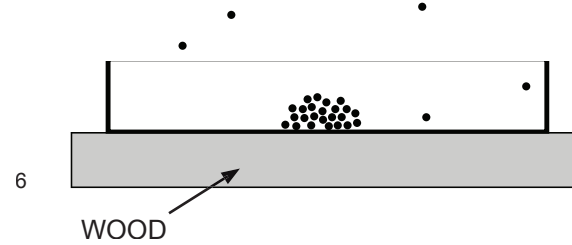
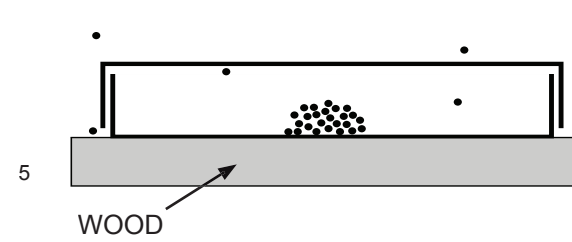
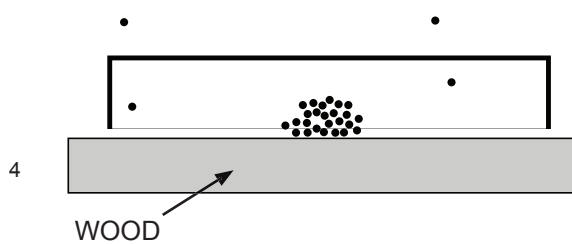
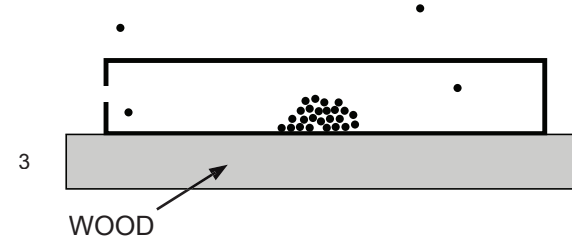
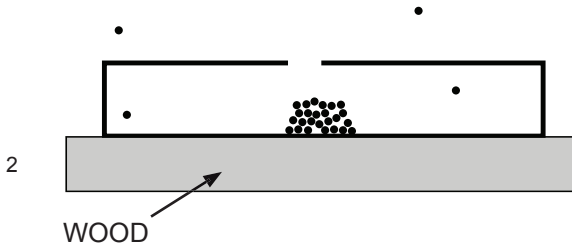
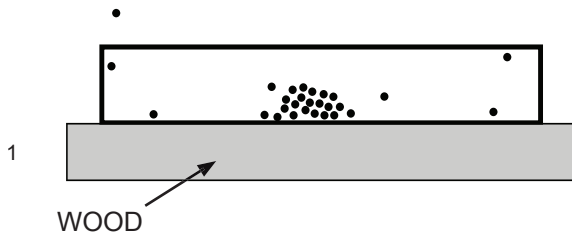


INTERNATIONAL SPACE STATION

CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

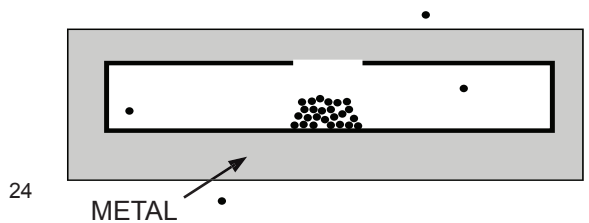
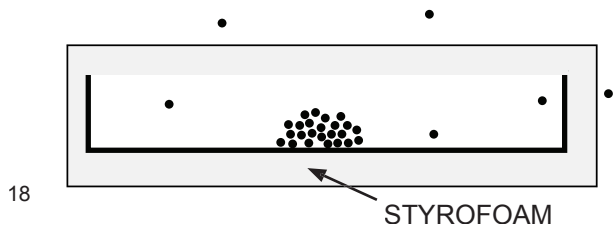
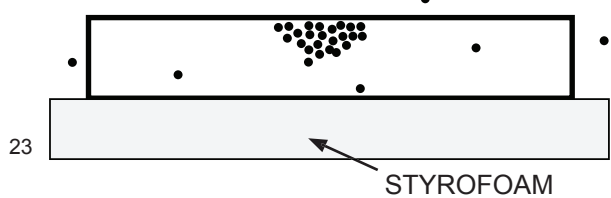
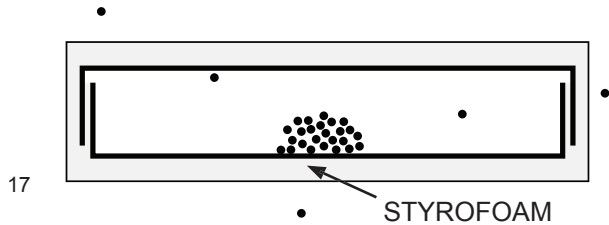
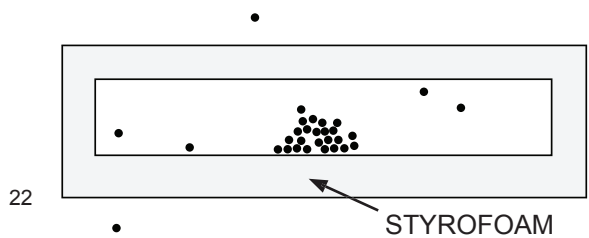
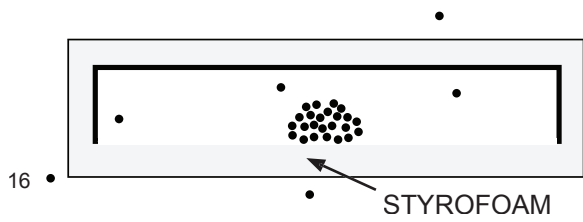
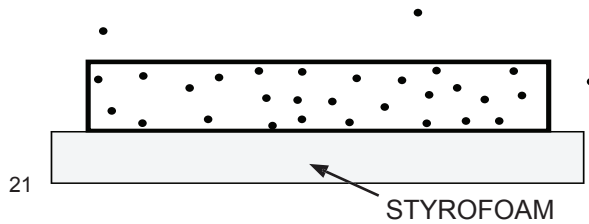
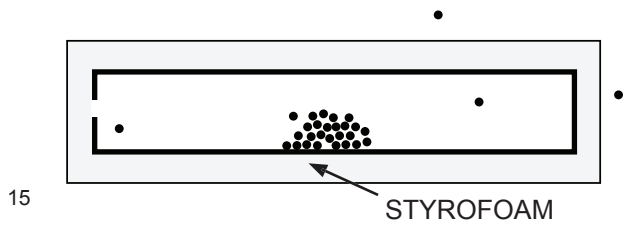
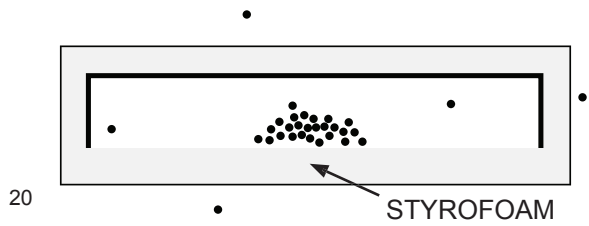
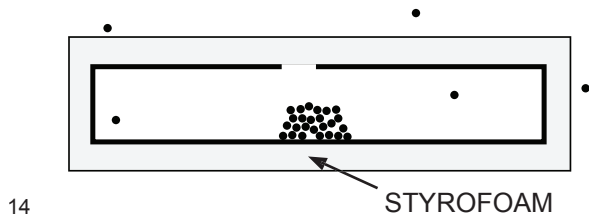
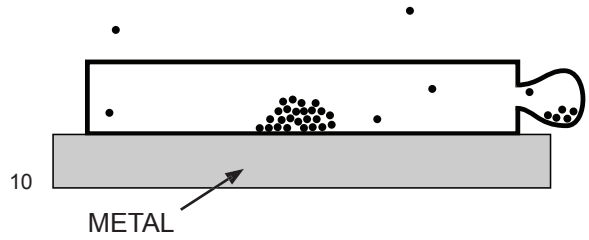
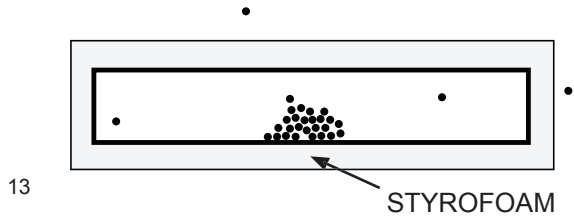
For drawings 1 through 12 define the system in words and draw an outline around the system. Explain whether the system is open, closed or isolated and discuss the reasons for your choice.



CHEMICAL ENERGETICS

SYSTEM AND SURROUNDINGS

For drawings 13 through 24 define the system in words and draw an outline around the system. Explain whether the system is open, closed or isolated and discuss the reasons for your choice.



CHEMICAL ENERGETICS

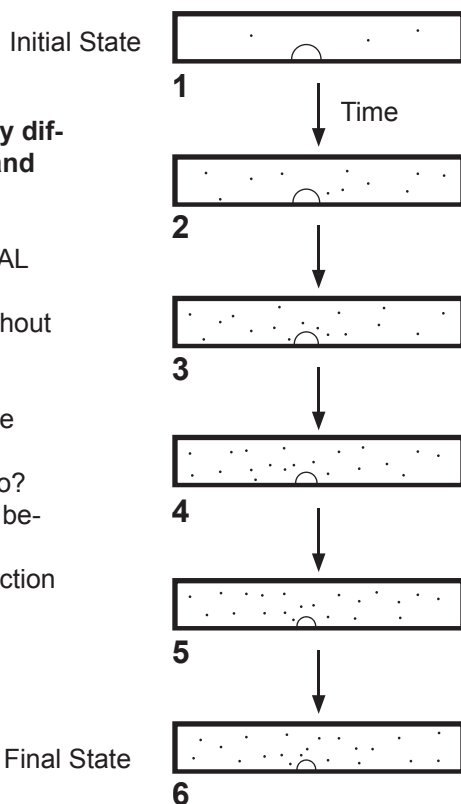
KINETICS AND THERMODYNAMICS

In the experiment shown on this page, a drop of water is placed in a petri dish which is then covered. The black dots represent water molecule in the air. The primary purpose of this page is to clarify the distinction between kinetics and thermodynamics.

THERMODYNAMICS
is concerned with the energy difference between the initial and final states of a reaction.

QUESTIONS OF CHEMICAL THERMODYNAMICS

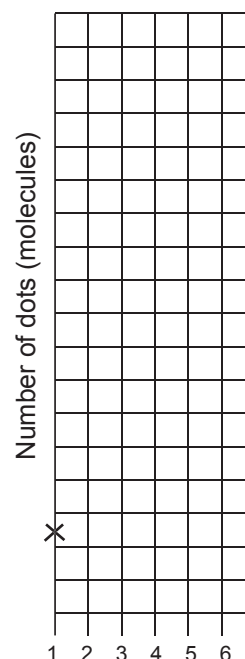
1. Can the reaction occur without additional energy?
2. How much energy will be released or absorbed when the reaction occurs?
3. How far will the reaction go? How much of the reactant will become product?
4. How can we make the reaction go further?



KINETICS
is concerned with the rate of a reaction and the intermediate steps between the initial and final state of a reaction.

QUESTIONS OF CHEMICAL KINETICS

1. What is the rate (speed) of the reaction?
2. How can the rate of the reaction be changed?
3. What is the reaction path, or mechanism, by which the reaction takes place.?



Using the experimental evidence provided by the pictures, explain why the state labelled final state is actually the final state.
If there were a state 7, subsequent to state 6, how would state 7 differ from state 6 and how would it be like state 6?

Using the pictures of the experiment, graph the number of evaporated molecules at each state. (The initial state is done for you.) Describe the rate of the reaction.

CHEMICAL ENERGETICS

ENERGY

Looking into various chemistry texts you will see energy defined as the capacity or ability to do work or that plus the capacity or ability to make heat flow or to cause change. Perhaps energy is too fundamental to give it a good definition. Yet in practice we examine different forms of energy, or energy change, in definite amounts.

The basic SI unit of energy is the Joule, which is defined as a Newton of force moving through a meter of distance. Although many forms of energy, such as chemical energy, may not appear directly as a force moving through a distance, all forms of energy are measured in Joules. A Joule is enough energy to lift your chemistry textbook a couple of centimeters (in earth's gravity). This is not very much energy so chemists usually use kiloJoules, kJ. If you weigh 50 kilograms, it will require about 5 kJ to climb 10 meters of stairs or hillside.

Consider time. There is no such thing as THE TIME. Not only are there different time zones but there are different time systems. For example, computer time is the number of milliseconds since midnight on January 1, 1970. Time is the difference between say, the present instant and the beginning of the system. Differences in time are real.

It is the same with energy, change in energy is real, the difference in energy between two situations is real. When the energy of a situation is given or measured, that always means the difference in energy between that situation and another situation which is arbitrarily set at zero energy. When the change in energy between two situations is measured, it is not necessarily to specify a zero point, but when a situation is said to have some energy, then it is necessary to know what the zero point situation is.

An essential principle of energy is that it is conserved. That is, energy can be neither created nor destroyed but only changed from one form into another. The only exception to this is the transformation between mass and energy according to Einstein's equation

$$E = mc^2$$

but scientists get around this by calling mass another form of energy. Then the principle holds exactly and it is also called The First Law of Thermodynamics.

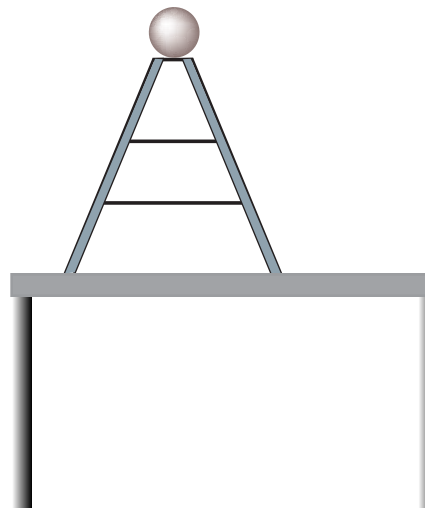
FORMS OF ENERGY:

- Kinetic energy of motion
- Potential energy
- Various forms of chemical energy
- Electrical energy
- Gravitational energy
- Nuclear energy
- Electromagnetic radiation
- Sound
- Heat

What are some other forms of energy?

EXAMPLE

An 8 kg bowling ball resting on a 3 meter high ladder will have a gravitational potential energy above the base of the ladder of 235.2 J. But if the ladder happens to be standing on a 3 meter high platform, the bowling ball will have a gravitational potential energy of 470.4 J above the base of the platform.

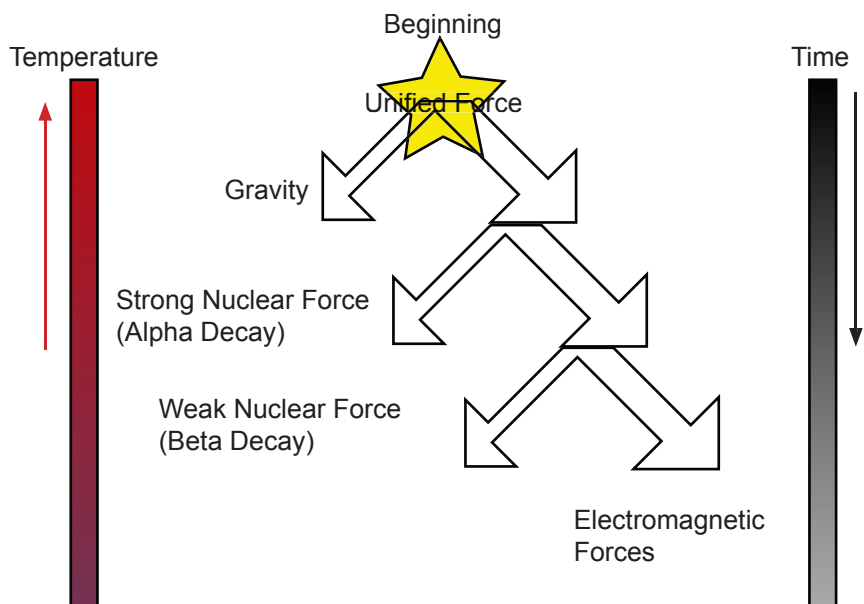


If the bowling ball rolls off of the ladder, into what forms of energy will the gravitational potential energy be changed? Answer this from you own experience, not from theory.

Suppose 10 Joules of light (electromagnetic energy) strikes a surface and 5 Joules of light is reflected from the surface and the rest of the light is absorbed into the surface, becoming heat. How much heat energy is absorbed by the surface?

CHEMICAL ENERGETICS

ENERGY AND FORCE



Energy and force are two different concepts which scientists use to analyze reactions and changes in systems. As there are various forms in which energy appears so there are different forces which arise in nature. In modern terms there are four known forces (although some astronomers have postulated a fifth force to explain certain aspects of the universe). The four forces are the electromagnetic force, the gravitational force, the weak nuclear force and the strong nuclear force. There also exists a theoretical unification of the electromagnetic and weak forces and it is also considered plausible that in the very early stages of the universe all of the forces were combined as one. It is useful to compare the different strengths and qualitative aspects of the different forces.

Gravity is the weakest of the forces but since it is only attractive it can accumulate great strength resulting from large masses.

Electromagnetic forces are about 100 thousand times as strong as gravity and are the forces which control most of our daily lives as well as essentially all of chemistry. There are two charges of which opposites attract and like charges repel, so the normal condition is opposite charges to balance each other.

The weak nuclear force is about 100 times as strong as electromagnetic forces and is responsible for beta decay.

The strong force is what holds fundamental particles like neutrons and protons together.

If gravity is such a weak force, why do we feel so heavy?

The unit of force is the Newton, abbreviated 'N'. By definition, one Newton is the force required to accelerate one kilogram one meter per second per second. According to Newton's third law every force has an equal and opposite force. So since earth's gravity has an acceleration of 9.8 ms^{-1} , the force required to hold up a one kilogram object against gravity is 9.8 N.

A common American unit of force is the pound, abbreviated lb. A pound is approximately equal to 4.45 N. In common usage 'pound' is often used when the mass is what is meant. Pound is the unit of force, or weight, not mass, but the two concepts are related - on Earth!

Many consumer items are marked with their 'weight' from which their mass can be easily derived. For example a weight of one pound, 1 lb, has a mass of 454 gm and a liter, L, of common drinks has a mass of approximately one kg. Read the labels on several packages and calculate the force required to hold them up.

An isolated system consists of an electron and a proton separated by a micron (10^{-6} m). Qualitatively describe the forces and energies involved and how they change over time.

CHEMICAL ENERGETICS

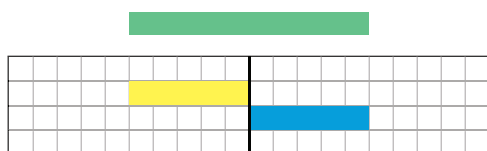
KINETIC AND POTENTIAL ENERGY

Energy comes in a variety of forms, including kinetic and potential energy. What is the difference between these two types of energies?

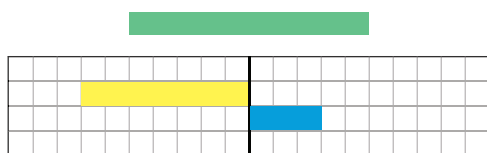
Kinetic energy is the energy due to motion. Potential energy is the energy due to position. The total energy of an object is the sum of its kinetic and potential energies.

When you climb a mountain your gravitational potential energy increases but your kinetic energy remains about the same (unless you fall off). What is the source of this increase in energy?

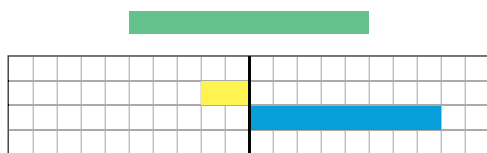
$$\text{Energy}_{\text{total}} = \text{Energy}_{\text{potential}} + \text{Energy}_{\text{kinetic}}$$



1



2



3

Could any of the Chem Logs above represent the energy of the bowling ball resting on top of the ladder? If so, which one and why.

If the bowling ball falls off of the ladder, in what sequence, i.e., first, second and third, might the Chem Logs show the kinetic and potential energies of the falling ball?

KINETIC ENERGY

Kinetic energy of an object is related to its mass and speed through the equation:

$$E_k = \frac{1}{2} mv^2$$

As an example, suppose an 8 kilogram bowling ball is falling at 10 meters per second. We can calculate its kinetic energy:

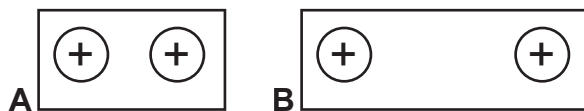
$$E_k = \frac{1}{2} 8 \text{ kg} \times (10 \text{ ms}^{-1})^2 = 400 \text{ J}$$

How much kinetic energy will a 500 kg volkwagon travelling at 20 meters per second have?

POTENTIAL ENERGY

No single equation can be given to determine the potential energy of an object because this energy depends on an arbitrary designation of the zero. However, potential energy can be determined in specific cases.

We looked at gravitational potential energy on the first page of this module but for chemists it is important to understand electrostatic potential energy. There is always electrostatic potential energy between two charged objects. If the objects have the same kind of charge, e.g., both positive, then the potential energy decreases as the distance between the objects increases. If the objects have opposite charges then the potential energy increases as the distance between the objects increases.



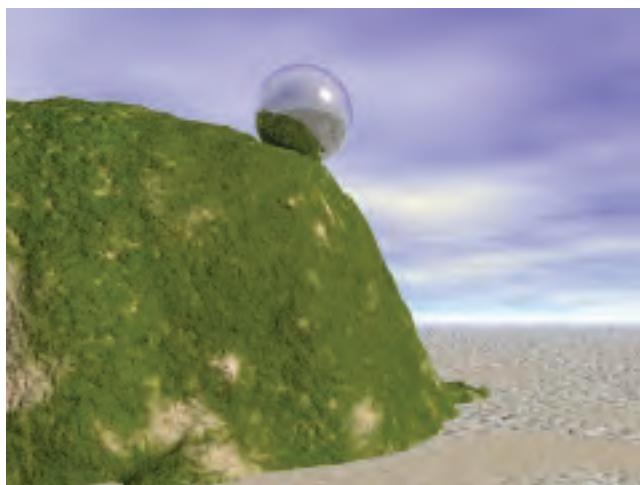
Assuming that the four positive charges above are equal, compare the potential energy of the situation in box A with that of the situation in box B. Which has more potential energy?



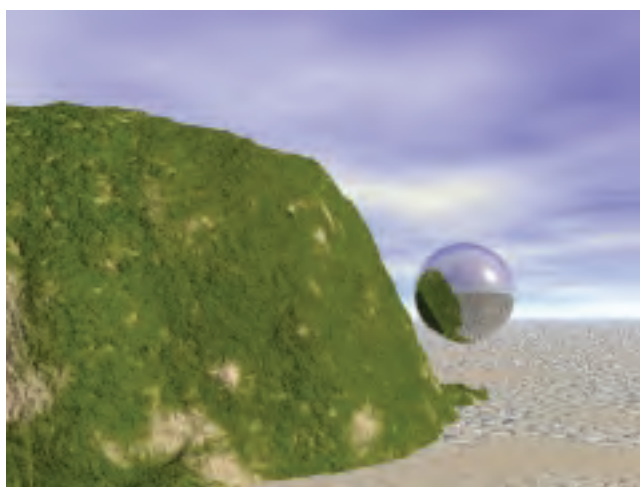
Assuming that the two positive charges above are equal in magnitude and that the two negative charges are equal in magnitude, which situation, A or B, has the greater potential energy?

CHEMICAL ENERGETICS

KINETIC AND POTENTIAL AND THERMAL ENERGY



POTENTIAL ENERGY

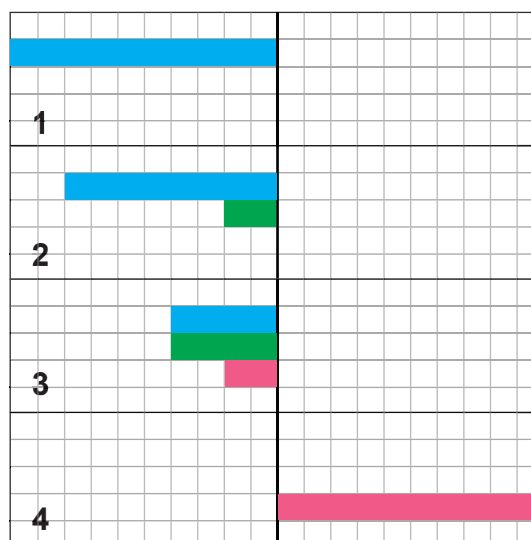


KINETIC ENERGY



THERMAL ENERGY

- Potential Energy
- Kinetic Energy
- Thermal Energy



For each of the four ChemLogs 1 through 4, find the total energy (by counting the colored squares).

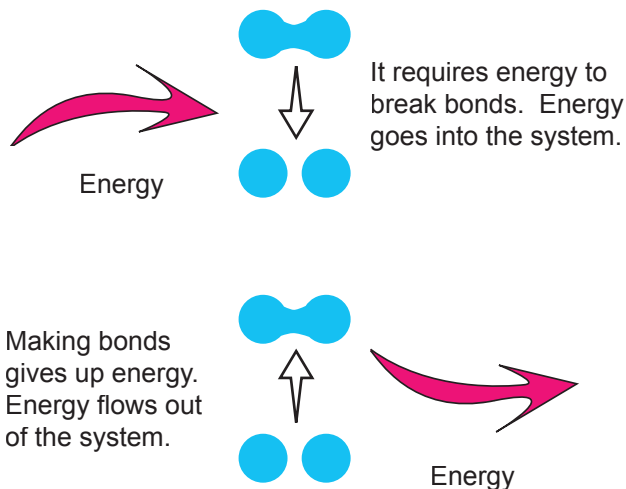
Describe the different forms of energy which occur in the process of hydroelectric power generation.

CHEMICAL ENERGETICS

CHEMICAL ENERGY

Chemical energy is the potential energy stored in the arrangements, or bonding, of atoms in a substance. Changes in chemical energy occur with chemical reactions. Chemical reactions generally involve a change in chemical energy. One important use of chemical energy is help form new materials by providing the energy needed for endothermic reactions.

In other cases there may be energy which is not reused as chemical energy. In an exothermic reaction, this often appears as heat energy but might also include other forms, such as the light absorbed by chlorophyll or the sound of a chemical explosion.



The combustion of methane can be represented by the formula $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$. List the bonds that are broken in this reaction and list the bonds that are formed.

ENERGY SCALES

SOME ONE MOLE INTERACTIONS

Chemical energies are usually expressed in kJ/mol, which is an abbreviation for kiloJoules per mole of substance. Here are some examples which compare chemical energies to other forms of energy.

Ionizing one mole of Argon (20 g) will require as much energy as a 50 kg person climbing two miles.

Dissociating one mole of gas phase dioxygen (32 g) into its constituent atoms will require as much energy as needed to light a 100 watt bulb for 3 hours, six minutes and 45 seconds.

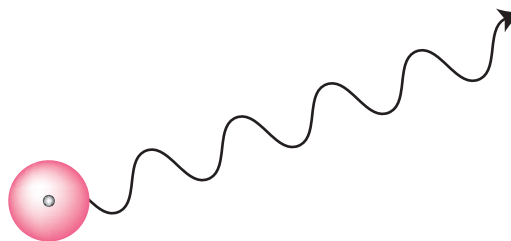
To make one mole of acetylene from its constituent elements would require as much energy as pumping one hundred liters of water up over 230 meters.

It can be seen from the examples that chemical energies are often (not always) quite large.

Describe some applications of chemical energy which are familiar in daily life.



While they are separated there is an electrostatic potential energy between the negatively charged electron (in red) and the positively charged proton (in black).

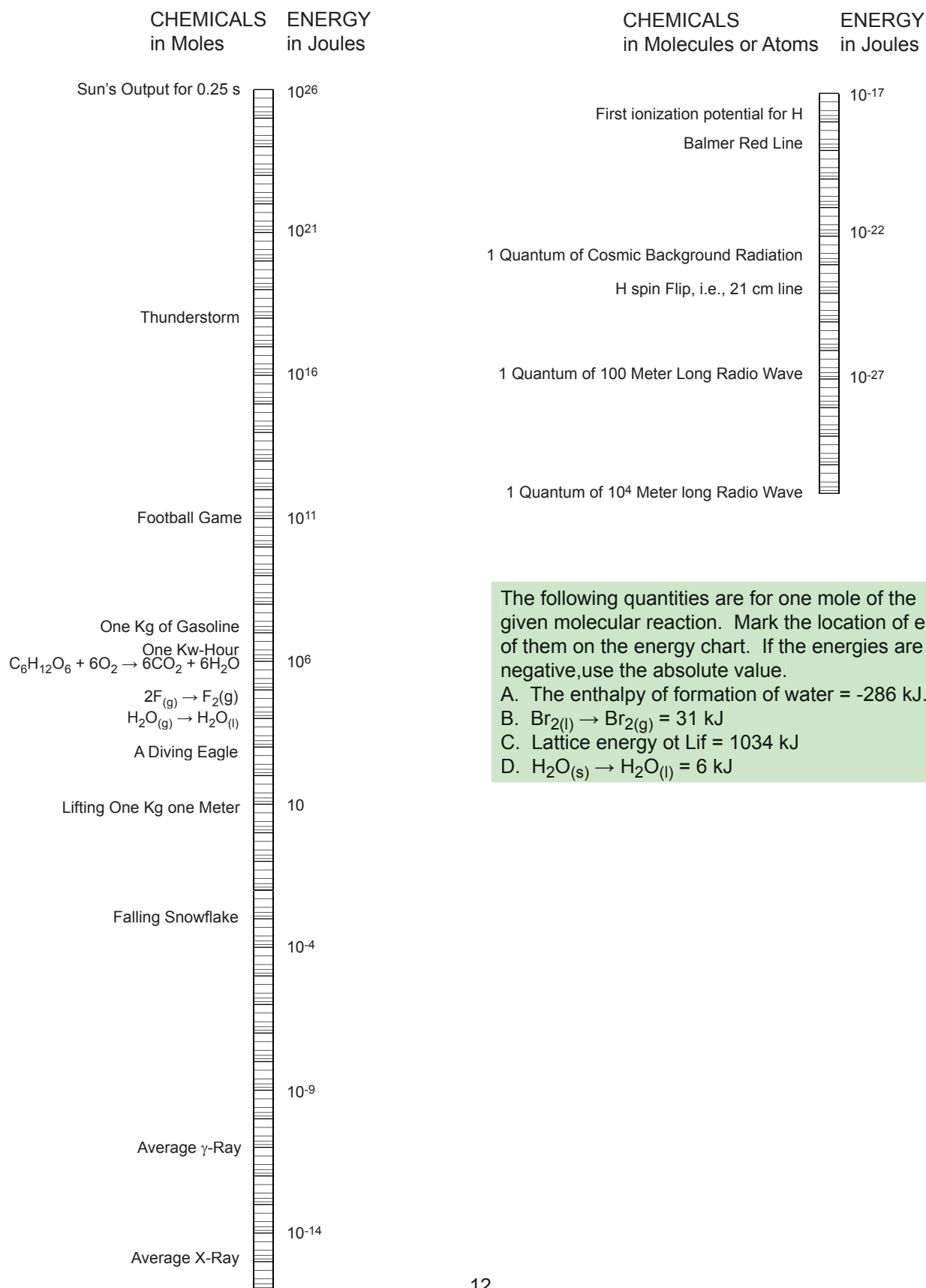


When the electron and proton come together, to produce a hydrogen atom, the electrostatic potential is reduced and that lost energy must still exist. In an isolated atom it is usually carried away by electromagnetic radiation.

Positive and negative charges are usually very closely balanced in nature. Explain why we know this is true and describe what might happen in a situation where they were far out of balance.

CHEMICAL ENERGETICS

ENERGY SCALE



The following quantities are for one mole of the given molecular reaction. Mark the location of each of them on the energy chart. If the energies are negative, use the absolute value.

- The enthalpy of formation of water = -286 kJ.
- $Br_{2(l)} \rightarrow Br_{2(g)} = 31$ kJ
- Lattice energy of $LiF = 1034$ kJ
- $H_2O_{(s)} \rightarrow H_2O_{(l)} = 6$ kJ

CHEMICAL ENERGETICS

SPONTANEOUS VS. NON-SPONTANEOUS REACTIONS

Some chemical reactions will occur spontaneously and some will not. The meaning of spontaneous reaction as we shall use it is “having the potential to proceed naturally without an input of energy from the outside.” We need to consider three questions:

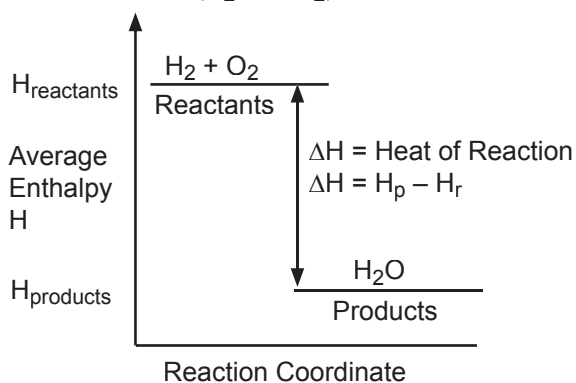
1. Can the reaction occur under any circumstances? Some reactions will not occur under any circumstances.

2. Can the reaction occur spontaneously? A nonspontaneous reaction is one that does not occur naturally, but it can potentially be made to occur by supplying outside energy.

3. Will the reaction actually occur? That is, will the reaction occur in a reasonable time?

The average chemical energy or heat content of a chemical system at constant temperature and pressure is called **enthalpy**, represented by the symbol H . The heat evolved or absorbed when a reaction occurs is the difference between the average enthalpy of the products and the reactants and is given the symbol ΔH . This difference in enthalpy is called the **heat of reaction**.

An exothermic reaction such as the reaction between dihydrogen gas and dioxygen gas to form water is accompanied by a decrease in enthalpy and heat is evolved to the surroundings. Thus, the heat of reaction, ΔH , is negative. This indicates that average bond strengths in and between the product molecules (H_2O) are stronger than the average bond strengths in and between the reactant molecules (H_2 and O_2).



Heat of reaction at constant pressure and temperature = Average enthalpy of products – average enthalpy of reactants.

Heat of reaction at constant pressure and temperature = $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

Exothermic Reaction : Heat evolved to surroundings
 ΔH_{system} is –
 Endothermic Reaction : Heat absorbed from surroundings
 ΔH_{system} is +

First Law of Thermodynamics – Law of Conservation of Energy

In all macroscopic chemical and physical changes, energy is neither created nor destroyed but only transformed from one form to another

or

In any process the total energy of the system plus its surroundings remains constant.

The Minimum Potential Energy Principle

Mechanical systems tend spontaneously to a state of minimum potential energy consistent with their surroundings.

The Minimum Chemical Energy Principle

Chemical Reactions tend spontaneously toward a state of minimum chemical energy consistent with its surroundings

or

Exothermic reactions “should” be spontaneous and endothermic reactions ‘should’ be nonspontaneous.

A Tentative Hypothesis—The Minimum Enthalpy Principle

Chemical reaction at constant temperature and pressure tend spontaneously toward a state of minimum enthalpy (H) consistent with their surroundings.

Spontaneous reactions are exothermic: ΔH is –
 Nonspontaneous reactions are endothermic: ΔH is +

a. Is the reaction of carbon dioxide (CO_2) and water (H_2O) plus heat to form glucose, a sugar, and dioxygen, exothermic or endothermic?

b. Is ΔH + or –?

c. What is the sign of ΔH for the reverse reaction of glucose and O_2 to form CO_2 and H_2O ?

d. According to the minimum enthalpy principle, which reaction should be thermodynamically spontaneous?

Forward reaction: $CO_2 + H_2O + \text{heat} \rightarrow \text{glucose} + O_2$
 or

Reverse reaction: $\text{glucose} + O_2 \rightarrow CO_2 + H_2O + \text{heat}$

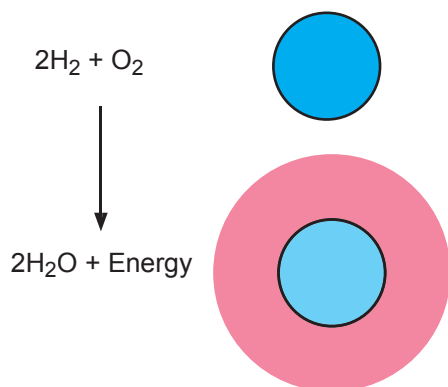
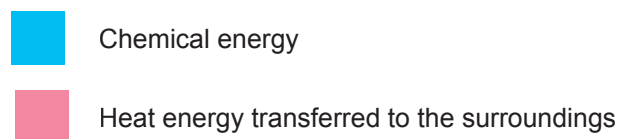
e. Which reaction should be nonspontaneous?

f. If the reaction is thermodynamically spontaneous in one direction, does this mean that this reaction *will* actually occur? Explain.

CHEMICAL ENERGETICS

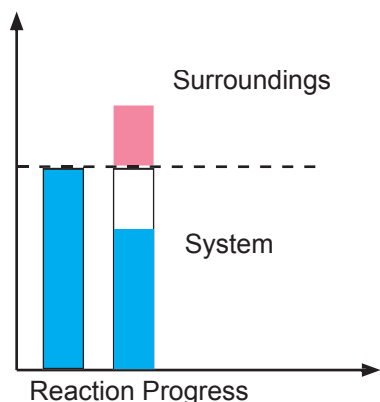
VIEWS OF THE FIRST LAW

EXOTHERMIC REACTION



The system is the interior of the circle, everything else is the surroundings. The exothermic reaction transforms chemical energy into heat energy. The final result is that the chemical energy of the system is lowered and the lost chemical energy becomes heat energy added to the surroundings.

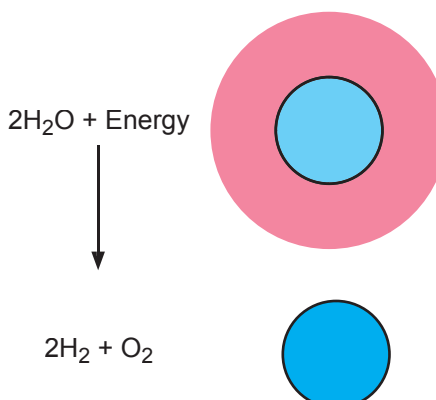
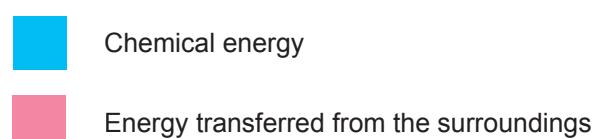
Another View of the Same Reaction



The system is a collection of hydrogen and oxygen atoms which are in H_2 and O_2 molecules before the reaction. After the reaction the system is the same collection of atoms formed into H_2O molecules plus energy. This energy is transferred to the surroundings.

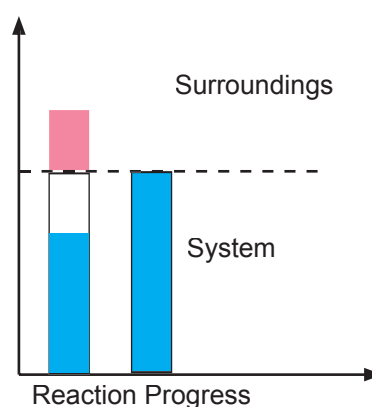
Does the energy transferred from the system to the surroundings in an exothermic reaction always end up as heat energy?

ENDOTHERMIC REACTION



The system is the interior of the circle, everything else is the surroundings. The endothermic reaction transforms energy from the surroundings into chemical energy in the system. The final result is that the chemical energy of the system is increased and the energy of the surroundings is decreased.

Another View of the Same Reaction



The system is a collection of hydrogen and oxygen atoms which are in H_2O molecules before the reaction. After the reaction the system is the same collection of atoms formed into H_2 and O_2 molecules. The chemical energy of the system has been increased by energy withdrawn from the surroundings.

What other forms of energy, besides heat, can be withdrawn from the surroundings to make an endothermic reaction occur?

CHEMICAL ENERGETICS

ORIGINS OF THE FIRST LAW OF THERMODYNAMICS

In 1798 Count Rumford published an article in the Philosophical Transactions of the Royal Society of London in which he described experiments about boring out brass cannon which showed that heat is not a substance, as previously thought, but a form of motion, or of what we would now call energy. He showed that an inexhaustible amount of heat could be produced with a finite amount of matter, which precluded that heat itself be a substance.

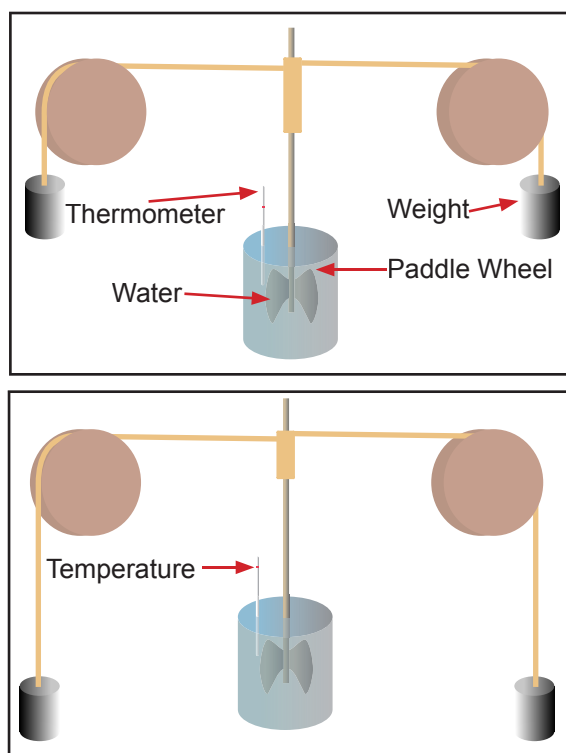
“Being engaged, lately, in superintending the boring of canon, in the workshops of the military arsenal at Munich, I was struck by the very considerable degree of heat which a brass gun acquires, in a short time. By being bored...

*The more I meditated upon these phenomena the more they appeared to me to be curious and interesting, a thorough investigating of them seemed even to bid fair to give a farther insight into the hidden nature of heat; and to enable us to form some reasonable conjectures respecting the existence, or non-existence, of an igneous fluid: a subject on which the opinions of philosophers have, in all ages, been much divided.... And, in reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of heat generated by frictions, in these experiments, appeared evidently to be **inexhaustible**. It is hardly necessary to add that anything which any insulated body, or system of bodies, can continue to furnish **without limitation** cannot possibly be a **material substance**: and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be **MOTION**.*

In the 1840's James Joule conducted a series of experiments measuring the relationship between different forms of energy, in particular electrical, mechanical and heat energy. The pictures below show an experiment in which the potential gravitational energy of the weights turns the paddle wheel as the weights fall, which in turn heats the water by friction. Joule's conclusion was that when energy is changed from one form to another, the amount of energy remains the same.

Now this principle has come to be accepted. It is called conservation of energy or the First Law of Thermodynamics.

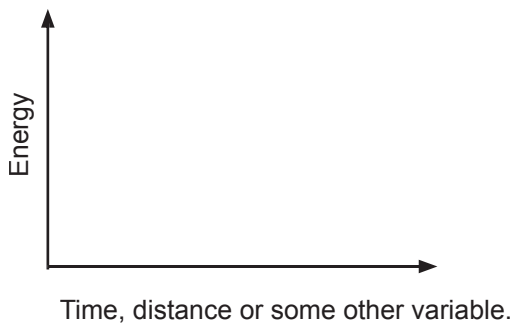
JOULE'S EXPERIMENTAL ARRANGEMENT



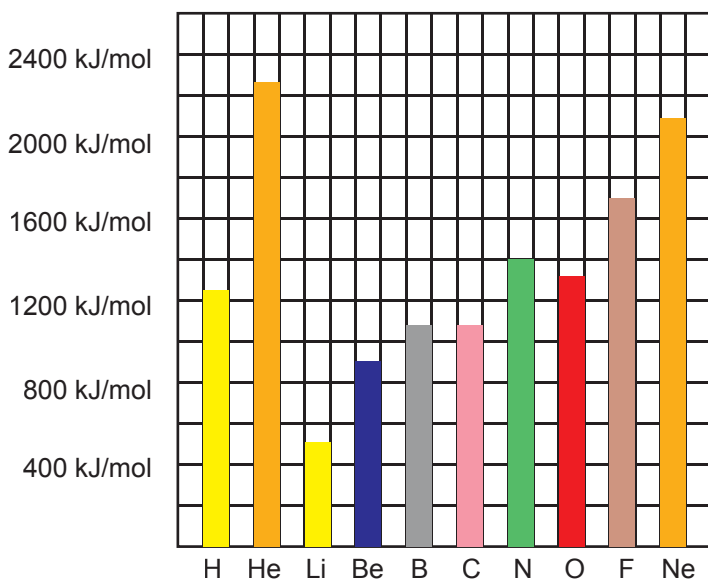
CHEMICAL ENERGETICS

ENERGY DIAGRAMS

It is standard in chemistry to show the energies of systems and energy changes between states by means of diagrams in which the vertical axis represents energy with the upward direction representing higher energy. The horizontal axis can represent changes in some other property or different systems.

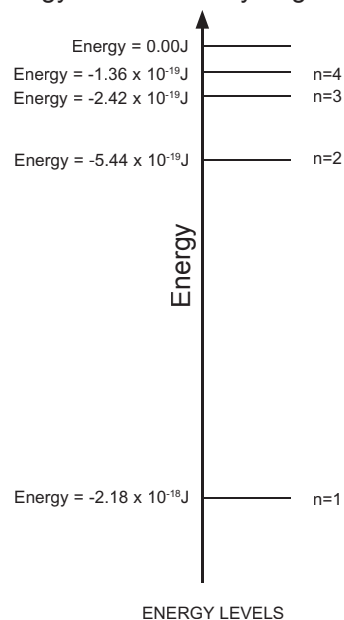


As an example of energy charts comparing different systems we show a chart of the energy required to ionize the first valence electron from the first ten elements. In this chart the vertical energy scale is in kilowatts per mole.



In the ionization energy chart the zero of energy was at the bottom of the chart. Sometimes this is not the case. Charts showing the energy levels of atoms, for example, may have the zero of energy near or at the top of the chart.

Energy levels of the Hydrogen atom.



In this example of the energy levels of the hydrogen atom, there is no real horizontal axis. We just need the space to write in. On the other hand, the other charts on this page do each have a meaningful horizontal axis.



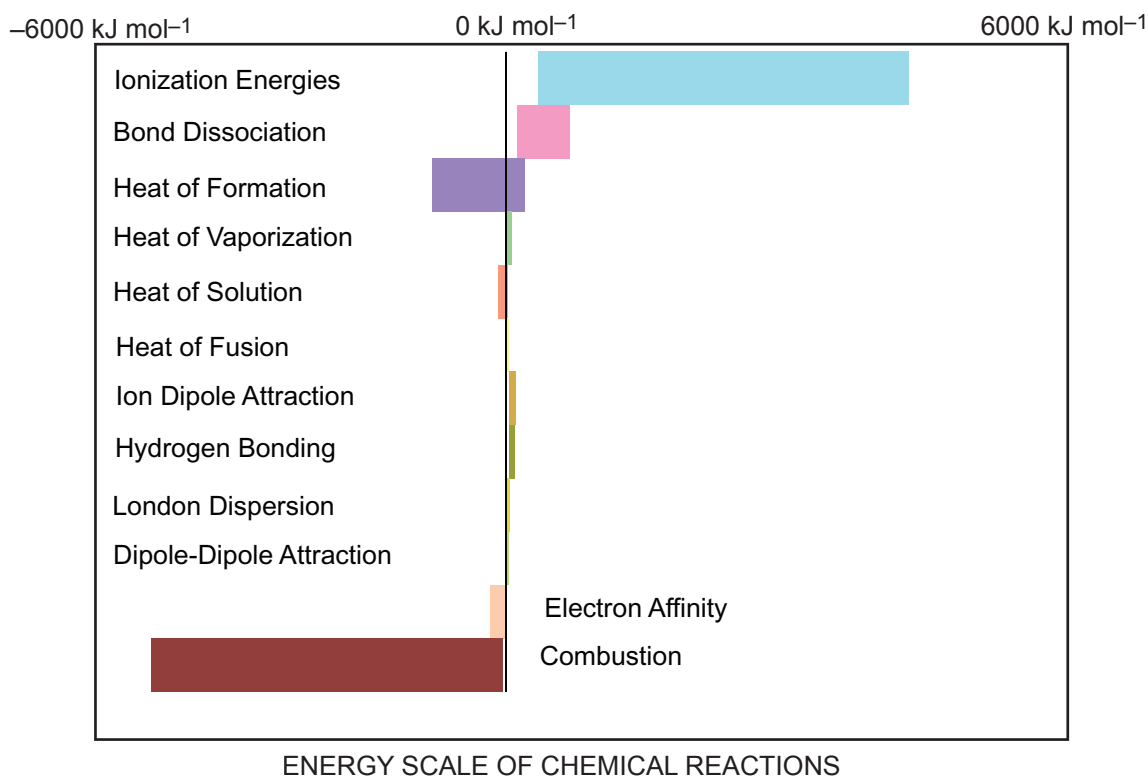
Suppose you are going from your home to chemistry class. In the box above draw a line or curve showing the changes in your gravitational potential energy as you go from home to chemistry class. Draw it from left to right, starting in the middle of the left hand side. Chemistry class is on the right hand side of the box but I don't know how high it is relative to your home.

CHEMICAL ENERGETICS

ENERGY CHEM LOGS

We have examined the common vertical axis representations of energy which you will find in most of your textbooks. However, in Powerful Pictures we have introduced the Chem Log, because sometimes a horizontal bar graph communicates information more intuitively than a vertical presentation.

Look into the media available to you, such as newspapers, magazines, books and the Internet, for examples of horizontal bar graphs. Compare and contrast these examples with Chem Logs.



If you have read our Chem Log tutorial you will know that there are also more sophisticated forms and uses of Chem Log but for our simple version used in this module you need to note that the zero of energy is in the middle and the amount of energy involved varies with the distance from the middle. In the Chem Log above, the left side shows negative, or exothermic reactions, while the right side shows positive, or endothermic, reactions.

Which of these types of chemical reactions are endothermic? Which are exothermic? Which include both endothermic and exothermic possibilities?

Write a list of the types of chemical reactions shown in the Chem Log, ordering it according to the range of energies associated with each type. For example, Heats of Formation occur over a wider range of energies than Bond Dissociation.

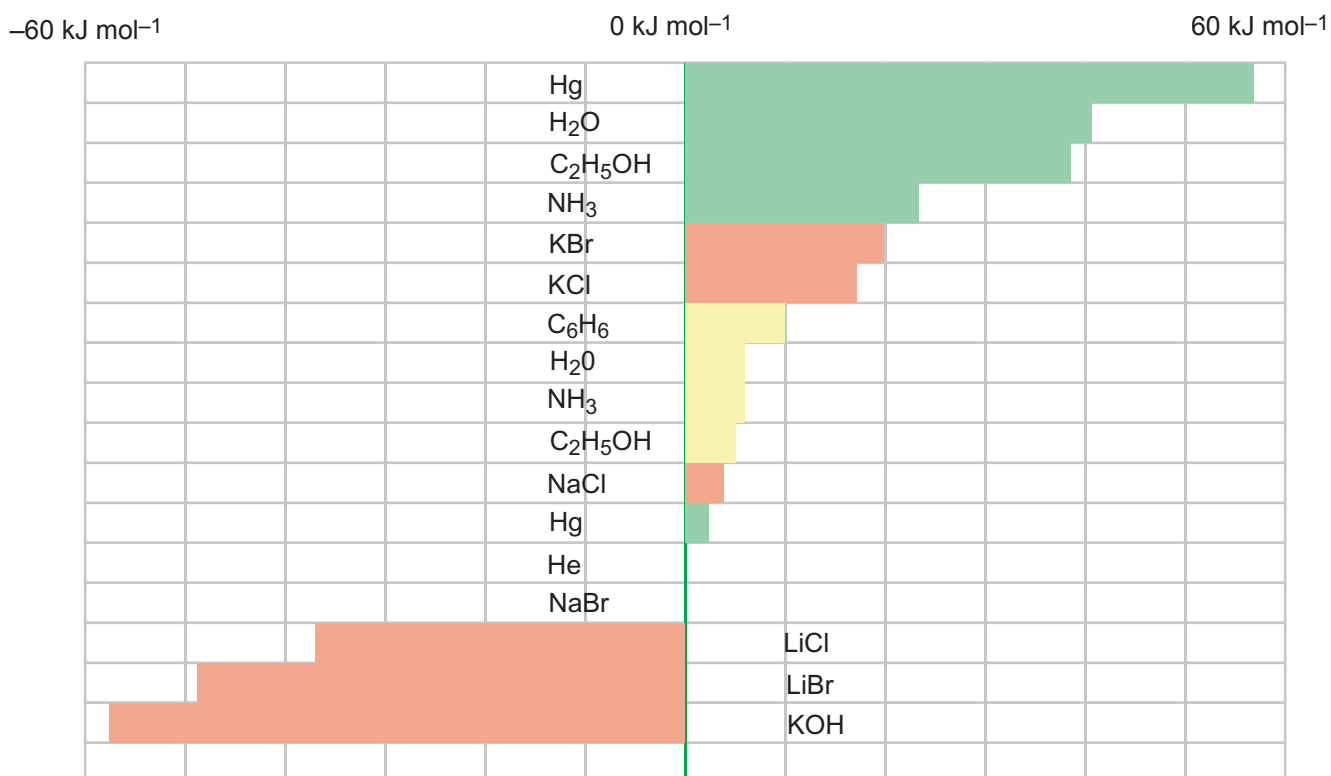
CHEMICAL ENERGETICS

ENTHALPY CHANGES

Enthalpy, H , is a thermodynamic quantity. H is the chemical energy or heat content of a system at constant temperature and pressure. What is important about enthalpy is its change, ΔH , when a chemical process occurs. Provided the process occurs at constant pressure (usually one atmosphere) and the only work done by the system is possibly the production of gas, then ΔH is equal to the heat energy produced or absorbed by the process. When $\Delta H > 0$ the process absorbs heat from its surroundings. When $\Delta H < 0$ the process produces heat.

The chart below shows the enthalpy changes produced by evaporation, melting and dissolving.

- Enthalpy change when a substance goes from the liquid to the gaseous state.
- Enthalpy change when a substance melts.
- Enthalpy change when a substance dissolves into water.



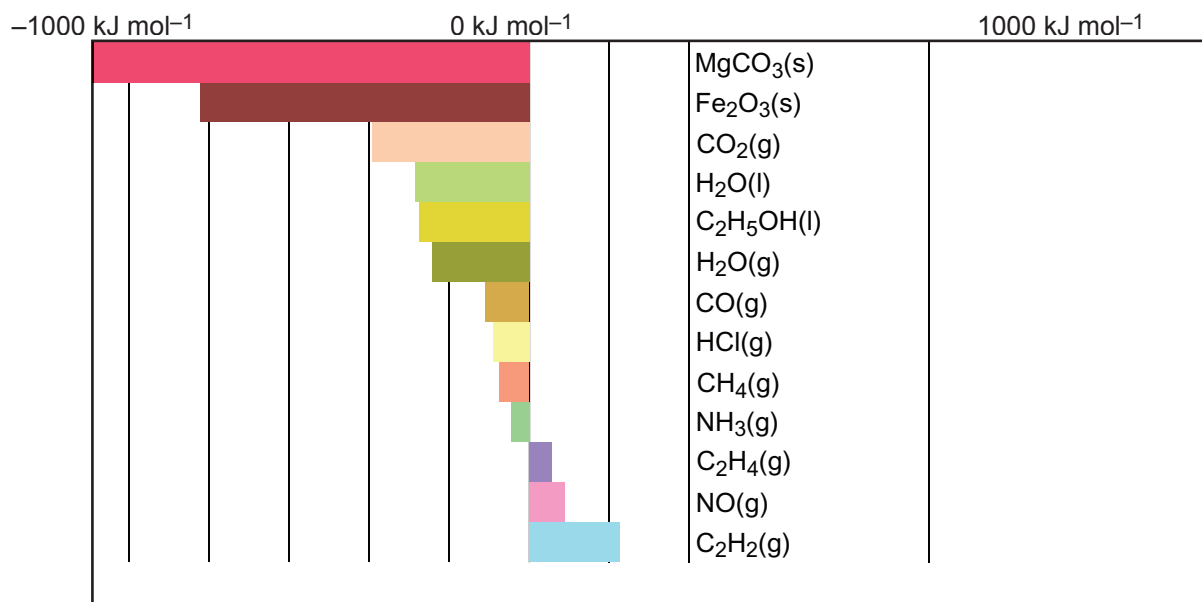
From the chart, would you expect KBr or LiBr to dissolve more readily in water?

Which of the processes shown in the chart are exothermic?

A cold winter day will often become somewhat warmer when snow starts falling. Give an enthalpic explanation of this phenomenon.

CHEMICAL ENERGETICS

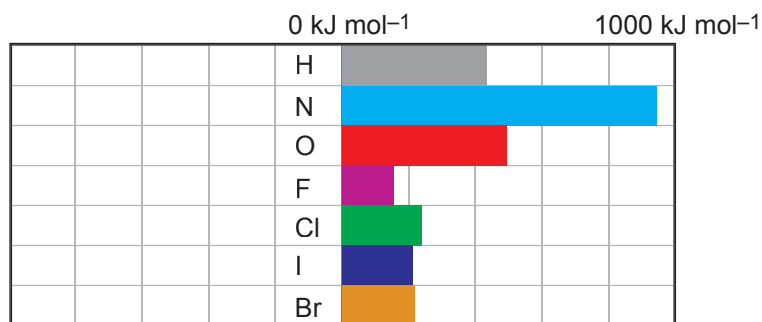
ENTHALPY OF FORMATION



The enthalpy of formation of a substance is the enthalpy change which occurs when a substance is formed from the most stable forms of its component elements. In several cases the most stable form of an element is a diatomic gas which must be decomposed in order to use the atoms in the formation of the substance. The next Chem Log shows the enthalpies of formation for several atomic gases from their more stable diatomic state.

Given its large negative enthalpy of formation, explain why rusting iron usually does not feel warm to the touch (unless it has been left in the sun).

Methane, CH₄(g) is a common fuel, making up a large part of natural gas. Given that we burn methane to produce heat, explain how that can be so when its enthalpy of formation is negative.

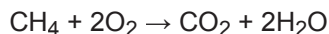


Discuss what effect the bond structures of N₂ and O₂ have in determining the enthalpies of formation of N and O.

CHEMICAL ENERGETICS

ENTHALPIES OF REACTIONS

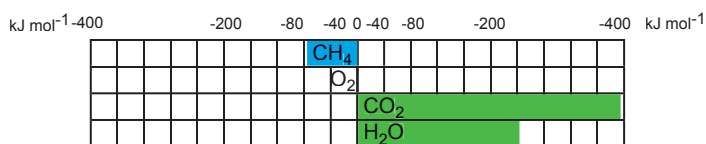
Consider the chemical reaction:



Since we know the enthalpies of formation of each of the reactants and each of the products we can find the enthalpy change in the reaction.

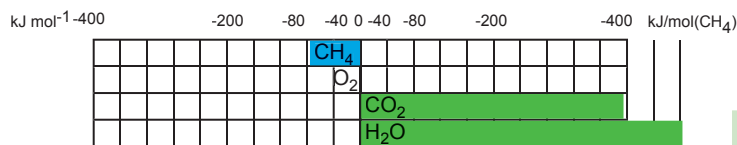
ENTHALPY OF FORMATION

Chemical	H in kJ mol^{-1}
CH_4	-74.8
O_2	0
CO_2	-393.5
H_2O	-241.8



ENTHALPIES OF FORMATION

The stoichiometry of the reaction requires two moles of water be formed, so we double the enthalpy of the water.



ENTHALPIES OF THE REACTION

In order to find the enthalpy change, ΔH , of the reaction we first sum the enthalpies of the products.



TOTAL ENTHALPY OF THE PRODUCTS

Then we subtract the enthalpy of the reactants.



DIFFERENCE OF ENTHALPIES

Which gives us the enthalpy change of the reaction.



ENTHALPY CHANGE OF THE REACTION

Tell whether the reaction is endothermic or exothermic and explain why.

Explain why the enthalpy of formation of O_2 is zero.

Find the total enthalpy of the products on the chart called TOTAL ENTHALPY OF THE PRODUCTS.

Find the enthalpy change of the reaction on the chart called ENTHALPY CHANGE OF THE REACTION.

The scale on the bottom four charts is labeled $\text{kJ/mol}(\text{CH}_4)$. This means kiloJoules per mole of CH_4 . Explain why it is labeled that way instead of kJ mol^{-1} and state an alternative label.

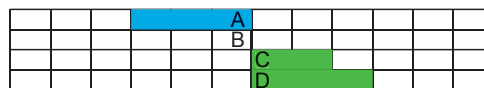
For the given products, what would have been the total enthalpy of the reactants for the reaction to be in equilibrium?

The charts below apply to a reaction in the type $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$

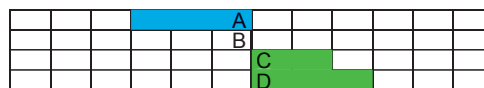
In the charts, draw in an enthalpy of reactant B that would be required in order for the reaction to

- Proceed to the left
- Be at equilibrium
- Proceed to the right.

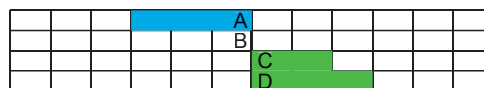
Assume that all the enthalpies are negative and that the enthalpy of B is NOT zero.



a. Proceed to the left.



b. Equilibrium



c. Proceed to the right.

CHEMICAL ENERGETICS

HESS'S LAW

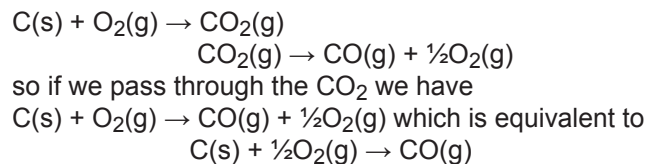
Hess's Law states that the enthalpy change in a given process is equal to the sum of the enthalpy changes of the several processes that, when added, yield the process of interest.

Because enthalpy, H, is a state function, enthalpy change, ΔH , between two states only depends upon the difference in enthalpy between the states and not upon how one state was changed into the other one. So we can use Hess's Law to determine ΔH for a reaction, R, if we can find a set of reactions which combine to give an equivalent reaction to R, even if these are NOT the actual processes by which R happens.

Suppose we want to find ΔH for the combustion of carbon to give carbon monoxide:

- a. $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H = ?$
 given that we know ΔH for the reactions
 b. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5 \text{ kJ}$
 c. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0 \text{ kJ}$

Here is the plot. Reaction b gives the enthalpy for combusting carbon into carbon dioxide. If we reverse reaction c we can get rid of the carbon dioxide and obtain carbon monoxide, which is what we are looking for.

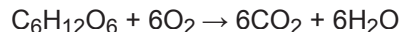


To get the ΔH of that reaction we subtract the ΔH of reaction c from the ΔH of reaction b.

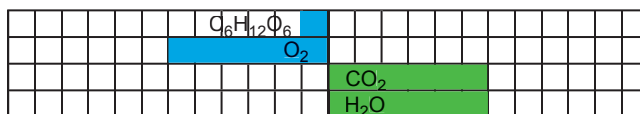
$$\begin{array}{r} \Delta H(\text{Reaction b}) \\ -\Delta H(\text{Reaction c}) \\ \hline \Delta H(\text{Reaction a}) \end{array} \quad \begin{array}{r} -393.5 \text{ kJ} \\ -(-282.0 \text{ kJ}) \\ \hline -111.5 \text{ kJ} \end{array}$$

State functions depend only upon the difference between two states and not upon the path between them. Suppose you climb a mountain. Which of the following quantities is a state function and which is not?
 The change in altitude between the bottom and top of the mountain?
 The distance traveled while climbing the mountain?

Consider the oxidation of glucose, which is a primary source of energy in our bodies, where it is also called respiration. The chemical formula is:



We can express this reaction by a ChemLog:



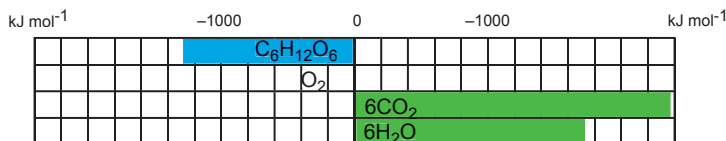
STOICHIOMETRY

We can now look at the enthalpy change involved in the reaction. We begin with the enthalpies of formation, ΔH_f
 $\Delta H_f(C_6H_{12}O_6) = -1273 \text{ kJ mol}^{-1}$
 $\Delta H_f(O) = 0 \text{ kJ mol}^{-1}$

$$\Delta H_f(CO_2) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f(H_2O) = -285.8 \text{ kJ mol}^{-1}$$

We can express the enthalpies as a chem log

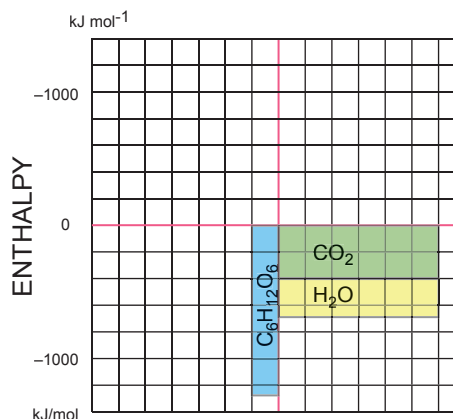


ENTHALPY

Now we introduce another variety of ChemLog where the height of the bar is the enthalpy in kJ mol^{-1} . Positive enthalpies appear above the horizontal axis and negative enthalpies appear below that axis.

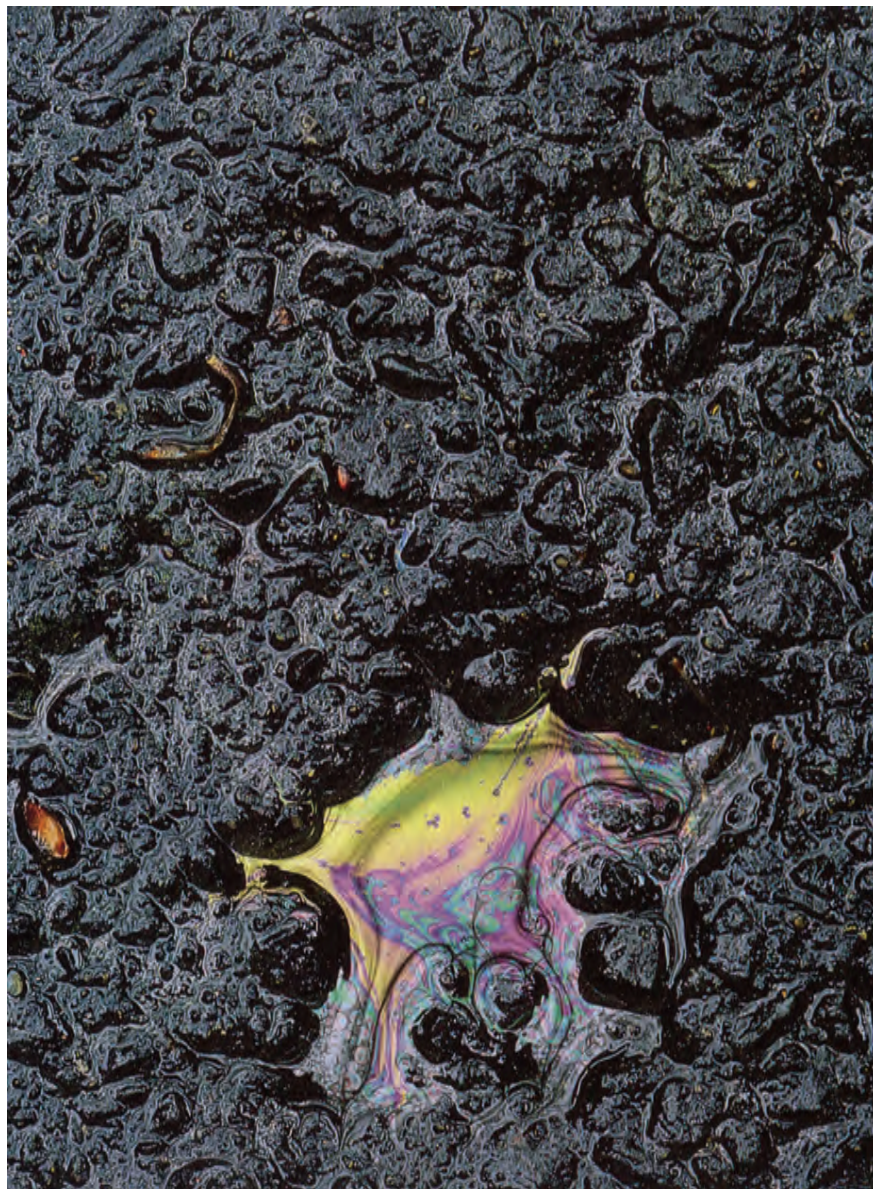
As we have done before the width of the bar is determined by the number of moles of the substance in the reaction: Reactants to the left of the vertical axis and products to the right of that axis.

The value of this kind of ChemLog is that the area of a bar is proportional to its enthalpy.



STOICHIOMETRY

DO MOLECULES EXIST AND HOW SMALL ARE THEY?



by **Dr. Stephen Thompson**
Mr. Joe Staley
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

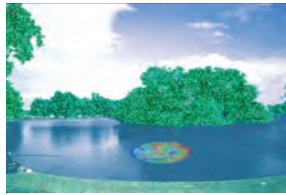
BENJAMIN FRANKLIN STILLS THE WAVES



1



2



3



4

Throughout his life Benjamin Franklin was interested in the calming effect of oil on turbulent water. In 1774, he described a series of experiments in which he poured oil on a pond in England. He observed that a teaspoon of olive oil poured on the surface spread to about one half of an acre. In an article in *Philosophical Transactions* 64, 1774, 445-460, he also reported, as seen in the excerpt given here:

Franklin searched for a scientific explanation of these phenomena because he was interested in the practical problem of saving the lives of sailors shipwrecked at sea in violent storms. He didn't realize that this simple experiment could actually be used to determine the size of olive oil molecules! Before determining their size, let's explore why olive oil molecules spread on water. This alone was fascinating to Franklin because on other surfaces, olive oil doesn't spread. How can this be?



5

In 1989, when the Exxon Valdez grounded at Prince William Sound and spilled 10.8 million gallons of oil into the sea, the clean-up process was expensive and difficult because of the simple fact that oil spreads on water. Several methods to clean Prince William Sound were employed, including the use of a boom, as seen in the following picture. The boom can be pulled across the surface to collect the oil but is usually employed more as a guard to protect an area.

[450]

After this, I contriv'd to take with me, whenever I went into the country, a little oil in the upper hollow joint of my bamboo cane, with which I might repeat the experiment as opportunity should offer; and I found it constantly to succeed.

In these experiments, one circumstance struck me with particular surprize. This was the sudden, wide, and forcible spreading of a drop of oil on the face of the water, which I do not know that any body has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking-glass that lies horizontally; the drop remains in its place, spreading very little. But when put on water it spreads instantly many feet round, becoming so thin as to produce the prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance. It seems as if a mutual repulsion between its particles took place as soon as it touched the water, and a repulsion so strong as to act on other bodies swimming on the surface, as straws, leaves, chips, &c. forcing them to recede every way from the drop, as from a center, leaving a large clear space. The quantity of this force, and the distance to which it will operate, I have not yet ascertained; but I think it a curious enquiry, and I wish to understand whence it arises.

Notice the color variation in the water. Describe the contaminated water. Are Franklin's observations similar to yours? Why or why not?

When oil is spilled on water, does it float on top, sink to the bottom, or get dispersed throughout the water?

What other methods have been used to clean up oil spills.
What new methods can you suggest?

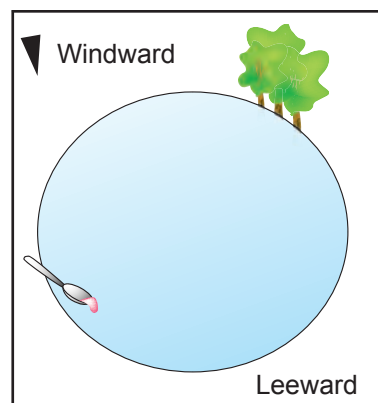
Read Benjamin Franklin's original discussion, which is included with your course resources.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ON CLAPHAM POND-1

Benjamin Franklin was interested in the effect of pouring oil upon troubled waters. As a practical man he thought that the effect might help prevent ships from sinking and sailors from drowning. The following quotes are from the 1774 Philosophical Transactions of the Royal Society.

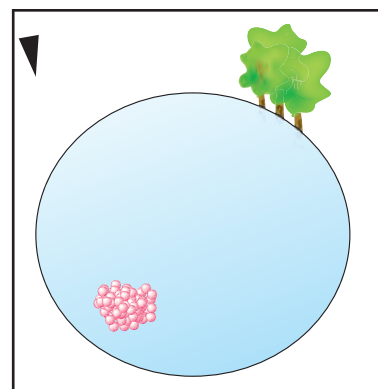
“At length being in CLAPHAM where there is, on the common, a large pond, which I observed to be one day very rough with wind, I fetched out a cruet of oil, and dropt a little of it on the water.”



6

“I saw it spread itself with surprising swiftness upon the surface; but the effect of smoothing the waves was not produced...”

Why not?

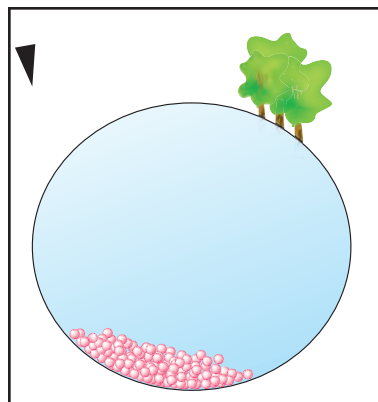


7

“...for I had applied it first upon the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore.”

What would you have done next after getting this result?

Why do you suppose the wind pushed the oil upon the shore when the wind does not push the water upon the shore. Or does it?



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ON CLAPHAM POND-2

Visit a small or medium sized pond on a windy day. Observe the character of the waves both on the leeward and the windward sides. Repeat Franklin's experiments on both sides of the pond and describe your results.

"I then went to the windward side, where they began to form..."

Olive oil is attracted to the water. How does this experiment support this statement?

Olive oil is attracted to itself. How does this experiment support this statement?

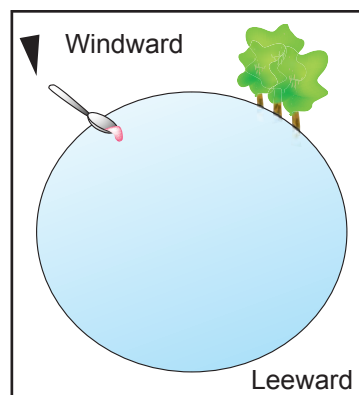
"...and there the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square..."

What do you think would happen if the olive oil molecules were smaller than water molecules?

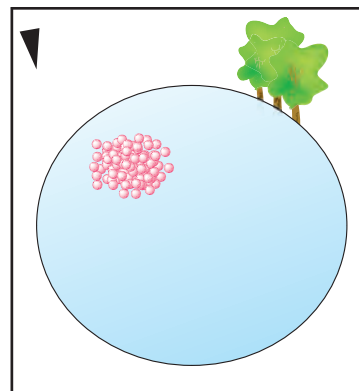
"...which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass."

You might suppose that the oil spread because it was blown by the wind. Do you think that there might have been another reason why the oil spread?

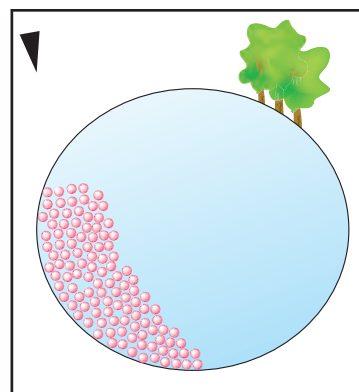
What do you think Franklin would have found if he had returned to look at the pond the next day? Why, from a molecular point of view do you think that?



9



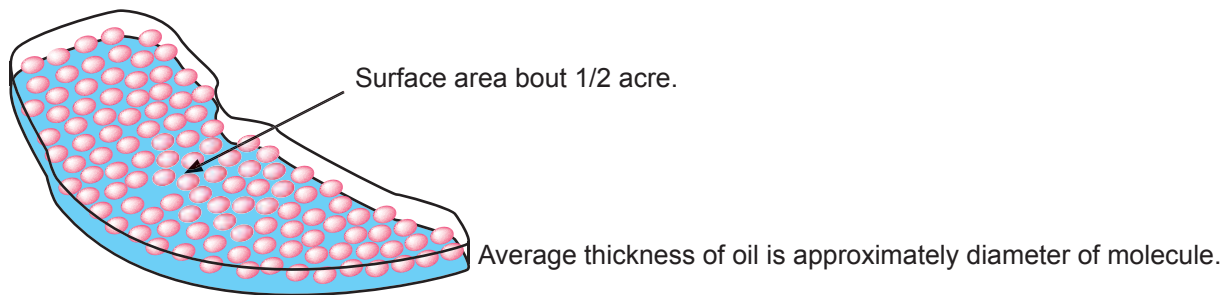
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

SURFACE AREA CALCULATION



12

One acre = 43,560 square feet = 4,840 square yards = 4047 square meters.

It is reasonable to approximate “perhaps half an acre” as 2000 square meters.
Call the surface area A
 $A = 2000 \text{ m}^2$
Call the diameter of the oil layer D .
Call the volume of the oil V .
From geometry, $V = AD$
But eighteenth century teaspoons in museums hold approximately two cubic centimeters, so we know that
 $V = 2 \text{ cm}^3$
Now we can put our facts together and see that
 $2 \text{ cm}^3 = 2000 \text{ m}^2 \times D$
You can finish the calculation.

Benjamin Franklin could have done this calculation but he did not. Why do you think that he did not? What implications would it have had for the development of science if he had?

A few years ago Professor Stephen Thompson of Colorado State University attempted to repeat Franklin’s experiment by dropping olive oil onto City Park lake in Fort Collins. It did not work. Why not?

We are assuming that the oil, after spreading to half an acre, was one molecular layer thick. Of what significance for our assumption is the fact that after spreading to half an acre the oil STOPPED spreading.

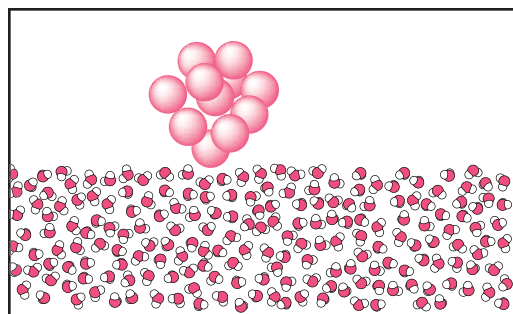
Calculate the number of molecules in Dr. Franklin’s teaspoonful.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

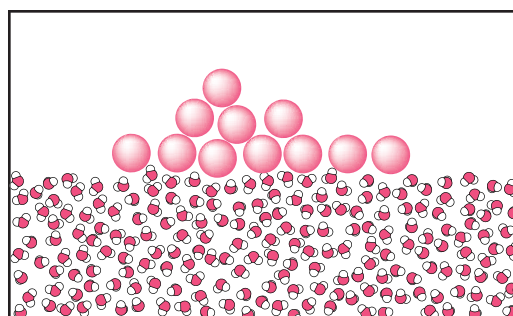
OIL ON WATER

If you look closely at the pictures on the right you will notice that the positions and/or orientations of (some of) the water molecules have changed. Did you try the experiment of placing a drop of oil on ice? Did the oil spread? Can you explain why the motion of the water molecules is necessary for the oil to spread? Could the spreading of the oil be simply due to the random motion of the water molecules? Could it be due to the weight of the oil pushing itself flat across the water?

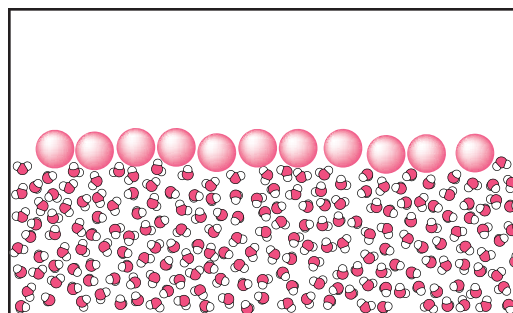
Did you try the experiment of placing a drop of mineral oil on water? Did it spread? How does that fact fit with the explanation of spreading as due to random molecular motion or to the weight of the oil?



13



14



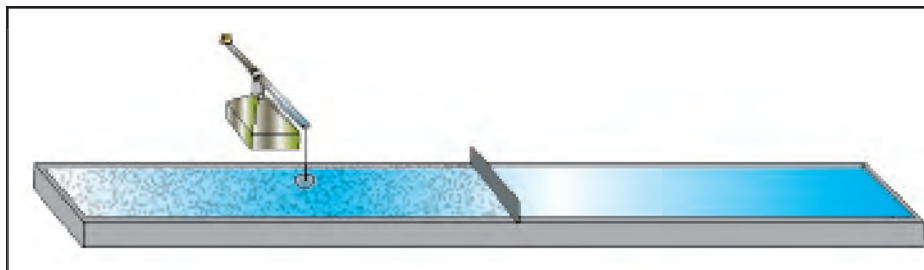
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AGNES POCKLES

In 1891 the famous scientist Lord Rayleigh (who won the 1906 Nobel Prize for the discovery of Argon) received a letter from an unknown German lady, Agnes Pockles. An English translation of the letter was published in Nature on March 12, 1891.

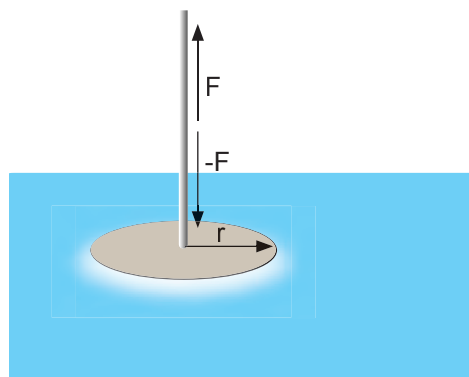
Pockles found experimentally that the surface tension of a saturated solution of sodium chloride was 15.4% greater than the surface tension of pure water. Can you give a molecular explanation for that fact?



16

Agnes Pockles experimental apparatus for measuring surface tension.

The picture on the right shows Pockles' method of measuring surface tension. From this method, discuss why the units of surface tension are Newtons per meter. Devise another method of measuring surface tension.



17

Among Pockles' results were the following:

"...that the surface layer of water can take up more of soluble substances than the internal liquid..."

and similarly

"...in which a thin disk of camphor, so hung that it is half immersed in the cleanest possible water surface, is cut through in the course of a few hours."

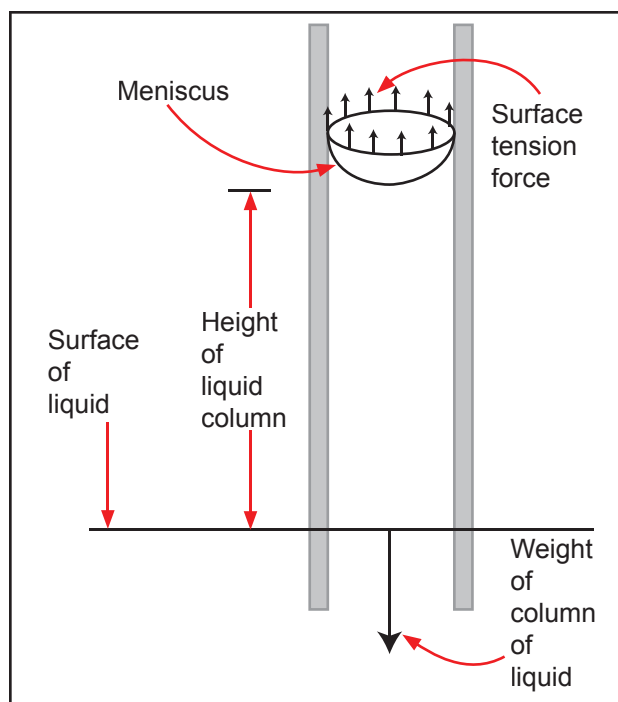
Explain what you can deduce about the molecular nature of water surfaces from these observations?

Read Ms. Pockles letter to Lord Raleigh, as translated and published in Nature, which is included in your course resources. Explain what you consider to have been her most significant or interesting results.

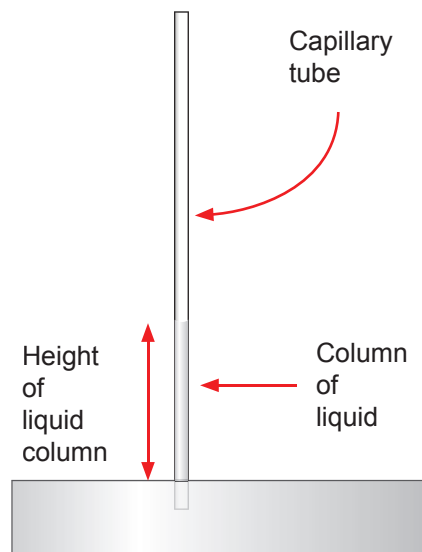
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MEASURING SURFACE TENSION BY THE CAPILLARY METHOD

The Pockles method of measuring surface tension is rather difficult to use but here is a simpler method, although it still requires careful technique.



18



19

Using the capillary method, measure the surface tension of different fluids, including distilled water, soapy water, tap water, an aqueous salt solution and ethanol. (The density of 95% by volume ethanol is 0.82g cm^{-3} .)

Why is careful attention to cleanliness essential for this measurement? When the liquid used is water, should the capillary tube material be hydrophilic or hydrophobic and what would happen if it were the opposite.?

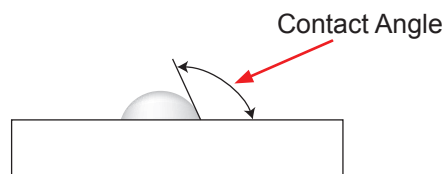
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

CONTACT ANGLES

We can often surmise the interaction between a liquid and a solid by observing the contact angle between a droplet of the liquid placed on the surface of the solid.

What can you determine about the relative hydrophilicity of the four surfaces illustrated in the drawings to the right? Assume that the droplet is made of water.

Place droplets of water on various surfaces, including both clean and dusty glass, different plastics and metals. Observe and draw the contact angles and discuss the hydrophobicity or hydrophilicity of the substances. Repeat the experiment with other liquids such as alcohol and various vegetable and mineral oils.



20



21



22



23



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

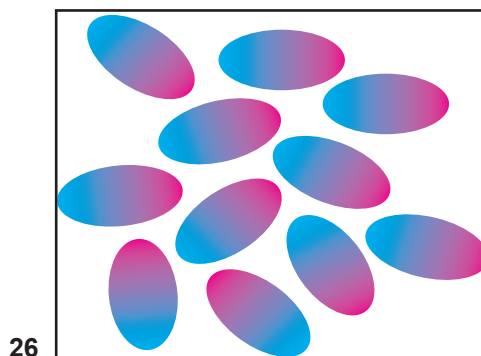
INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the structure of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?
Why is it more important in liquids than in gases?
Can homonuclear diatomic molecules such as H_2 , O_2 and N_2 have dipole-dipole forces?



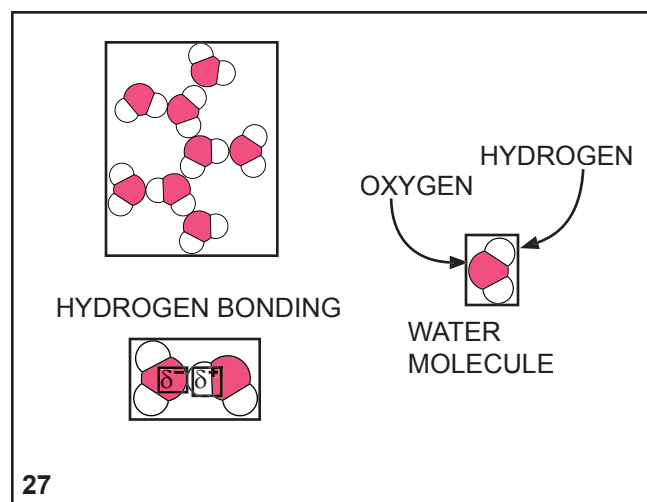
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DIPOLE DIPOLE INTERACTION

HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom.

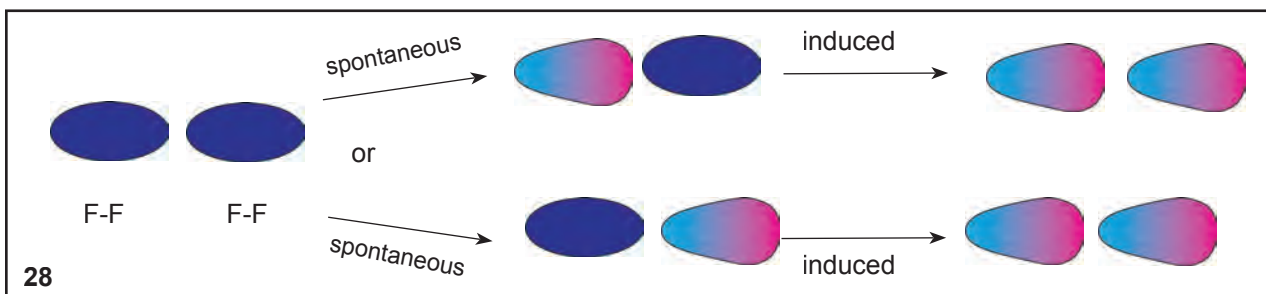
Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.



27

LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecule so that the two molecules have opposite charges on their near sides and attract each other.



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

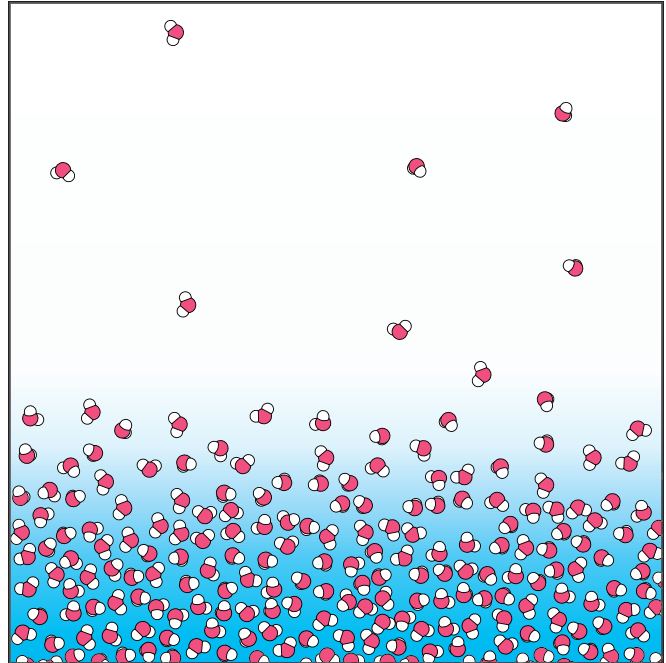
SURFACE TENSION

In the drawing on the right, circle a water molecule in the bulk of the water, a water molecule in the air and a water molecule in the surface layer of the water.

We know that it takes energy to evaporate water and that water molecules in air have a higher energy than water molecules in the liquid. What about water molecules in the surface layer?

What happens, in terms of energy, when we move more molecules from the bulk into the surface by stretching the surface layer?
What does this imply about the shape of a water/air interface, i.e. a surface?

The surface tension of water is 7.2×10^{-3} Newtons per meter. Multiply this by one square meter. What is the resulting unit? What kind of thing is that? (e.g. force, energy, viscosity,...?)



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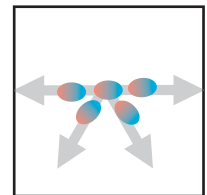
DISPELLING THE MYTHS

Some people may think of surface tension as implying some sort of skin or film on the surface, but we know that is almost the opposite of the truth.

A more sophisticated myth, because it is in the chemistry and physics textbooks, is that surface tension arises because, while a molecule in the bulk of the liquid is pulled equally in all directions by its neighboring molecules, a molecule on the surface is not pulled in the upward direction. This is a true statement about forces but its result is to keep the surface a surface and has nothing to do with surface tension.

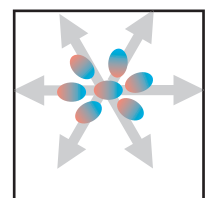
With the model of surface tension presented here it is possible to deduce whether surface tension would increase or decrease with increasing temperature, say from 300 K to 310K. Which is it?

In what direction is the resultant force on the surface molecule?



30

Forces on a surface molecule.



31

Forces on a bulk molecule.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AMPHIPHILIC OIL ON WATER

What are the three types of inter-molecular forces involved in this system? (Hint: water-water (hydrogen bonding) is one.)

By referencing these three forces, how does palmitic acid spread into a monolayer? How do the relative strengths of these three forces compare to each other?

Does the surface tension of the water increase or decrease at the palmitic acid/water interface?

Using a similar molecular force description, why doesn't motor oil spread into a monolayer on water?

Draw a picture of what a "puddle" of motor oil on water might look like.

Draw a molecular picture of what the interface of the motor oil/water puddle might look like.

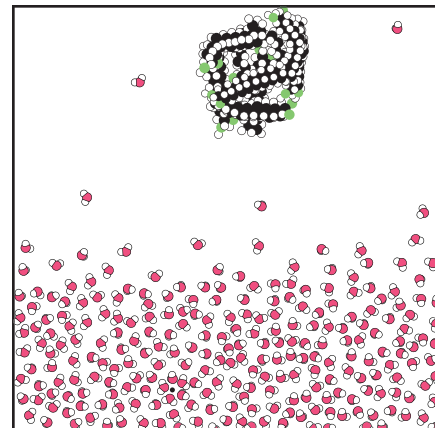
Why does the palmitic acid form a monolayer? Why don't individual palmitic acid molecules "break off" from the edges? (Or water penetrate the interior of the mono-layer, separating portions of it?)

Why is the constant molecular motion of the water surface necessary for the oil to spread? Incidentally, this is why oil will not spread to form a mono-layer on a glass surface.

Devise an experiment to show whether the time required for the oil to spread is dependent on the temperature of the water. What is your hypothesis?

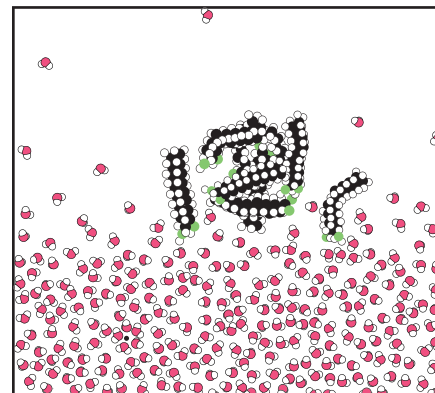
Perform the experiment. Report your results.

Why are there individual water molecules "floating" in the air above the surface?



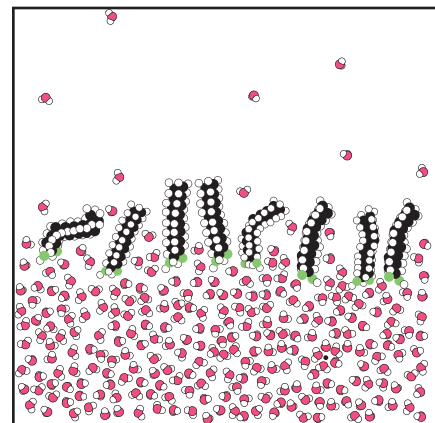
34

A small drop of palmitic acid falling towards a water surface.



35

The palmitic acid reaches the surface.



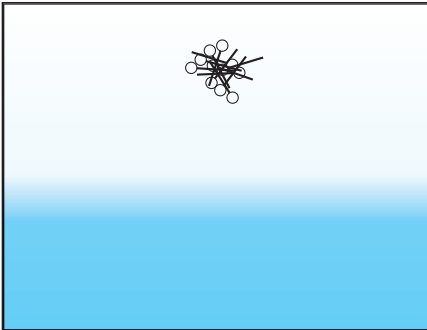
36

The palmitic acid spread into a monolayer.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

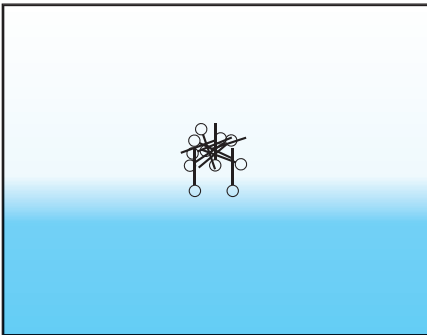
AMPHIPHILIC OIL ON WATER

37

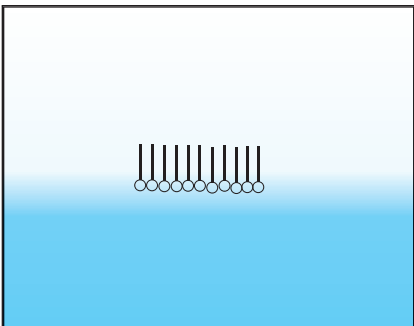


Using a simplified form such as the ones shown here - and it might be easier to put in the water with a blue marker- draw the sequence of molecular events if a drop of mineral oil were placed on water. Remember to modify the oil molecules to show that they are nonpolar.

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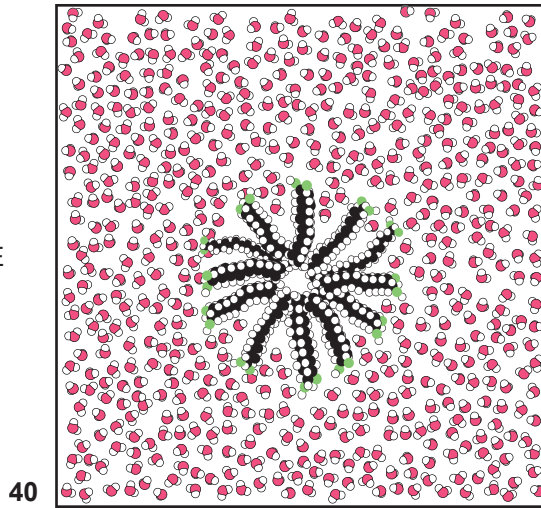
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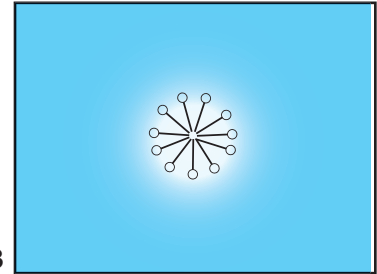
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AMPHIPHILIC OIL AND WATER

MICELLE

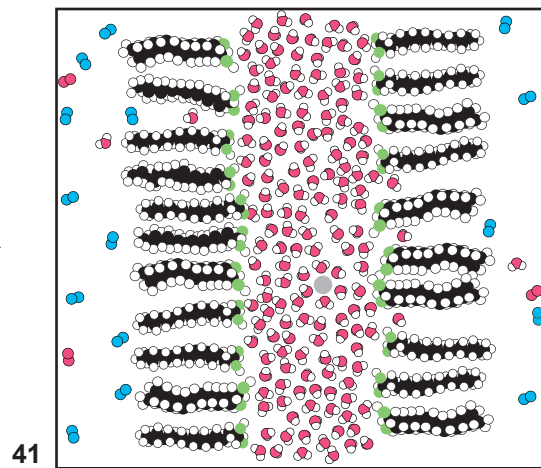


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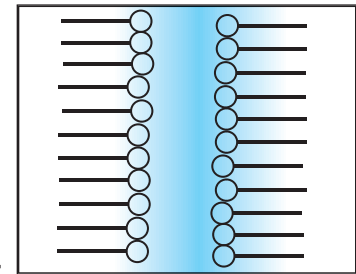


Investigate and describe occurrences of micelles, bilayers and vesicles. Give a molecular explanation for their occurrence and properties.

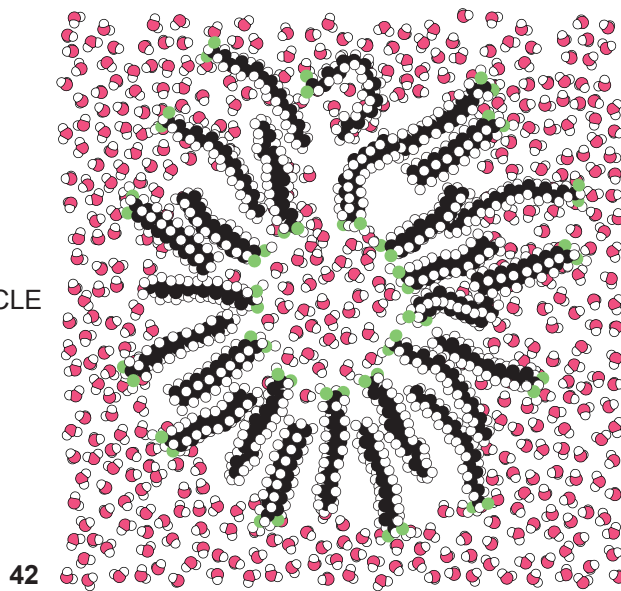
BILAYER



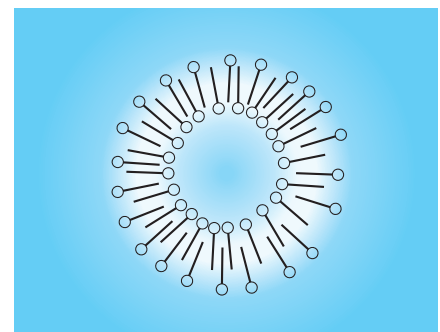
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VESICLE



45



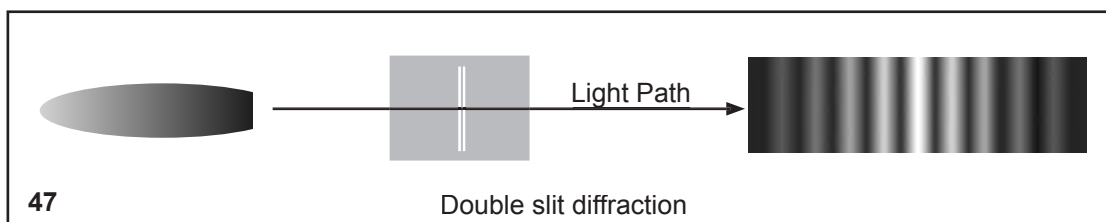
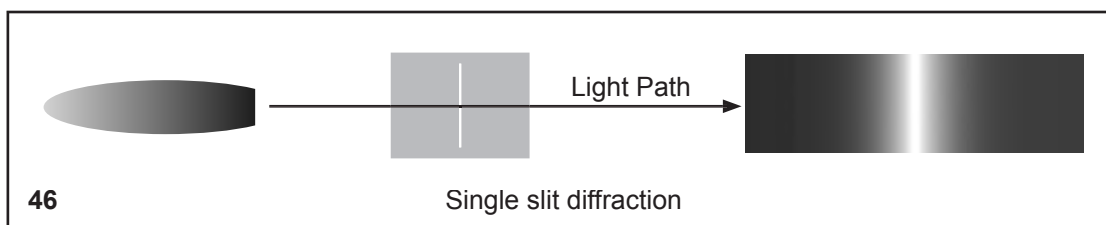
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MODERN MOLECULAR IMAGING

We began investigating molecules through the simple technology of placing oil on water and we have seen Ms. Pockles device. But this is the 21st century and we can now look at molecules directly. Among the modern methods of seeing molecules we will look at x-ray diffraction, atomic force microscopy and the scanning tunneling microscope.

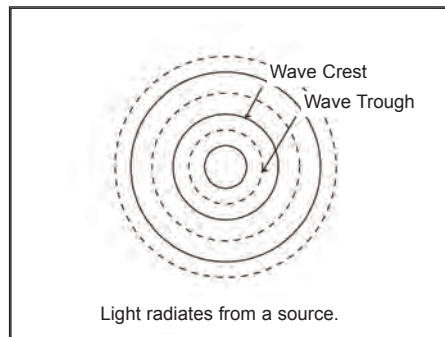
DIFFRACTION

Hold a sharp edge object, such as a pencil, at various distances away from a flat white surface in direct sunlight. From observing the shadows produced, what can you deduce about the nature of light?

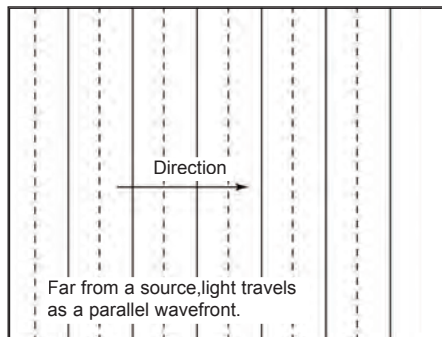


DO MOLECULES EXIST AND HOW SMALL ARE THEY?

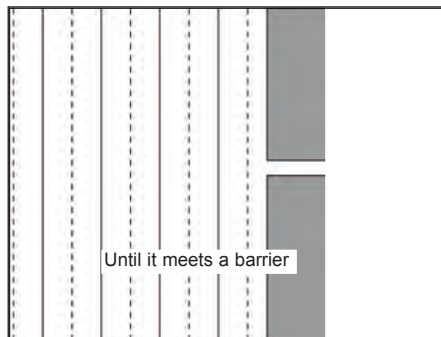
DIFFRACTION



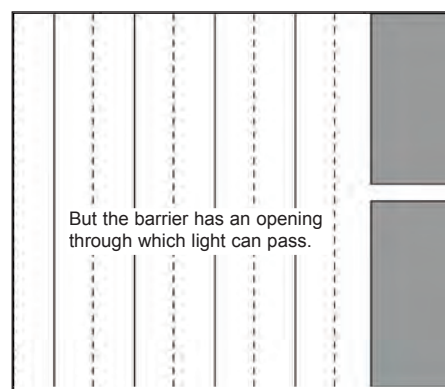
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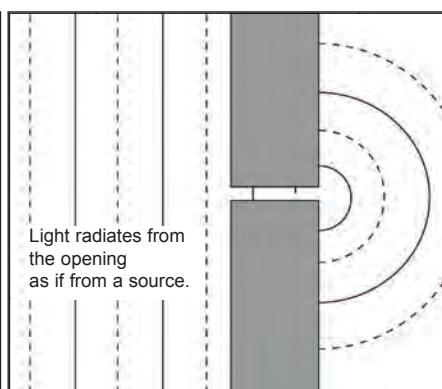
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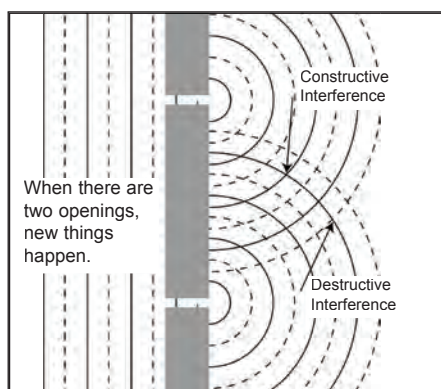
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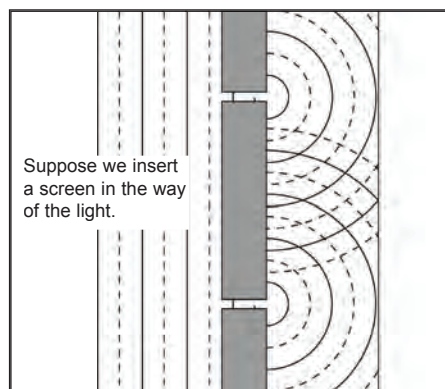
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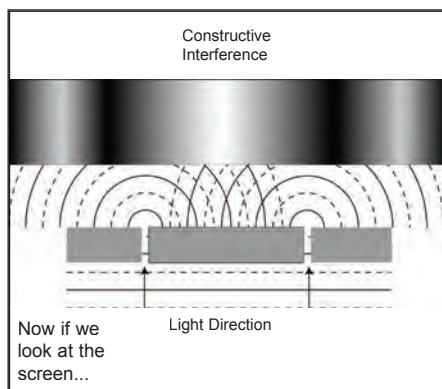
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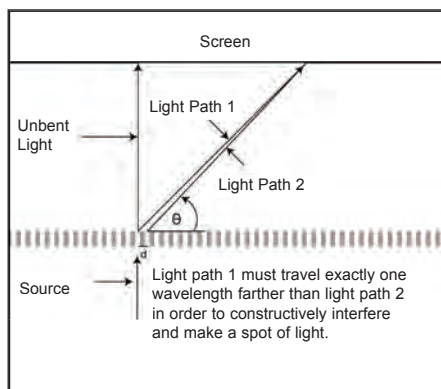
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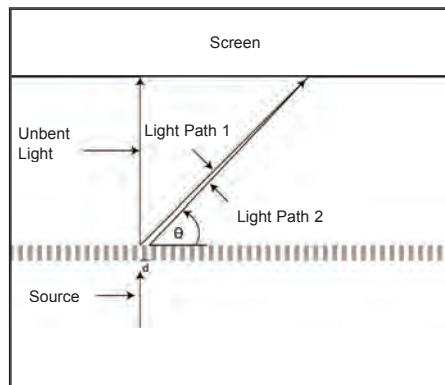
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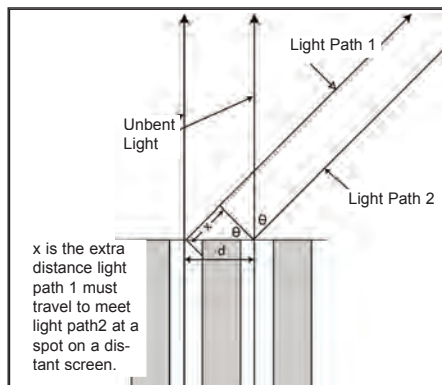
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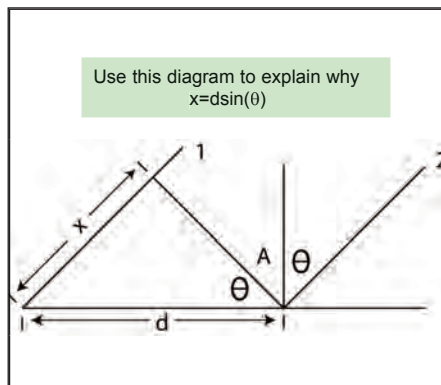
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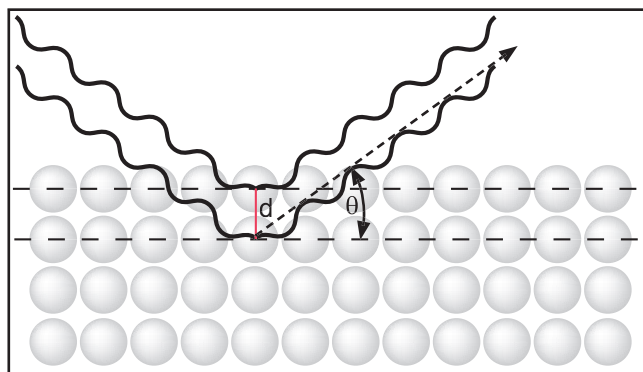
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

X-RAY DIFFRACTION

There are several methods of X-ray diffraction but they all depend upon the wavelength of X-rays being the same order of magnitude, or smaller, than atomic sizes or the spacing between atoms.

Also, X-rays are reflected from the electron clouds of atoms and molecules, rather than from the nuclei.



In the picture above two x-rays arrive and are reflected from the substance at the same angle θ . When the angle is just right, the bottom wave will travel exactly one wavelength farther than to top wave and so the two waves will be in phase and interfere constructively, giving a dot on a screen. The relationship which connects the angle of reflection, the wavelength, λ , of the x-rays and the distance, d , between atomic (or molecular) planes is given by Bragg's Law.

$$n\lambda = 2d\sin(\theta)$$

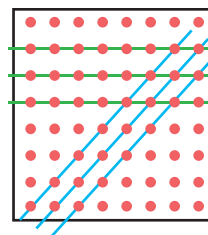
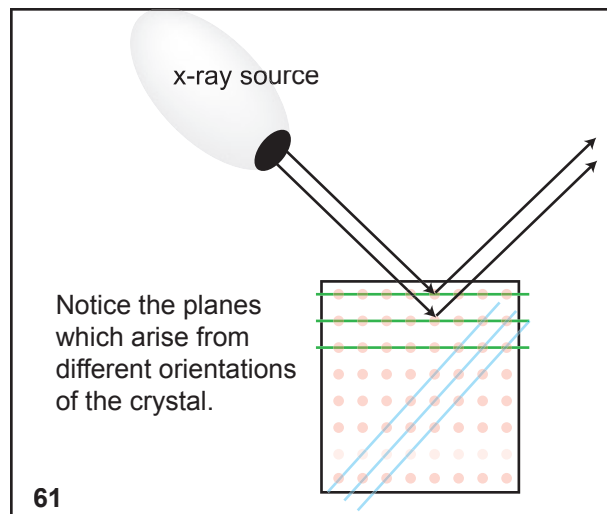
where n is a small positive integer.

When we are trying to find the separation d , which is effectively the atomic or molecular size, we solve the equation for d and then substitute experimentally determined values for λ and θ .

$$d = \frac{n\lambda}{2\sin(\theta)}$$

Compare the process of using x-ray diffraction for deducing crystal structure to the process of using a diffraction grating for spectroscopy. In what ways are the processes alike and in what ways do they differ?

Why can visible light waves not be used to measure atomic sizes?



Find some other planes in the pattern shown.

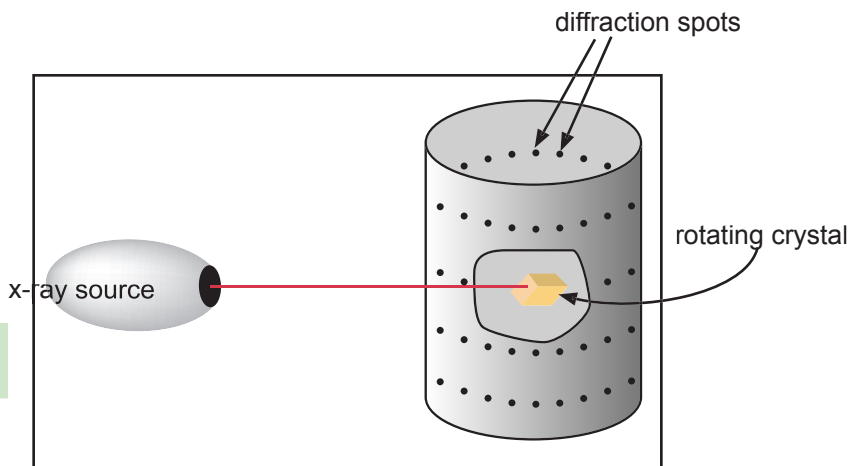
Suppose you could see at one meter wavelength. Describe, preferably by drawing, what the world would look like.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

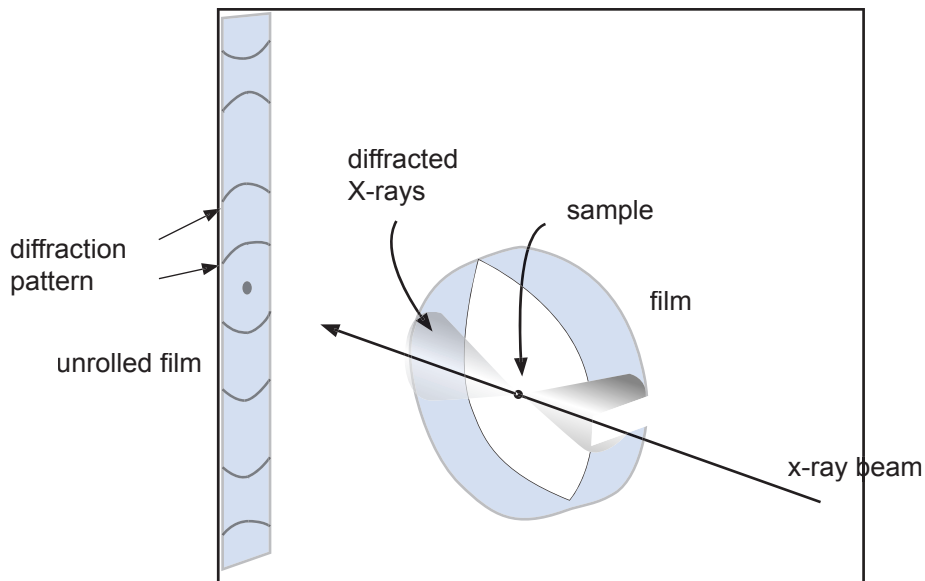
X-RAY DIFFRACTION

Explain why it is necessary to use a single crystal in the rotating crystal method?

How would you use x-ray diffraction to distinguish between glass and quartz?



63 Rotating Crystal Method



64 Powder Diffraction

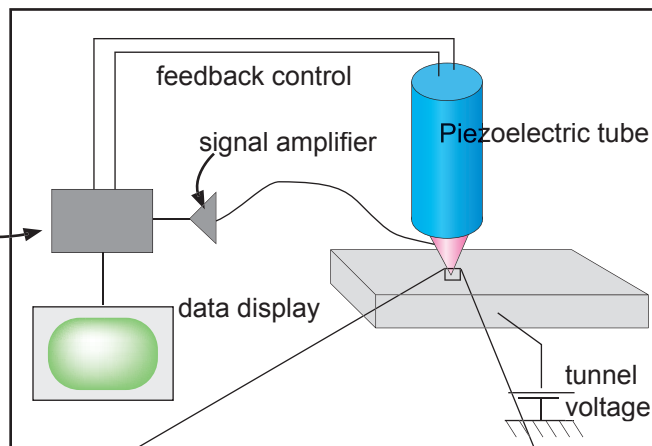
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

THE SCANNING TUNNELING MICROSCOPE

The scanning tunneling microscope (STM) measures the minute current between the atomic surface and the tip of a very fine probe. Because the current is very sensitive to the distance between the probe and the surface, the STM can recognize the bumps on the surface caused by single atoms.

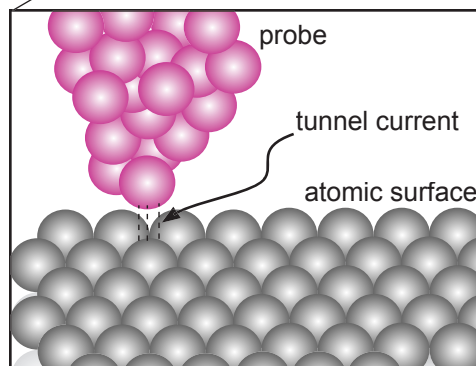
What limitations to the use of STM are implied by the necessity of using a tunneling current?

distance control
and scanning unit



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The piezoelectric effect in some materials provides a transduction between electric currents and mechanical vibrations. Quartz exhibits the piezoelectric effect.

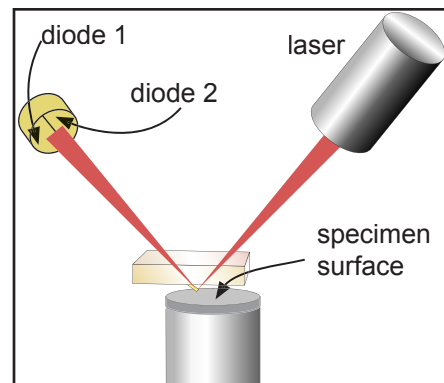


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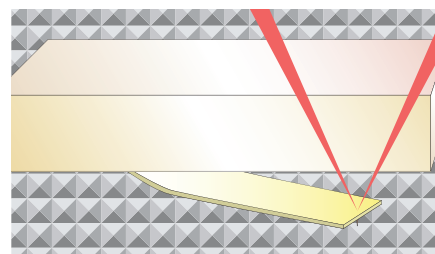
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ATOMIC FORCE MICROSCOPY

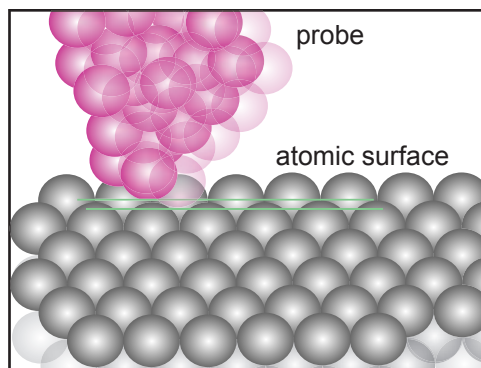
Atomic Force Microscopy relies upon direct contact, or near contact, between a finely pointed probe and an atomic surface. As the probe is moved across the surface, or vice-versa, the probe is pushed or pulled up and down by the variations in height between the top of an atom and the interstices between atoms. This motion is transmitted to a cantilever beam. The effect can be magnified several thousand times by a laser beam reflected off of the cantilever and measured by the relative strength of reception between two adjacent light measuring diodes.



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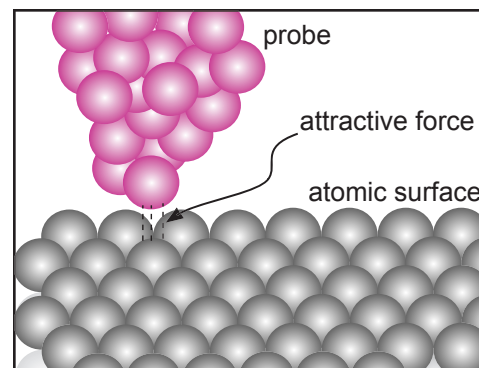


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Contact Mode

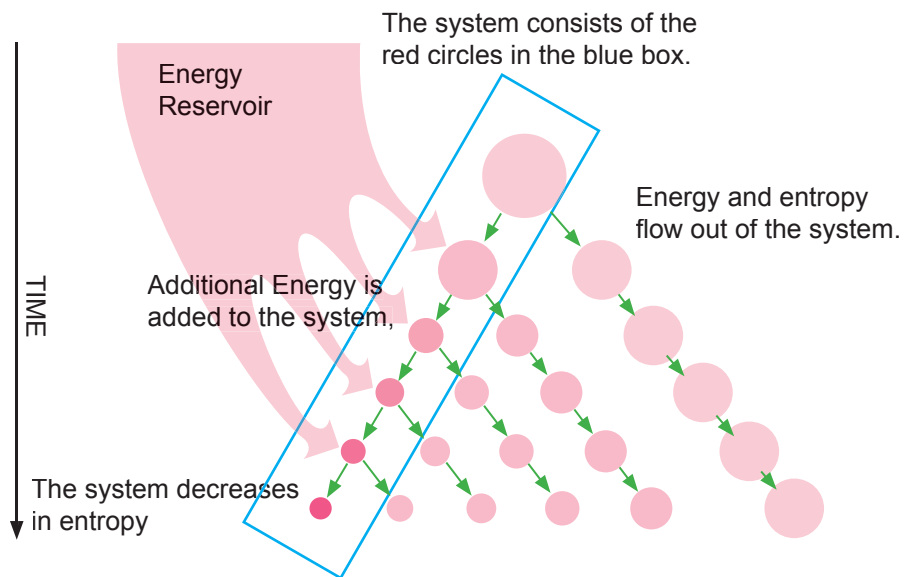


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Attractive Mode

There is a link on our website to another site which offers explanations of several other forms of modern molecular study techniques. Visit at least one of these sites, study the material and write an explanation of the process. Preferably draw it.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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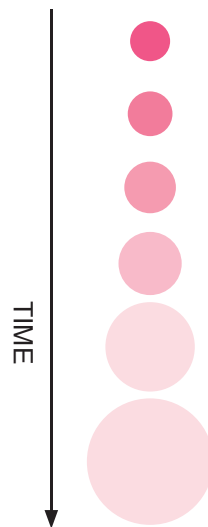
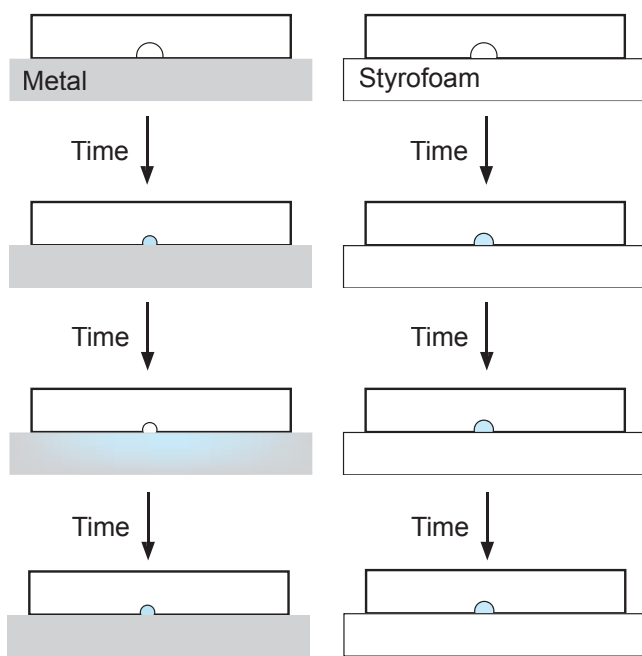
ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

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6	Configurational Entropy
7	Configurational Entropy: Cellular Representation
8	Configurational Entropy: Combined Representation
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19	Periodic Entropy Of The Elements

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

INTRODUCTION TO ENTROPY ENERGY DISPERSES



In the picture above the red ink represents energy. As time proceeds there is the same amount of ink (energy) but it spreads out, becomes less concentrated, disperses. Entropy is the measure of this dispersal. The second law of thermodynamics says that the opposite change is impossible in an isolated system.

In the experiments pictured above, the blue represents cooling, or loss of thermal energy. Is the evaporation of water exothermic or endothermic? What is the evidence? If it is endothermic, how can it proceed spontaneously in the isolated system where the petri dish is placed on styrofoam?

Spontaneous endothermic reactions do occur and that means that there must be another factor than enthalpy involved. Scientists call this factor **entropy**.

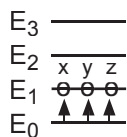


We have personal experience of entropy when we feel the coolness of evaporation.

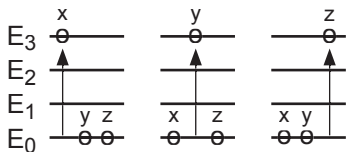
ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

ENTROPY

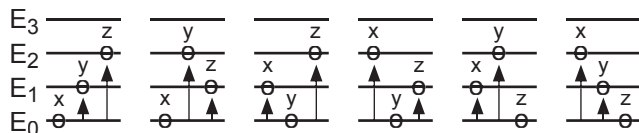
Suppose three molecules have a total of three quanta of energy to share between them and that each molecule can occupy one of four energy states requiring zero, one, two or three quanta to occupy.



Macrostate 1 has one possibility, that is, one microstate.



Macrostate 2 has three possibilities, that is, three microstates.



Macrostate 3 has six possibilities, six microstates.

Suppose each microstate is as likely to be occupied as any other microstate.

What is the most likely macrostate to be occupied? Suppose that the system shifts from one microstate to another at random times, what proportion of the time will the system be in macrostate 1? in macrostate 2? in macrostate 3?

Assume the three quanta of energy are distributed among *four* molecules. How many macrostates will there be and how many microstates will there be for each macrostate? Suggestion: use drawings like the ones above to figure this out.

Assume four quanta of energy are distributed among four molecules with four available energy states.

How many macrostates will there be and how many microstates to each macrostate?

In chemistry there are several different means by which energy can be dispersed and thus entropy created.

These include:

1. The number of molecules among which the entropy can be shared.

The rest of these examples refer to the same number of molecules:

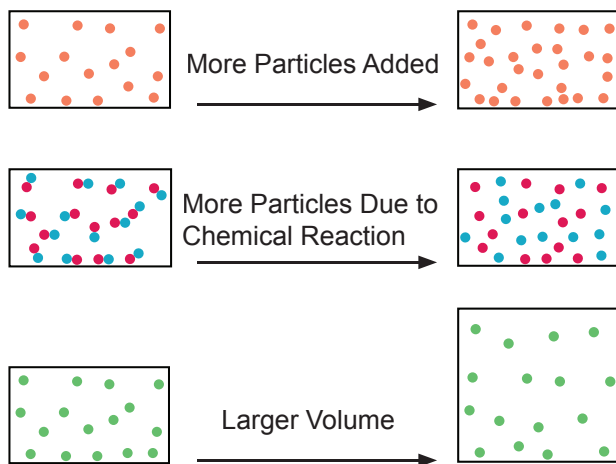
2. The volume of space which the molecules can occupy.

3. The freedom with which the molecules can move about that space, e.g., the difference between a solid and a liquid. This would include the freedom to change location and, in the case of nonspherical molecules, the freedom to change orientation or rotation.

4. The amount of energy available, which determines the range of energy states which the molecules can occupy.

5. The complexity of the molecules, which determines how many rotational and vibrational states they can have.

A modern way to describe entropy is to say that entropy increases with the number of ways energy can be distributed in a system.



In each of the above sets of pictures, there is a change between the left hand side and the right hand side. Explain how the change would increase the number of ways energy can be distributed in the system..

We have described several sources of entropy. You describe several conditions that can restrain the growth of entropy or reduce it in a system.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

ENTHALPY AND ENTROPY

Consider this experiment: a drop of water is placed in a clean Petrie dish and the cover is put on. What happens and what are the causes?

The system is the Petrie dish and its contents. The surroundings include the table and the air outside of the Petrie dish.

In the pictures below, each column shows the same state of the system, but from a different perspective. The first column shows just the changes in molecular location. The second column shows changes in energy (temperature) and the third column shows changes in entropy.



Temperature Increase



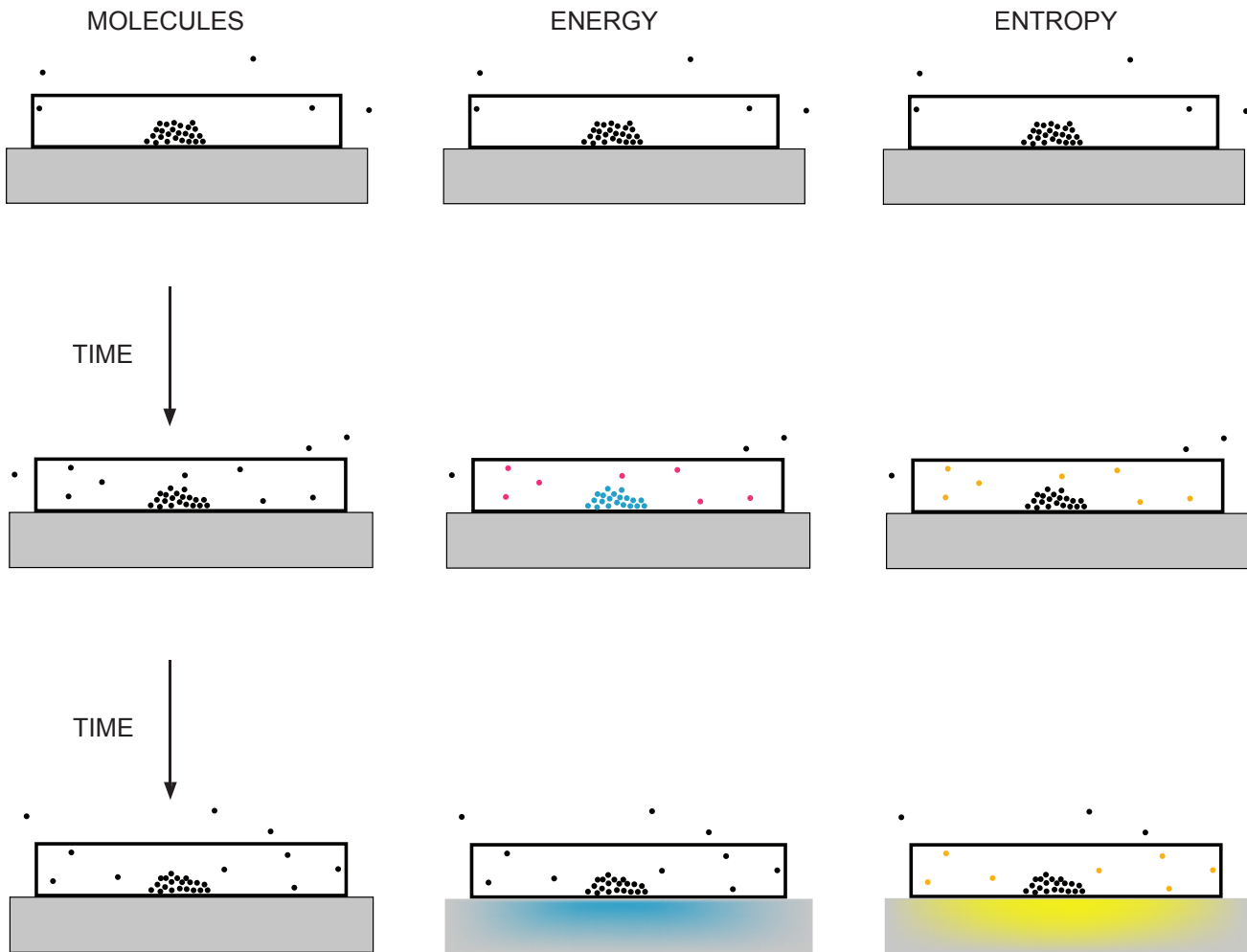
Entropy Increase



Temperature Decrease



Entropy Decrease



Describe what is happening to the molecules. What do you think will happen later?

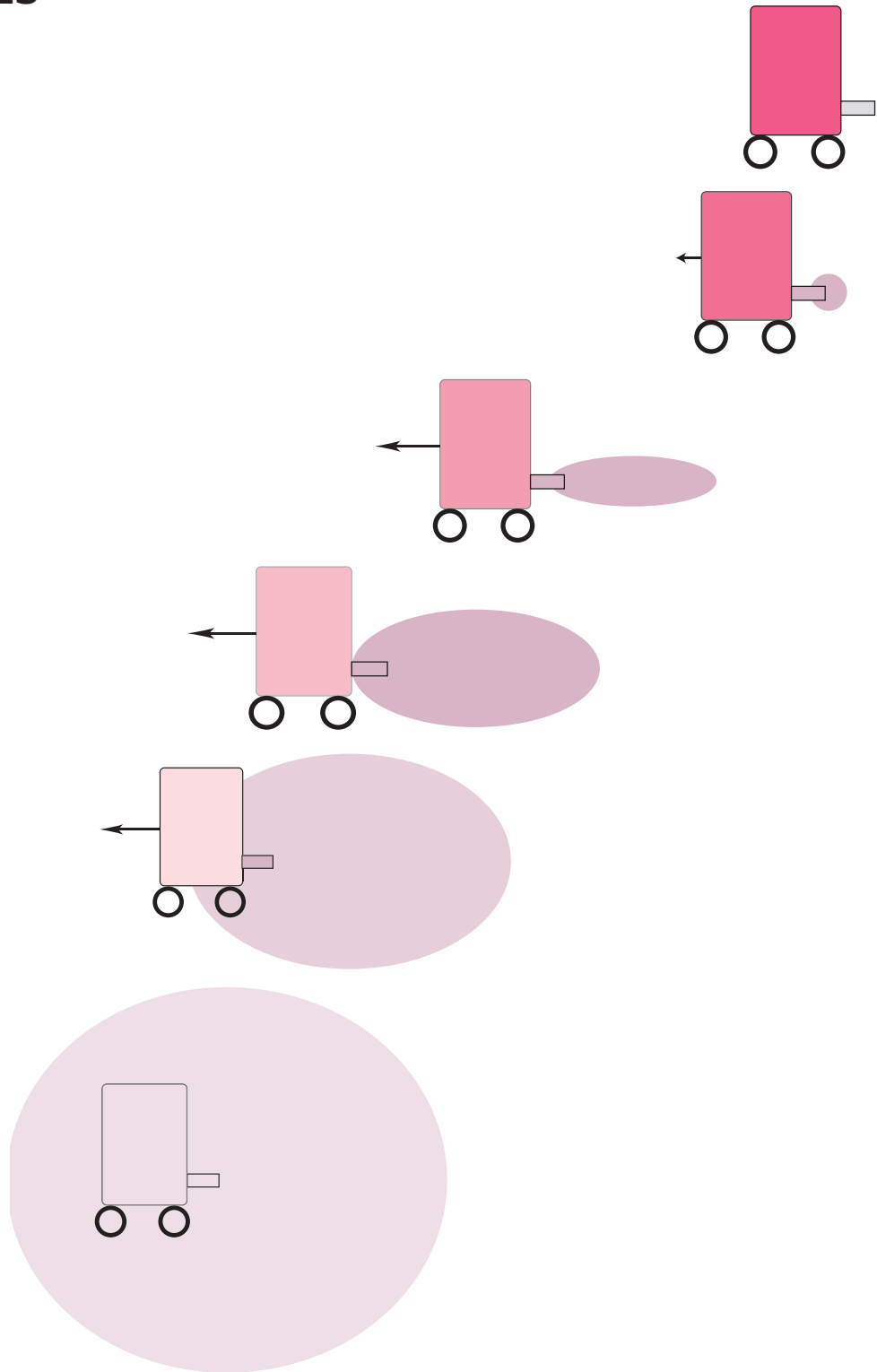
Why are the gas phase molecules warmer than the liquid phase in the intermediate time. Why do they return to equal temperature?

In the energy column, the gas phase molecules return to their original temperature. Why doesn't the same hold true for entropy? Is entropy conserved?

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

THERMAL ENTROPY

FUEL TO FUMES

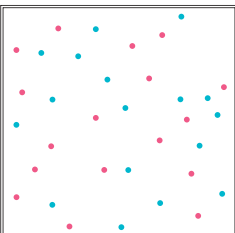
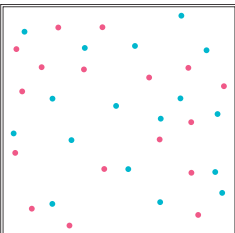
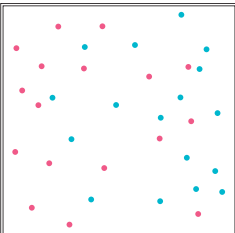
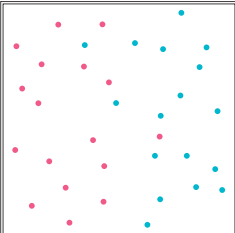
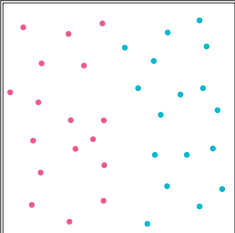
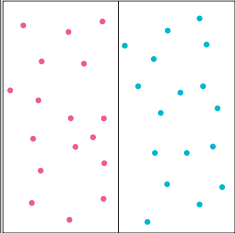


ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

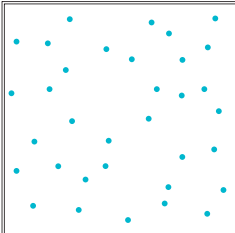
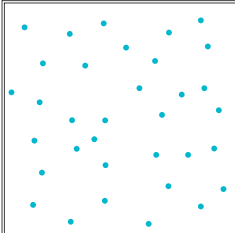
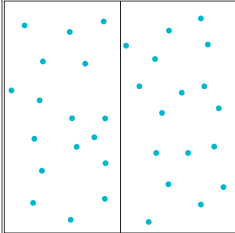
CONFIGURATIONAL ENTROPY

MIXING OF GASES

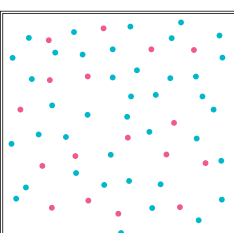
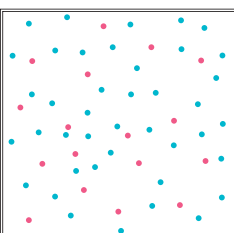
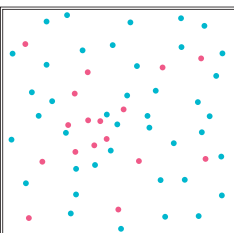
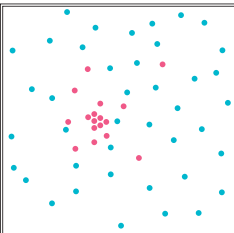
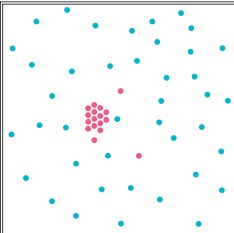
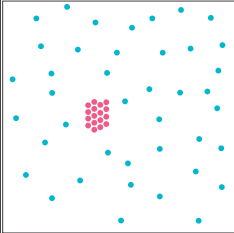
UNLIKE



LIKE



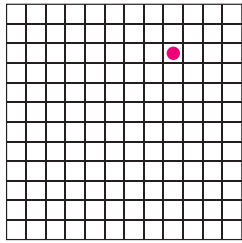
SOLUTION



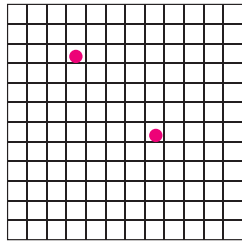
ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

CONFIGURATIONAL ENTROPY: CELLULAR REPRESENTATION

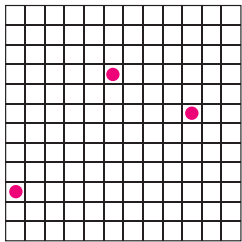
NUMBER OF MOLECULES



$$\Omega = 144$$

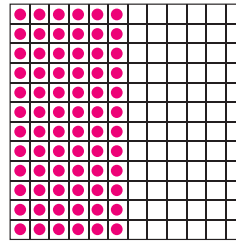


$$\Omega = 144 \times 143$$

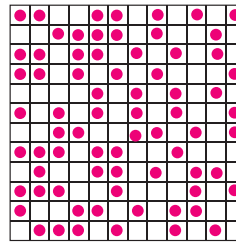


$$\Omega = 144 \times 143 \times 142$$

NUMBER OF STATES

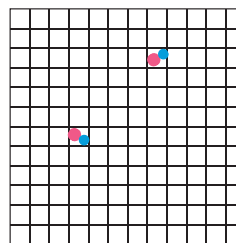


$$\Omega = 4$$

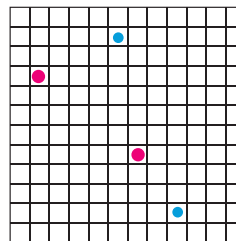


$$\Omega = \frac{144!}{72!}$$

MOLECULAR DISSOCIATION



$$\Omega = 144 \times 143$$

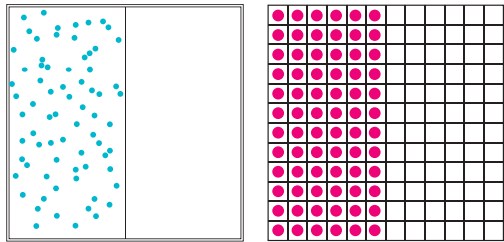


$$\Omega = 144 \times 143 \times 142 \times 141$$

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

CONFIGURATIONAL ENTROPY: COMBINED REPRESENTATION

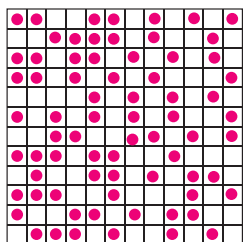
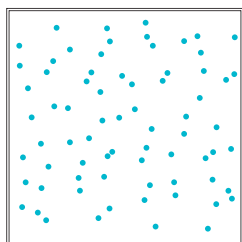
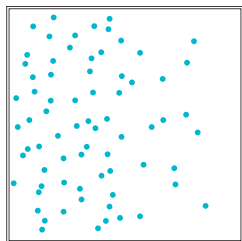
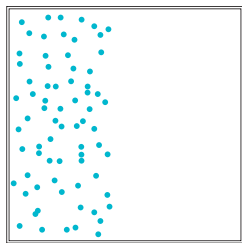
EXPANDING GAS



$$\Omega = 1$$

Molecule Molecular Weight

- Water 18
- Dinitrogen
- Dioxygen
- Argon
- Carbon Dioxide




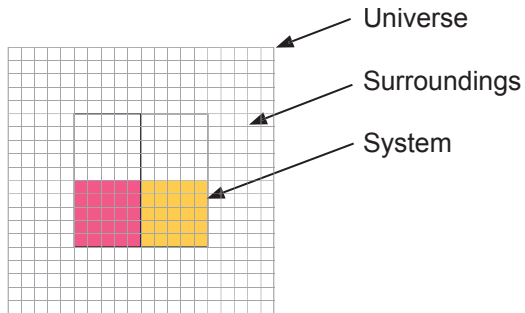
$$\Omega = \frac{144!}{72!}$$

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

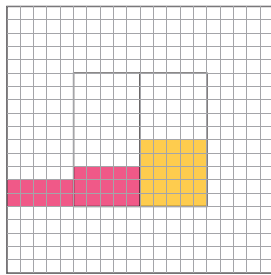
DISPERSIBLE ENERGY

 Enthalpy

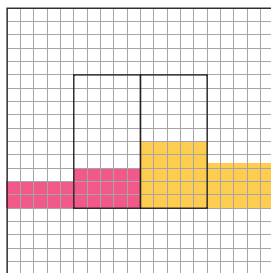
 Entropy



In this pictorial representation, the system is shown qualitatively with an original enthalpy and entropy. In the surroundings - the rest of the universe - the original state is shown blank, since the actual amount of enthalpy and entropy in the universe is uncalculated and since it is the change which is relevant.



$$\Delta H_{\text{Surroundings}} = -\Delta H_{\text{System}}$$

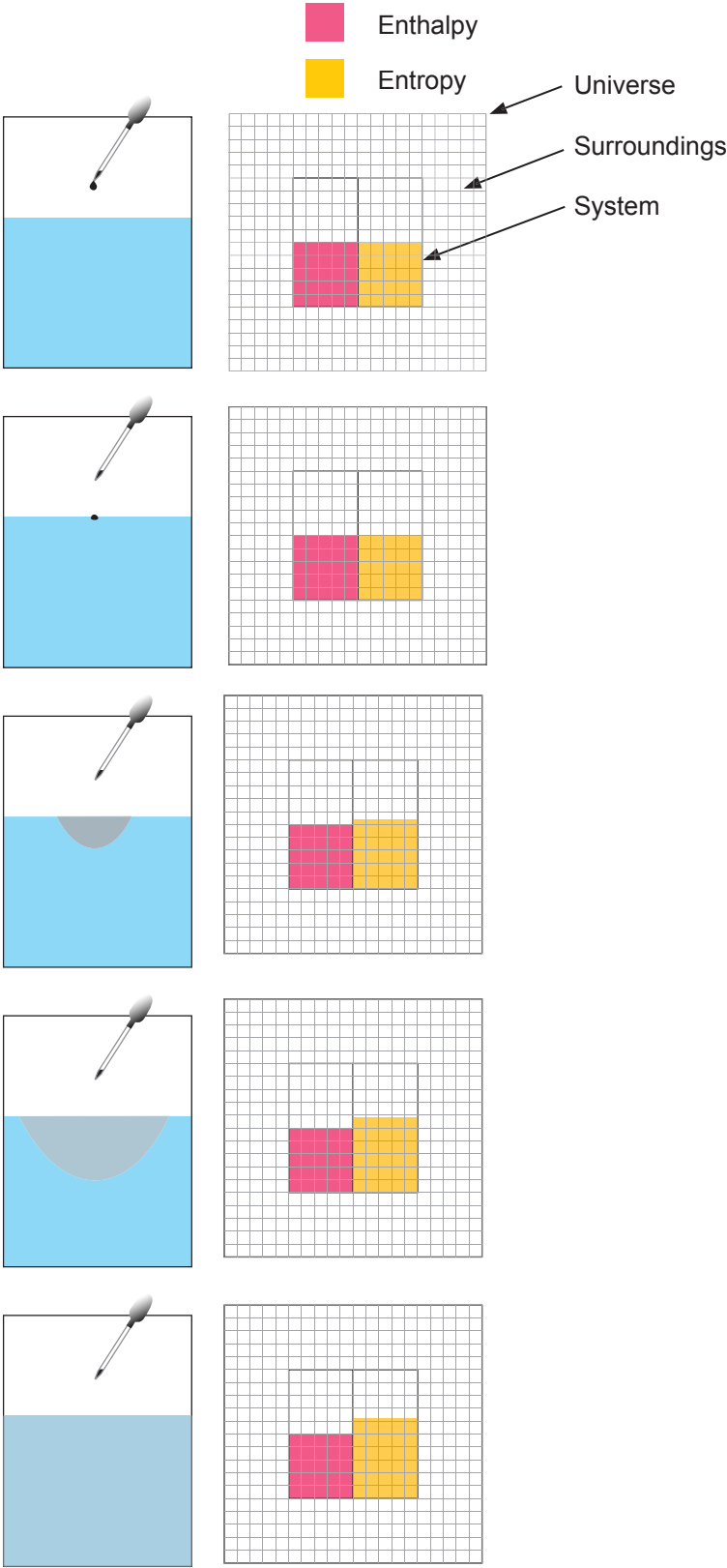


If $\Delta S_{\text{System}} = 0$, then

$$\Delta S_{\text{Universe}} = \Delta S_{\text{Surroundings}} = -(\Delta H/T)_{\text{System}}$$

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

DIFFUSION

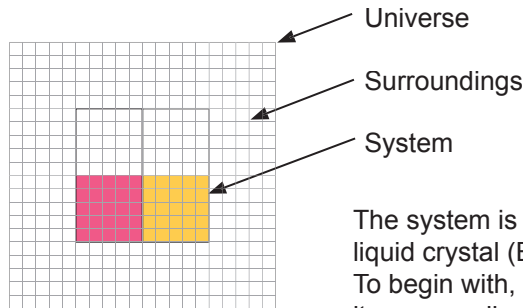
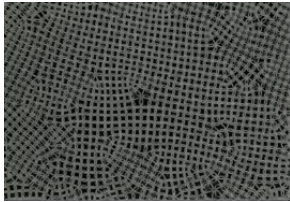


ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

LIQUID CRYSTAL

EXPERIMENT

INTERPRETATION



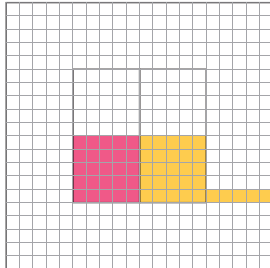
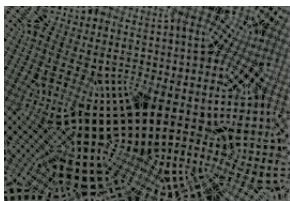
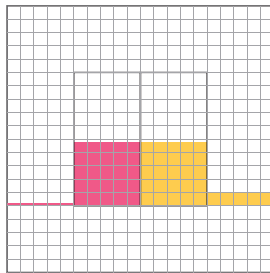
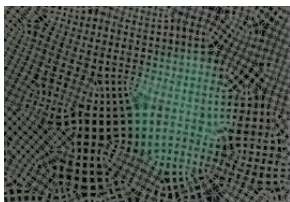
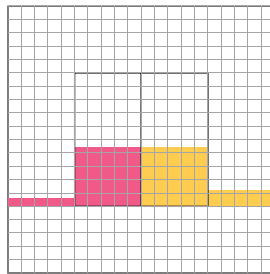
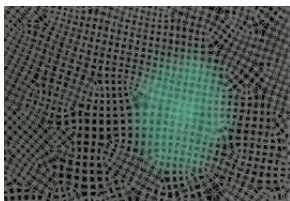
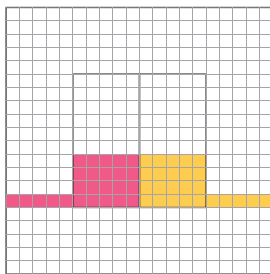
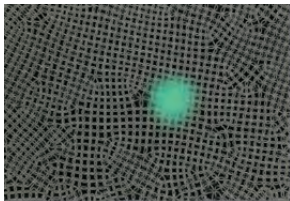
Universe

Surroundings

System

Enthalpy

Entropy



The system is a horizontal rectangle of encapsulated liquid crystal (ELC).

To begin with, the ELC is in thermal equilibrium with its surroundings. The surroundings include the surface upon the which ELC rests and the air above and around it.

A drop of water is placed upon the surface of the ELC. Assume that the water is originally at the same temperature as the system and surroundings (the water is part of the surroundings). **Experiment** shows that the ELC cools beneath the drop as the drop evaporates and then that the cool region both spreads and diminishes in intensity. After the drop is completely evaporated the ELC eventually returns to its equilibrium temperature.

The cooling is due to a warmer than average fraction of the water molecules escaping from the drop; although they lose energy to the work function of the water surface, they nevertheless retain enough energy to cool the drop.

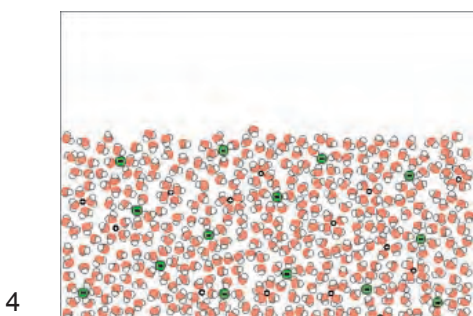
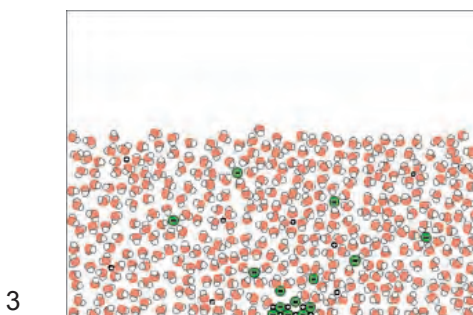
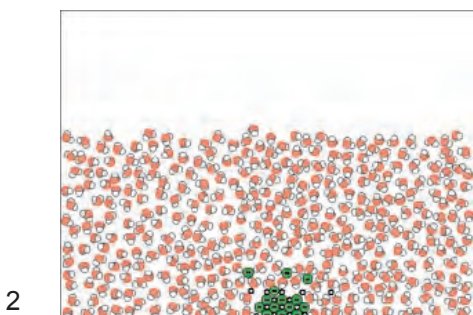
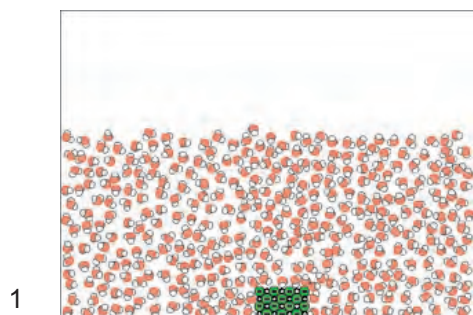
Since the ELC is cooled its entropy is decreased, unless there is an increase in some configurational entropy. The entropy of the water is configurationally increased by evaporation by the energy drawn from the ELC. And since the water is part of the surroundings, the entropy of the surroundings is thereby increased. Also, the thermal energy of the surroundings is increased.

Eventually **we see**, as and/or after the water finishes evaporating, the cool region of the ELC spreads out, diminishing in intensity, and eventually disappears, from which we conclude that the ELC returns to thermal equilibrium with its surroundings.

The entropy of the ELC also re-arises to its original level through absorption of heat from the surroundings. The surroundings will correspondingly return to its same energy level but will retain an increase in entropy; consider that the water which was once a liquid drop is now a gas. Lorem quiscip umsan heniametum ipit,

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

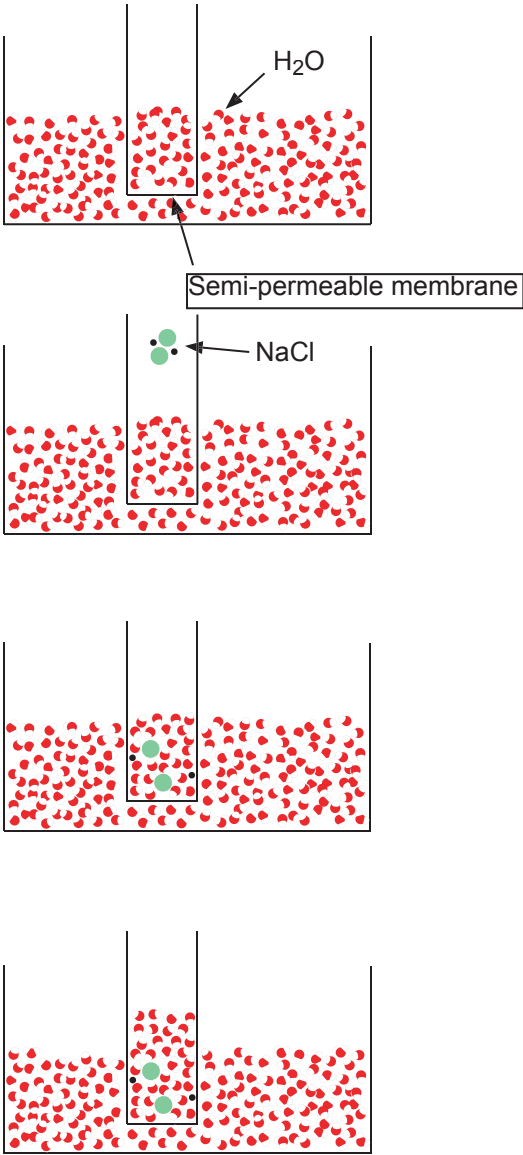
SALT DISSOLVING IN WATER



Ionic solvation in water has a dual entropy effect. The entropy is increased by the additional space occupied by the salt ions, e.g., Na^+ and Cl^- and the entropy is decreased by the orientation of the water molecules about the ions.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

THE PFEFFER TUBE



ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

THE SECOND LAW OF THERMODYNAMICS

In Thermochemistry we have seen that reactions are influenced by the comparative enthalpies of reactants and products. Reactions tend to occur which lower the enthalpy. However, this is not the whole story; there is another factor involved, called entropy.

Entropy has often been described as disorder, which is only partially correct. Here we will look at some types of entropy which are relevant to chemical reactions.

In classical thermodynamics, e.g., before about 1900, entropy, S , was given by the equation

$$\Delta S = \Delta Q/T$$

where ΔS is the entropy change in a system, ΔQ is heat energy added to or taken from the system, and T is the temperature of the system. The units for entropy are Joules/Kelvin, except in chemistry we work with the quantity of a mole, so in chemistry the units of entropy are Joules/mole-Kelvin.

Around 1900 Boltzmann found another basis for entropy as the number of ways a system can be in a given state (actually the logarithm of that number). For example, there are vastly more ways the air molecules in a room can be spread out all over the room than there are ways in which they would all be in one side of the room. Nature just does the most likely thing, when nothing prevents that. This is formally called the Second Law of Thermodynamics and can be stated as follows: **For combined system and surroundings, entropy never decreases.** Actually, it always increases. This is really what makes things happen. The first law of thermodynamics, that energy is conserved, just tells us what can happen; it is the second law that makes things go.

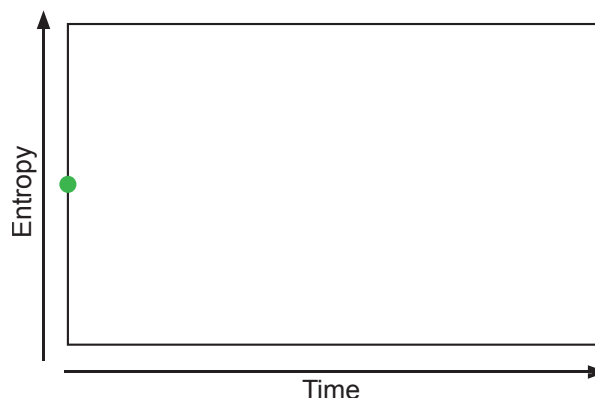
One of the early statements of the Second Law of Thermodynamics is that heat always flows 'downhill'. More exactly, if two bodies are in thermal contact, heat energy will always flow from the warmer to the cooler one.

In terms of heat energy, describe what happens when two bodies at the same temperature are brought into thermal contact? Does it depend upon the sizes of the bodies? Explain your answer.

Compare and contrast the flow of heat energy according to the Second Law of Thermodynamics with the flow of water on earth.

Describe some of the ways the world would be different if heat energy could flow from a cooler to a hotter body. Or what if that always happened?

Another statement of the Second Law is that there is a state variable called entropy which never decreases and, in effect, always increases.



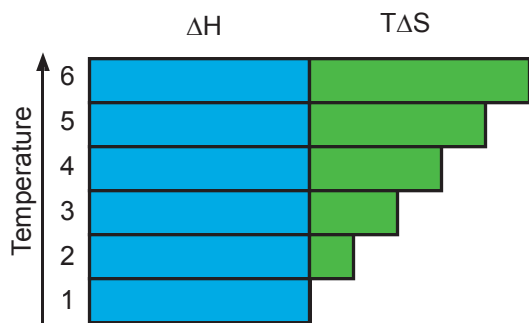
In the box outlined above, the green dot represents the entropy at some starting time. Time passes as we go to the right. Draw a line or curve from the green dot to the right side of the box which represents a *possible* chart of the amount of entropy.

Suppose you know that over a certain interval of time the entropy of a system decreased by the amount, A . What can you say about the entropy of the surroundings over that same interval of time?

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

GIBBS FREE ENERGY

The enthalpy of a system is the energy of the system at constant temperature and pressure. However, not all of that energy is available for the system to do work or contribute to a chemical reaction. There is another factor, which we have introduced as entropy. In order to relate the entropy to the enthalpy we need to multiply the entropy by the temperature (in Kelvin).



Gibbs' free energy, G is defined by $G = H - TS$ where H is the enthalpy, T is the temperature (in Kelvins), and S is the entropy. In a chemical reaction, $R \rightleftharpoons P$ (R are reactants and P are products) at a constant temperature we have $\Delta G = \Delta H - T\Delta S$.

If $\Delta G < 0$ the reaction may proceed spontaneously to the right.

If $\Delta G = 0$ the reaction is in equilibrium.

If $\Delta G > 0$ the reaction may proceed spontaneously to the left.

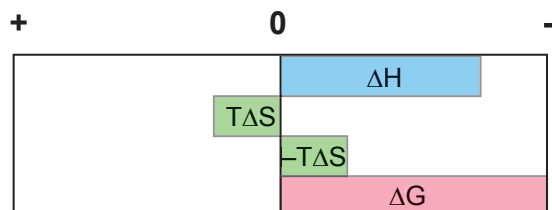
The bar graph above shows ΔH and $T\Delta S$ for the same chemical reaction at different temperatures. At which temperature is the reaction in equilibrium? Which temperature will maximize the reactants? Which temperature will maximize the products?

Since S (entropy) has units of $\text{kJ mol}^{-1} \text{K}^{-1}$ (kilojoules per mole-Kelvin), when we multiply it by K (temperature in Kelvin) we get units of kJ mol^{-1} (kiloJoules per mole), which are the same units as energy. Entropy times temperature is not actually an energy but it controls the availability of energy to do work, such as making chemical reactions happen.

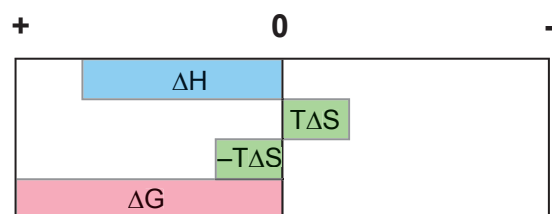
These four ChemLogs show four possible sign combinations for Gibb's Free Energy:

$$\Delta G = \Delta H - T\Delta S$$

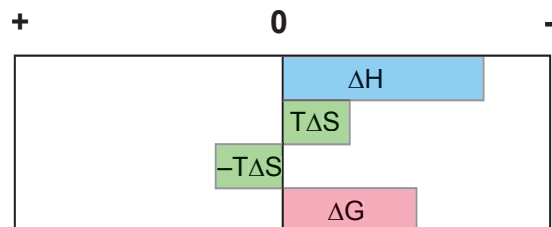
REACTION TYPE ONE



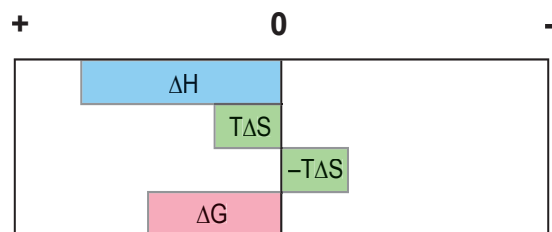
REACTION TYPE TWO



REACTION TYPE THREE



REACTION TYPE FOUR

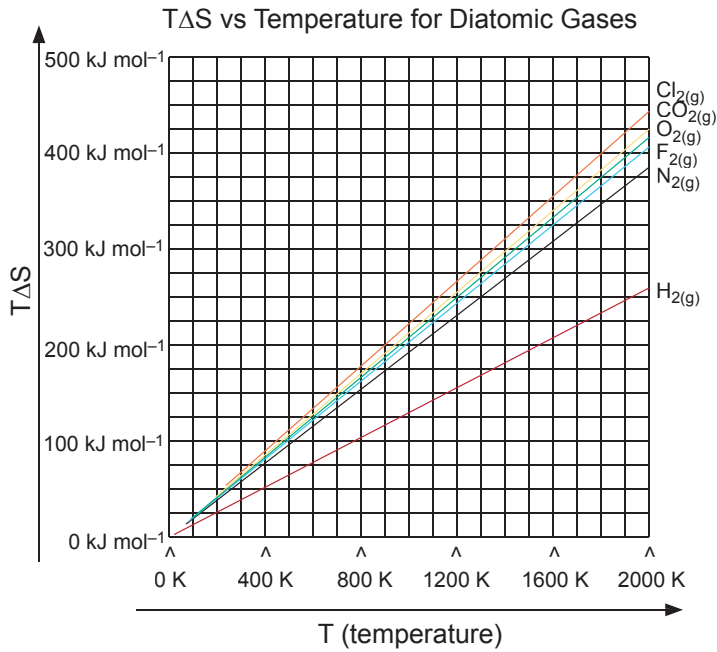


Which of the four reaction types above would be thermodynamically spontaneous? Why? Tell which reaction type each of the following reactions would fit into and explain why.

1. $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$
2. $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
3. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

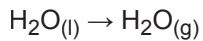
ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

GIBB'S FREE ENERGY AND TEMPERATURE



Using the chart above, describe the relationship, if any, between entropy and molecular weights.

EVAPORATION OF WATER

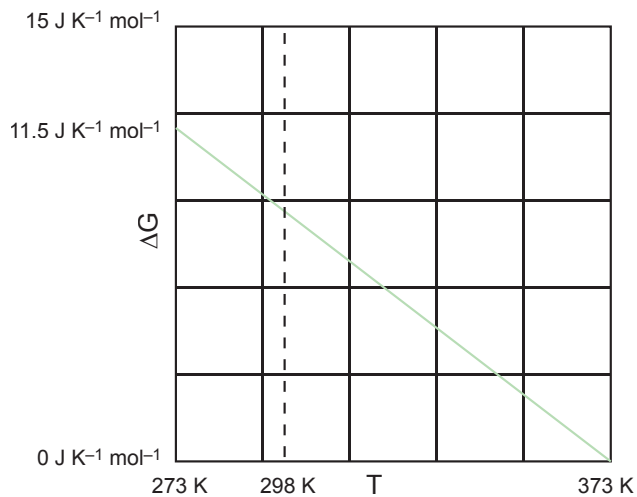


$$\Delta H_f^\circ = 44 \text{ kJ/K mol at } 298.15\text{K}$$

$$\Delta S^\circ = 119 \text{ J/K mol at } 298.15 \text{ K}$$

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ$$

If we make the reasonable approximation that ΔH and ΔS do not (significantly) vary between $T = 273 \text{ K}$ and $T = 373 \text{ K}$, then we can produce the following chart:



ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

GIBB'S FREE ENERGY AND TEMPERATURE

We know that when $\Delta G < 0$ a reaction is spontaneous and when $\Delta G > 0$ a reaction is nonspontaneous. However, ΔG is composed of two terms, an enthalpy term and an entropy term. When both terms pull ΔG in the same direction, then situation is clear, but what can we say in general about situations where the enthalpy and entropy terms are of opposite effect?

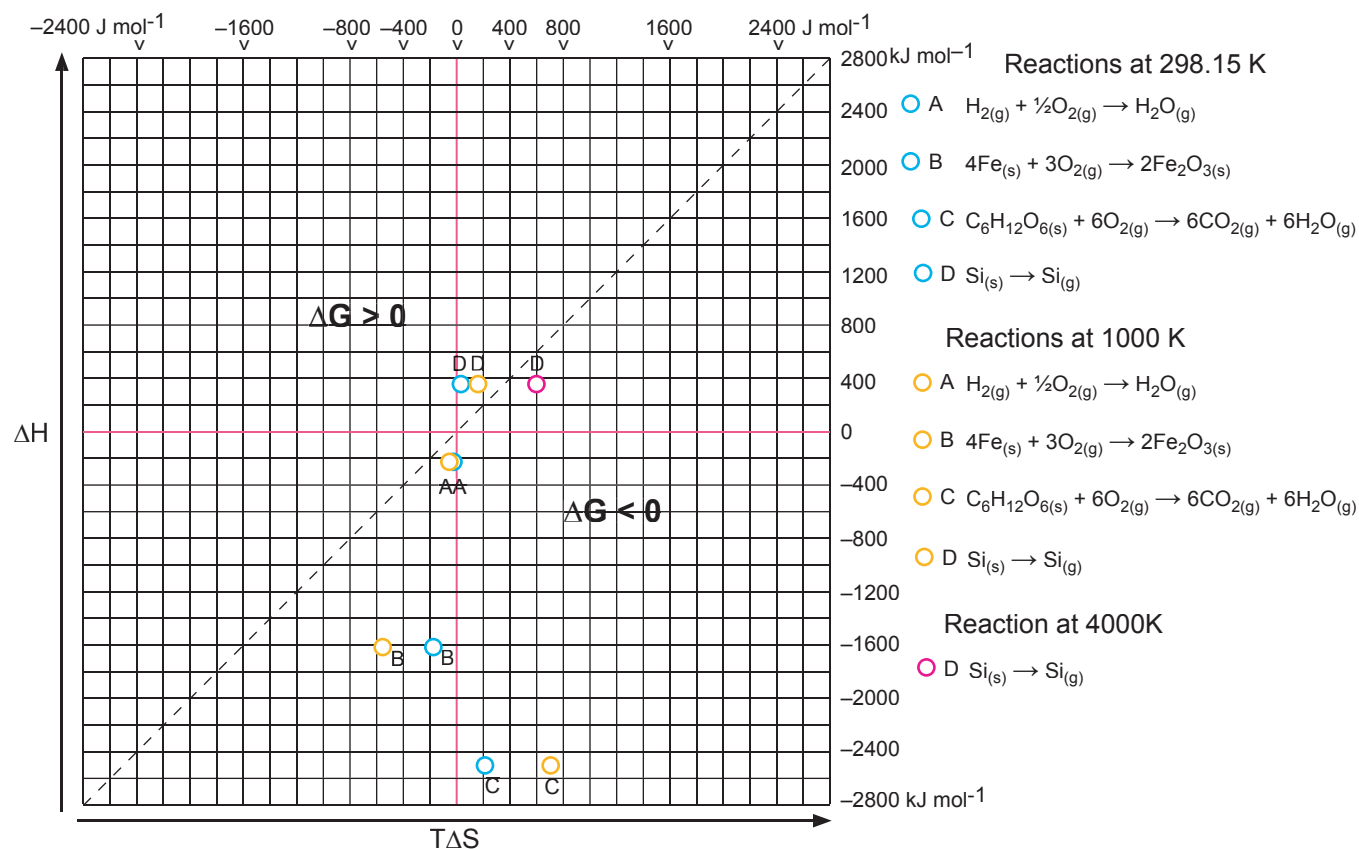
Because the entropy term, $T\Delta S$, is the entropy multiplied by the temperature, we would expect temperature to be an important contributing factor and we are right.

The Effect of Temperature on Spontaneity

1. At high temperatures the entropy factor, $T\Delta S$, predominates
2. At low temperatures the enthalpy factor, ΔH , predominates.

The chart below shows the separate terms, ΔH and $T\Delta S$, which combine to give Gibb's free energy.

Reactions below the dashed line are spontaneous, those above it are nonspontaneous.



You can see that the transition from solid silicon to gaseous silicon (reaction D) moves to the right on the table as the temperature increases. For what values of ΔS will this be true?

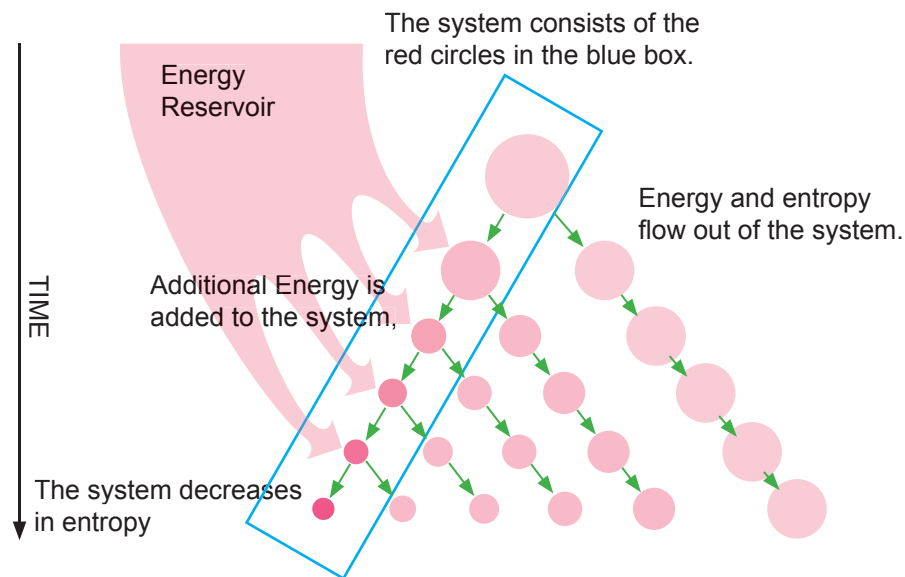
The reaction $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$ has $\Delta H = 3 \text{ kJ mol}^{-1}$ and $\Delta S = 93 \text{ J K}^{-1} \text{ mol}^{-1}$. Mark its location on the graph.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

HOW ENTROPY CAN DECREASE (IN A SYSTEM)

One way of stating the second law of thermodynamics is to say that in any (nonreversible, i.e., real) process the entropy of the system plus the entropy of the surroundings must always increase.

If energy disperses and entropy increases how is it possible that some systems, such as living beings, can maintain their energy and not be quickly dissolved by entropy? There are even systems in which entropy decreases; for example, water can be frozen into ice. This can happen if energy flows out of the system, carrying entropy with it.



Name some systems and processes where entropy decreases in the system.

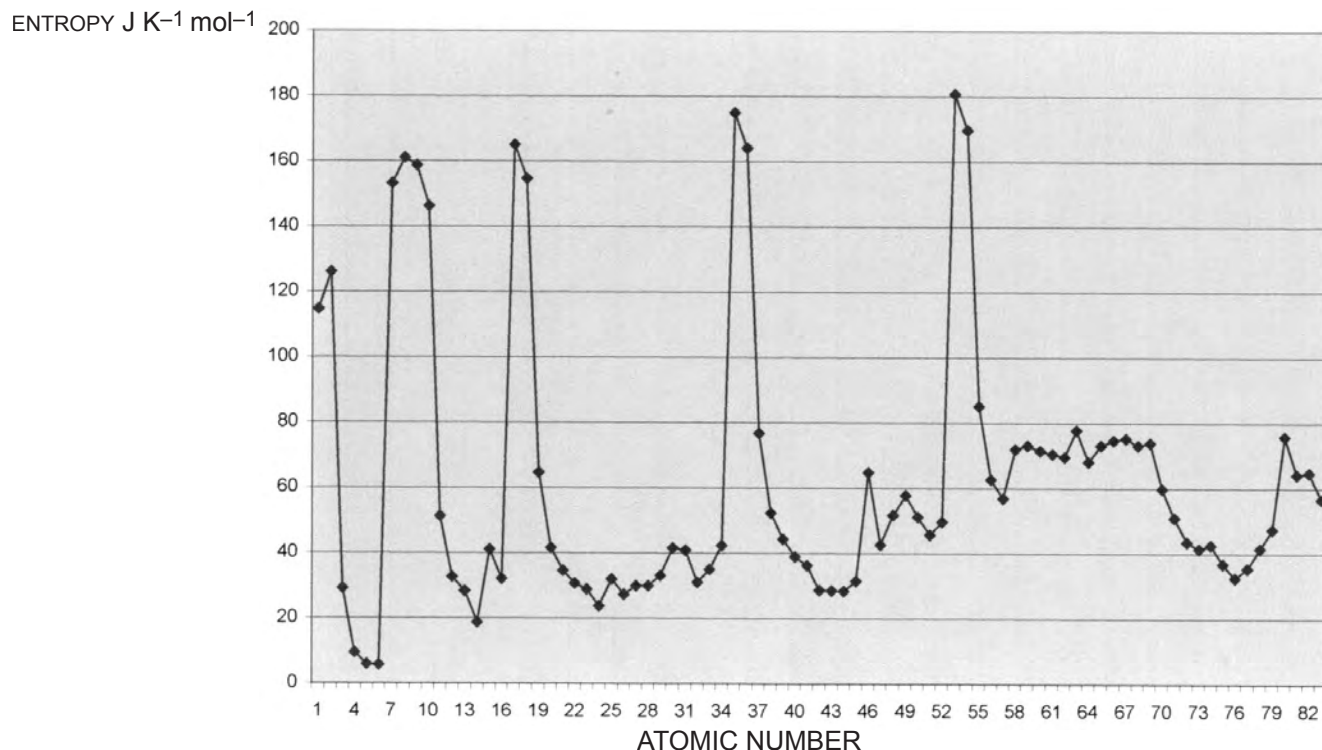
Carefully distinguish between the system and the surroundings and describe the energy and entropy changes which occur when entropy decreases in the system.

As the universe expands its temperature decreases. It is now about 2.7 K. And yet the second law of thermodynamics says that the entropy of the universe always increases. How can these facts be reconciled?

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

PERIODIC ENTROPY OF THE ELEMENTS

ENTROPY OF THE ELEMENTS



In the ENTROPY OF THE ELEMENTS CHART you can see that several of the elements have much higher entropy than the rest. Using the atomic numbers, determine and list what elements these are. Describe what they have in common which results in their high entropies.

ENTROPY INCREASING EVENTS

The following events either always or ordinarily involve an increase in entropy, either in the system or the surroundings or both.

Heating any substance.

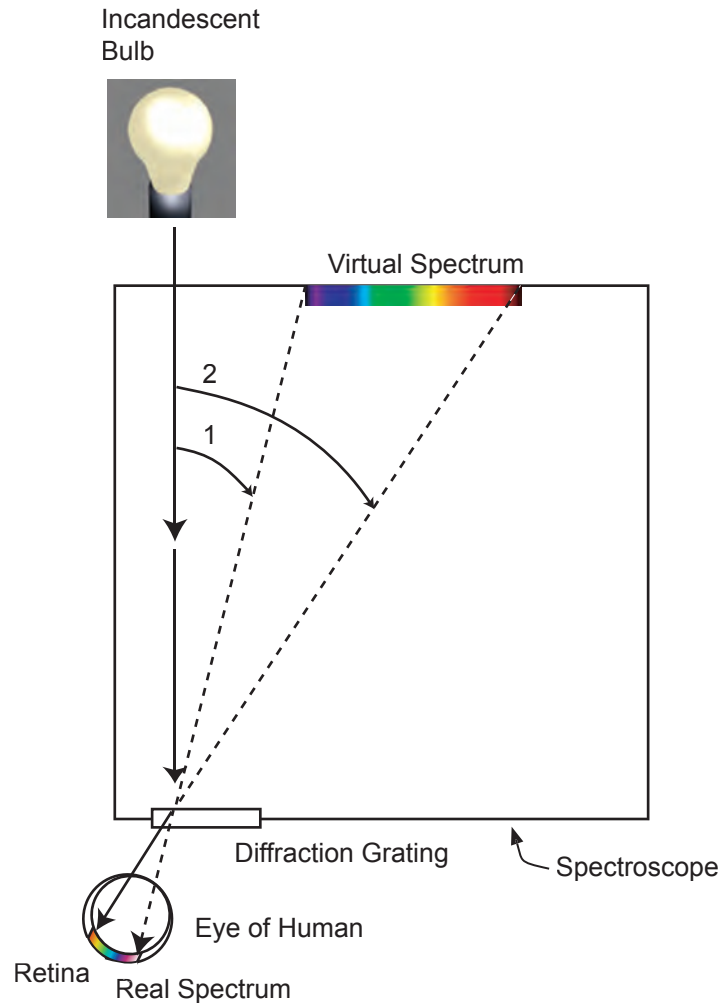
Phase change from solid to liquid and from liquid to gas.

Any reaction that increases the number of moles of gas molecules.

Mixing two different liquids or two different gases.

Dissolving solids in liquids.

FOUNDATIONS OF SPECTROSCOPY



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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FOUNDATIONS OF SPECTROSCOPY

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2	Introduction
3	Electromagnetic Radiation Ruler: The ER Ruler
4	Numbering Electromagnetic Radiation
5	Waves
6	Frequency And Wavelength
7	Questions For The ER Ruler
8	Fundamental Processes
9	Spectroscope
10	Interference: The Principle By Which Light Is Broken Up
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13	Fluorescent Lights
14	Continuous Emission
15	The Origins Of Band Spectra
16	Origins Of band Spectra
17	The Frank-Condon Principle
18	Band Spectra
19	Lasers
20	Simple Spectra
21	Complex Spectra
22	Spectral Questions

FOUNDATIONS OF SPECTROSCOPY

INTRODUCTION

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. When matter is energized (excited) by the application of thermal, electrical, nuclear or radiant energy, electromagnetic radiation is often emitted as the matter relaxes back to its original (ground) state. The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum and the science is appropriately called emission spectroscopy.

Another approach often used to study the interaction of electromagnetic radiation with matter is one whereby a continuous range of radiation (e.g., white light) is allowed to fall on a substance; then the frequencies absorbed by the substance are examined. The resulting spectrum from the substance contains the original range of radiation with dark spaces that correspond to missing, or absorbed, frequencies. This type of spectrum is called an absorption spectrum. In spectroscopy the emitted or absorbed radiation is usually analyzed, i.e., separated into the various frequency components, and the intensity is measured by means of an instrument called a spectrometer.

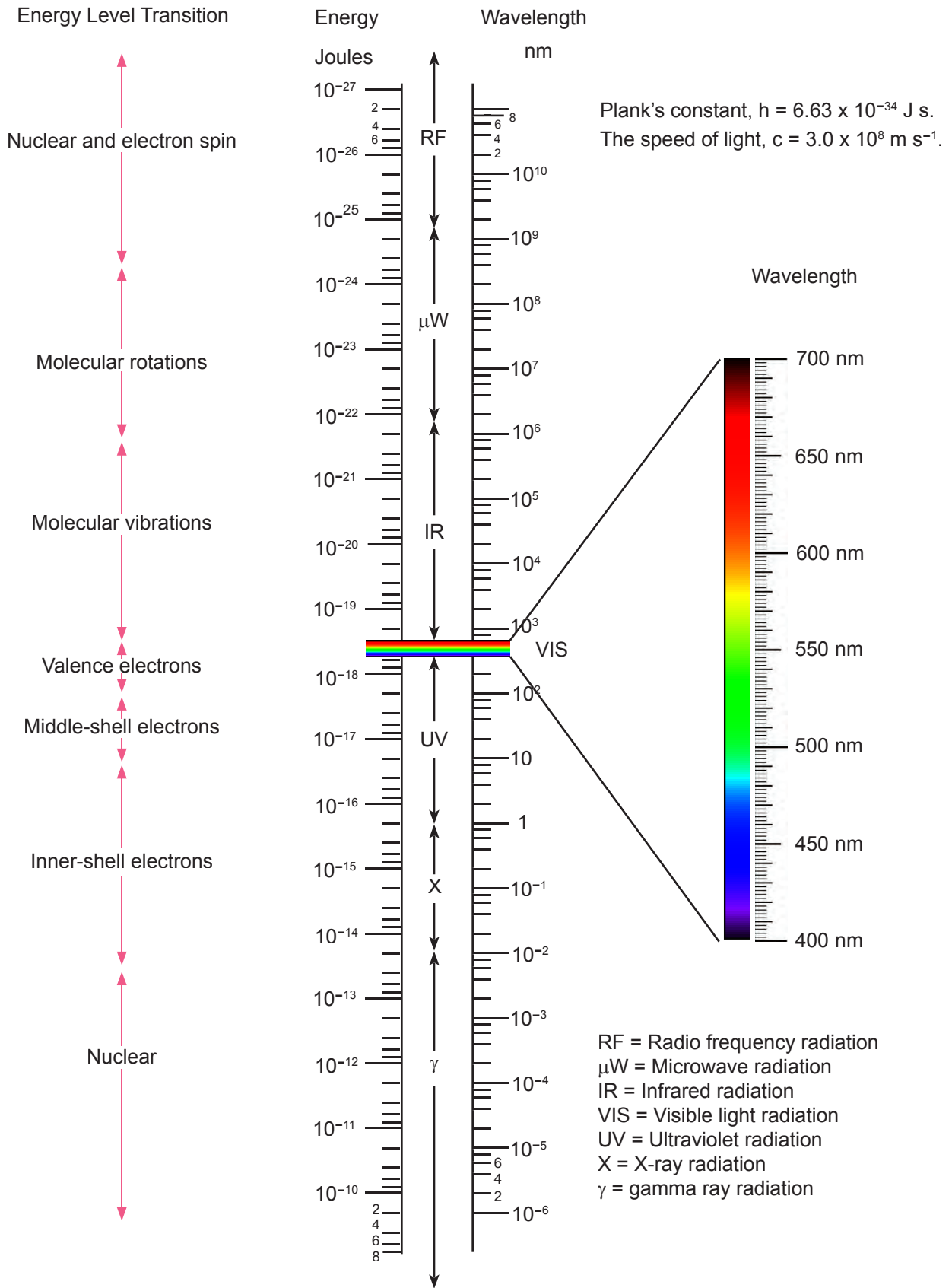
The resultant spectrum is mainly a graph of intensity of emitted or absorbed radiation versus wavelength or frequency. There are in general three types of spectra: continuous, line, and band. The sun and heated solids produce continuous spectra in which the emitted radiation contains all frequencies within a region of the electromagnetic spectrum. A rainbow and light from a light bulb are examples of continuous spectra. Line spectra are produced by excited atoms in the gas phase and contain only certain frequencies, all other frequencies being absent. Each chemical element of the periodic chart has a unique and, therefore, characteristic line spectrum. Band spectra are produced by excited molecules emitting radiation in groups of closely spaced lines that merge to form bands.

These categories of emission and absorption spectra contain tremendous amounts of useful information about the structure and composition of matter. Spectroscopy is a powerful and sensitive form of chemical analysis, as well as a method of probing electronic and nuclear structure and chemical bonding. The key to interpreting this spectral information is the knowledge that certain atomic and molecular processes involve only certain energy ranges. Page 3 shows the regions of the electromagnetic spectrum and the associated energy transitions that occur in atomic and molecular processes.

Much of the scientific knowledge of the structure of the universe, from stars to atoms, is derived from interpretations of the interaction of radiation with matter. One example of the power of these techniques is the determination of the composition, the velocities, and the evolutionary dynamics of stars. The source of the incredible amount of energy produced by the sun is nuclear fusion reactions going on within the hot interior (temperature $40 \times 10^6\text{K}$). Two fusion cycles, the carbon cycle and the proton cycle, convert hydrogen nuclei into helium nuclei via heavier nuclei, such as carbon 12 and nitrogen 14. The enormous radiation of energy from the hot core seethes outwards by convection. This radiation consists of the entire electromagnetic spectrum as a continuous spectrum. Towards the surface of the sun (the photosphere), the different elements all absorb at their characteristic frequencies. The radiation that shoots into space toward earth is a continuous emission spectrum with about 22,000 dark absorption lines present in it (Fraunhofer lines), of which about 70% have been identified. These absorption lines - i.e., missing frequencies - prove that more than 60 terrestrial elements are certainly present in the sun.

FOUNDATIONS OF SPECTROSCOPY

ELECTROMAGNETIC RADIATION RULER: THE ER RULER



FOUNDATIONS OF SPECTROSCOPY

NUMBERING ELECTROMAGNETIC RADIATION

Radiation may be described in one of two ways: either as a stream of energy pulses (photons) or as energy waves sent out from a source at the speed of light. Scientists use whichever interpretation works best to explain an experiment involving radiation. The photon and wave theories are linked by Planck's law:

$$E = h\nu$$

where E is the photon energy in Joules (J), ν is the frequency of the radiation (Hz or s^{-1}) and h is Planck's constant (6.63×10^{-34} J s).

Wavelength and frequency are related by

$$c = \lambda\nu$$

where c is the speed of light (3×10^8 m s^{-1}), λ is the wavelength of the radiation (often reported in nm), and ν is the frequency.

How many meters are in a nanometer?

How many megabytes in a gigabyte? How many kilobytes in a terabyte?

What is the frequency of a one nanometer photon? What is its energy?

A rough calculation suggests that there might be 10^{25} stars in the observable universe. How many Yotta stars is that?

Could you see a 500 nm speck of dust? Why?

You can calculate the kinetic energy, in Joules, of a moving object by multiplying its mass, in kilograms, times the square of its velocity, in meters per second, and dividing the result by two. What is the kinetic energy of a 1.0 Mgram elephant flying at 10 meters per second? Of a 10 gram meteoroid moving at Mmeters per second?

PREFIXES AND SCIENTIFIC NOTATION

Prefix	Symbol	Value
Yotta	Y	1,000,000,000,000,000,000,000,000
Zetta	Z	1,000,000,000,000,000,000,000,000
Exa	E	1,000,000,000,000,000,000,000
Peta	P	1,000,000,000,000,000,000
tera	T	1,000,000,000,000
giga	G	1,000,000,000
mega	M	1,000,000
kilo	k	1,000
hecto	h	100
deka	da	10
		1.0
deci	d	0.1
centi	c	0.01
milli	m	0.001
micro	μ	0.000001
nano	n	0.000000001
pico	p	0.000000000001
femto	f	0.0000000000000001
atto	a	0.0000000000000000001
zepto	z	0.0000000000000000000001
yocto	y	0.000000000000000000000001

Notation

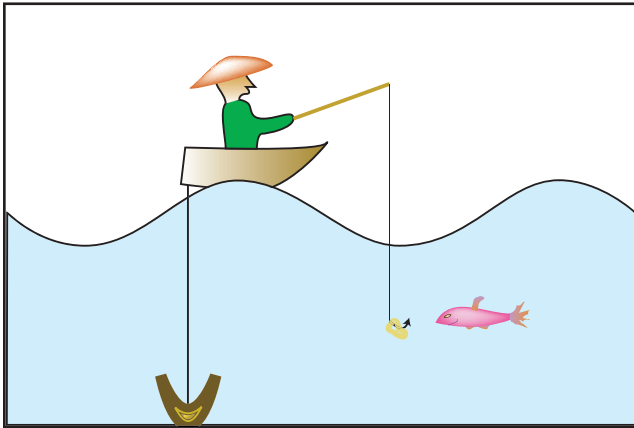
10^{24}
10^{21}
10^{18}
10^{15}
10^{12}
10^9
10^6
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-6}
10^{-9}
10^{-12}
10^{-15}
10^{-18}
10^{-21}
10^{-24}

Some Greek letters which we will use:

- α = "alpha"; as in α particle.
- β = "beta"; as in β particle.
- γ = "gamma"; as in γ ray.
- δ = "delta"; used with a plus or minus sign to represent partial charges in polarized molecules.
- Δ = "delta"; a capital delta is used for a change in a quantity.
- λ = "lambda"; used for wavelength.
- ν = "nu"; used for frequency.
- μ = "mu"; used for the prefix micro.
- π = "pi" is the ratio of the circumference of a circle to its diameter.
- Ω = "omega"; a capital omega is used for electrical resistance.

FOUNDATIONS OF SPECTROSCOPY

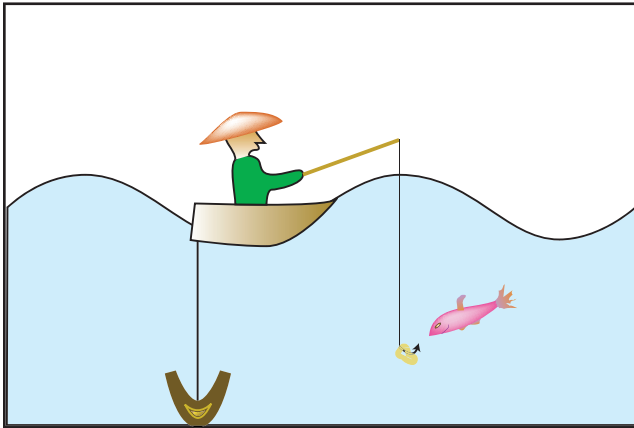
WAVES



The fisherman rises and falls with the passing waves. The (vertical) distance the fisherman moves through is called the amplitude of the wave. The distance between crests of the wave is called the wavelength. The time it takes for the fisherman to go from one wave top (crest), down to the bottom (trough) and back up to the top is called the period; its inverse is called the frequency. If the sea is choppy we could say that the number of waves going by the fisherman in a second is the frequency.

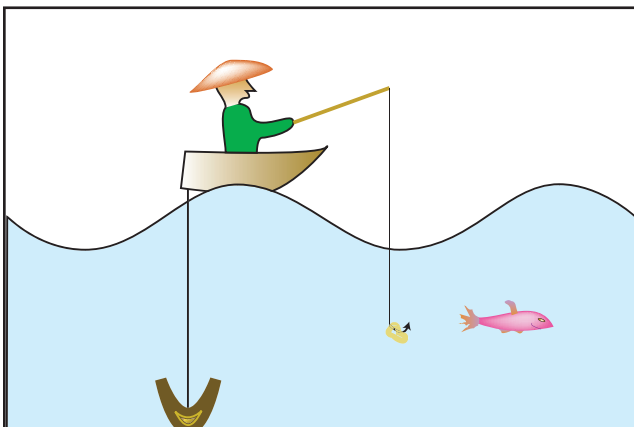
There is a general relationship for all waves that the velocity of the wave is the product of the wavelength times the frequency.

$$v = \lambda \nu$$



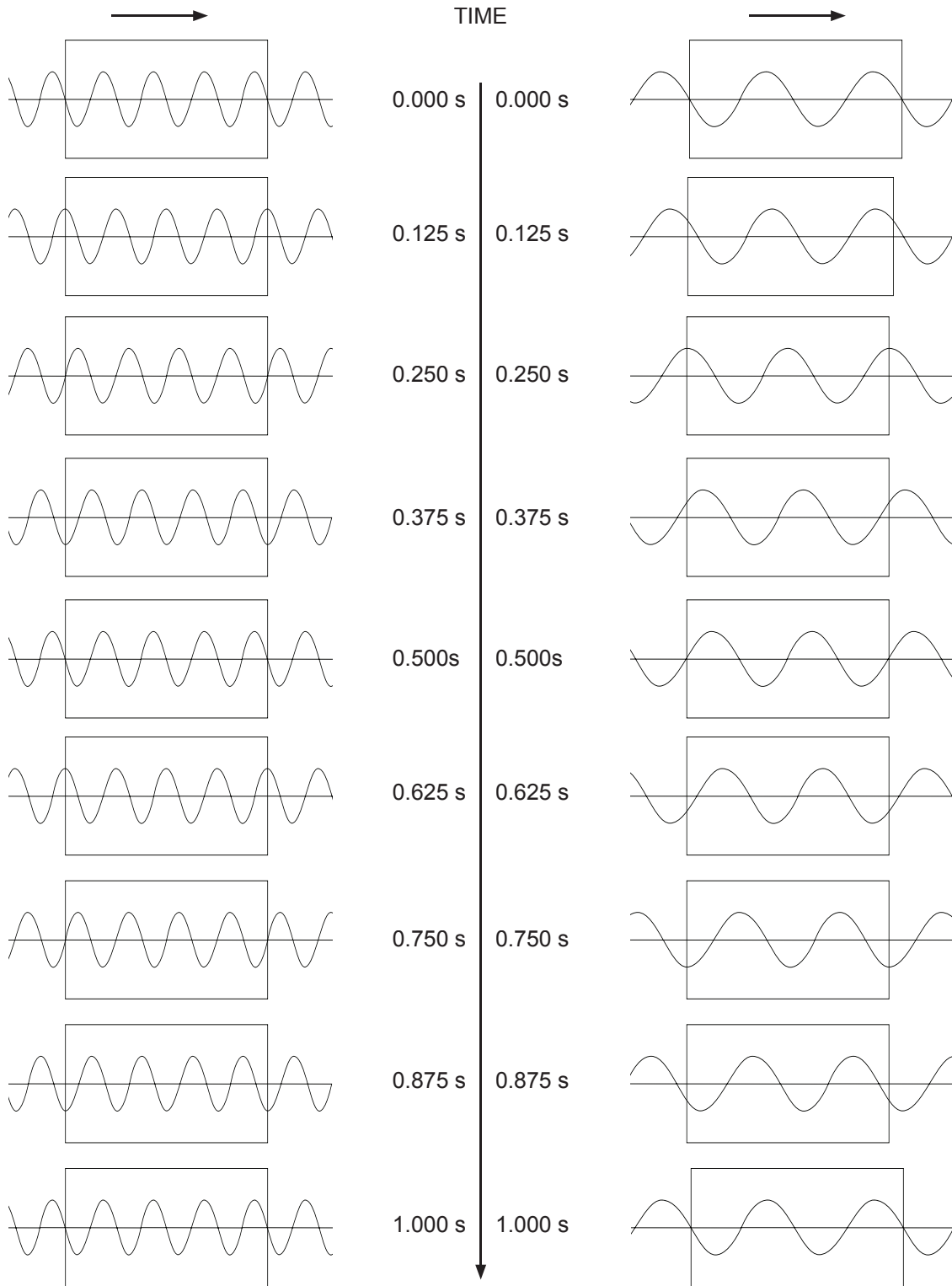
Measure the wavelength and amplitude, in centimeters, of the fisherman's wave.

If the frequency of the wave is 2.5 Hz, calculate its velocity.



FOUNDATIONS OF SPECTROSCOPY

FREQUENCY AND WAVELENGTH



Each of the vertical sequences of pictures above shows a wave moving to the right. Since electromagnetic radiation always travels at the same velocity (in vacuum and nearly so in air) and that velocity is equal to the product of wavelength and frequency, then increasing the frequency must decrease the wavelength.

Does the wave on the left have the same velocity as the wave on the right?

FOUNDATIONS OF SPECTROSCOPY

QUESTIONS FOR THE ER RULER

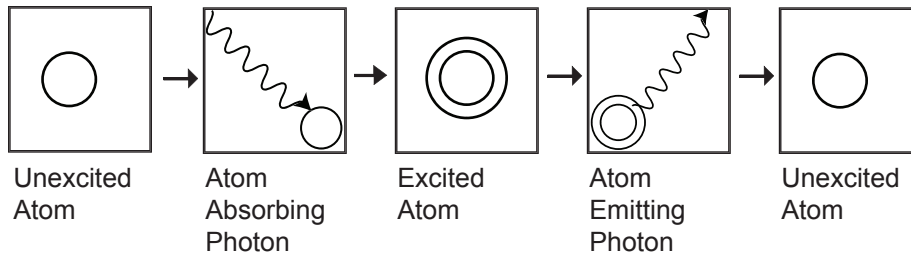
Plank's constant, $h = 6.63 \times 10^{-34} \text{ J s}$.

The speed of light, $c = 3.0 \times 10^8 \text{ m s}^{-1}$. This is the speed of all electromagnetic radiation in a vacuum.

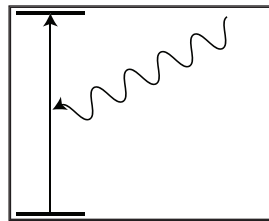
1. A solid state laser has a wavelength (λ) of 650 nm. What color is the laser light? Calculate the frequency (ν) and energy (E) of this light.
2. What is the wavelength range for visible light. Use the ER ruler.
3. Give the approximate wavelength range for yellow light. Use the ER ruler.
4. Give the approximate wavelength range for infrared radiation.
5. Which has the higher energy, red light or blue light?
6. Give the approximate frequency range for visible light.
7. What is the frequency and energy of electromagnetic radiation with a wavelength of $1.0 \times 10^4 \text{ nm}$? What type of radiation is it?
8. Noting that on the ER ruler the wavelength and energy scales go in opposite directions, if you added a frequency scale, would it go in the direction of the wavelength scale or the energy scale?
9. Atoms have diameters of approximately 0.1 nm. What kind of radiation would have a wavelength of 0.1 nm?
10. What type of radiation has an energy of $2.0 \times 10^{-7} \text{ J}$?
11. My favorite FM radio station has a frequency of 100 MHz. Calculate the wavelength and energy of the electromagnetic radiation broadcast by my station.
12. X-rays travel at a speed of $3.0 \times 10^8 \text{ m s}^{-1}$. What speed do radio waves travel at?
13. A microwave oven produces radiation with a frequency of $2.5 \times 10^9 \text{ Hz}$. This radiation stimulates water molecules to rotate. Calculate the wavelength and use the ER ruler to find the energy of this microwave radiation.
14. A cell phone has an operational frequency of 840 MHz. What type of radiation is this? Calculate the energy of the radiation. Can this radiation go through walls? Why?
15. Would you rather be in a beam of gamma (γ) rays or radio waves? Explain your answer.
16. Suggest the wavelength for the light emitted from the top light in a traffic light.
17. The red Balmer line in the atomic emission spectrum of hydrogen has an energy of $3.03 \times 10^{-19} \text{ J}$. Calculate the wavelength of the red light in a) m; b) nm; and c) μm . Also calculate the frequency in a) Hz; b) MHz; and c) GHz.

FOUNDATIONS OF SPECTROSCOPY

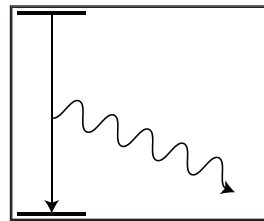
FUNDAMENTAL PROCESSES



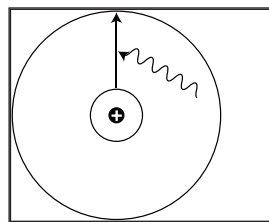
Absorbing a photon increases the energy of a system.



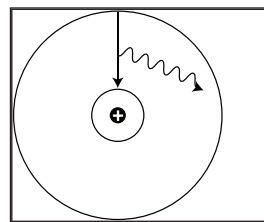
Emitting a photon decreases the energy of a system.



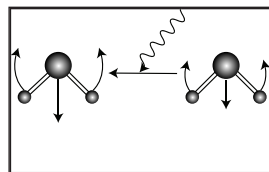
Absorbing a photon increases the size of an electron orbital.



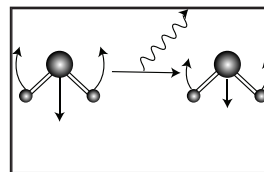
Emitting a photon decreases the size of an electron orbital.



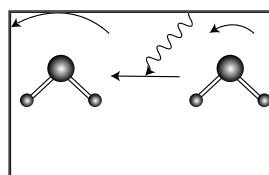
Absorbing an infrared photon can increase the vibrational energy of a molecule.



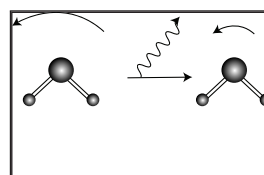
A vibrating molecule can emit an infrared photon and decrease its rate of vibration.



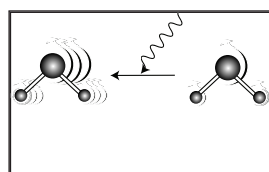
Absorbing a microwave photon can increase the rotational energy of a molecule.



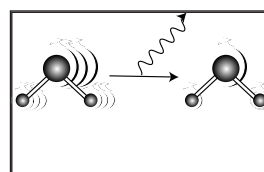
A rotating molecule can emit a microwave photon and decrease its rate of rotation.



Absorbing a photon can increase the translational energy of a molecule.



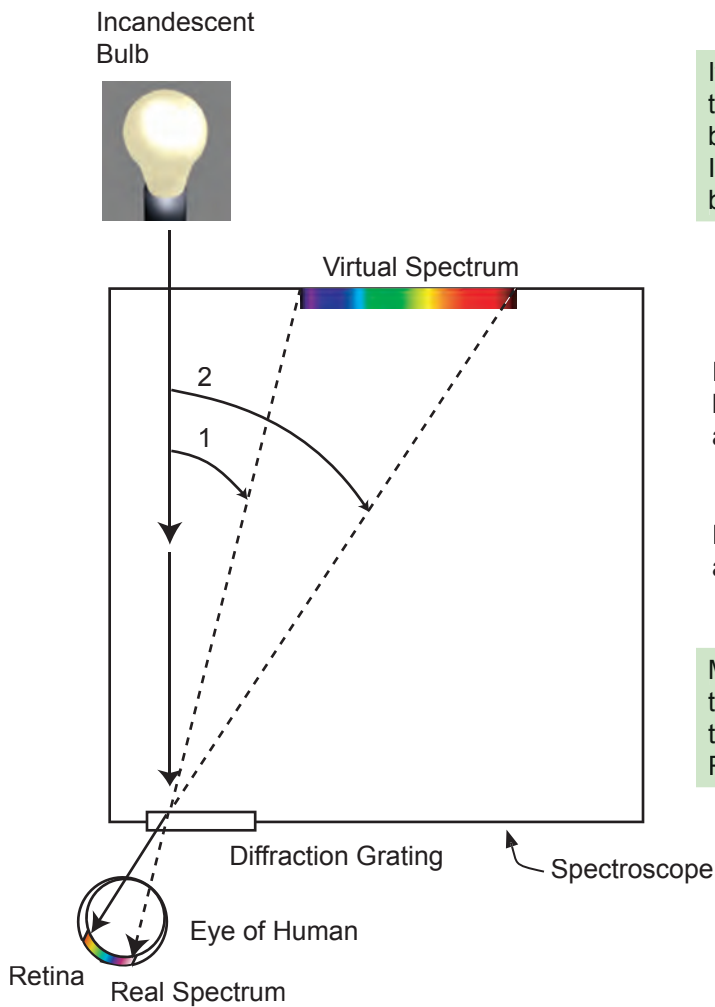
A moving molecule can emit a photon and slow up.



FOUNDATIONS OF SPECTROSCOPY

SPECTROSCOPE

The separation of light into its spectral components can be done by refraction or diffraction. The separation of light into its component colors is accomplished by a spectroscope. A spectroscope is simply a box with a slit at one end (to let in light) and a light-separating device at the other end.



If you put a camera at the position of the virtual spectrum and pointed it at the diffraction grating, would you be able to photograph the spectrum?
 If you put the camera in place of the eye, would you be able to photograph the spectrum?

For a diffraction grating with the width of the lines given as d , for light of wavelength λ , the angle of diffraction is given by the equation

$$n\lambda = d \sin\theta$$

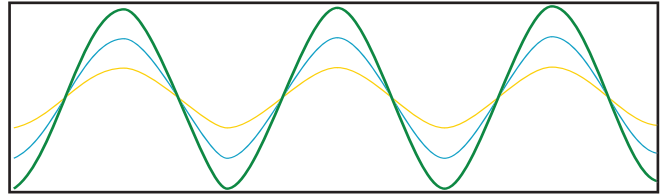
Here n is called the order of diffraction (usually 1) and θ is the angle of diffraction.

Measure the angle at which the blue end of the spectrum is diffracted(1). Use the equation for diffraction to calculate the spacing of the diffraction grating. Repeat for the red end of the spectrum(2).

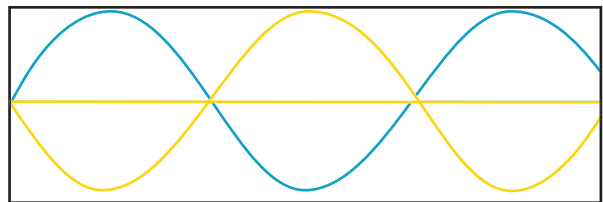
FOUNDATIONS OF SPECTROSCOPY

INTERFERENCE: THE PRINCIPLE BY WHICH LIGHT IS BROKEN UP

Unlike solid objects waves can occupy the same space at the same time. When they do their amplitudes add. This is strictly true for both electromagnetic waves and the waves of quantum mechanics. But the amplitudes of both kinds of waves are signed, that is, they are both positive and negative. When amplitudes of the same sign are superimposed upon each other then the combined amplitude is greater. This is called constructive interference. When amplitudes of opposite signs are superimposed upon each other then the net amplitude is decreased and sometimes cancelled. This is called destructive interference.



In this example of CONSTRUCTIVE INTERFERENCE the green curve is the sum of the yellow and blue curves.



In this example of DESTRUCTIVE INTERFERENCE the flat line is the sum of the yellow and blue curves. If the yellow and blue curves were light waves then the sum would be dark.

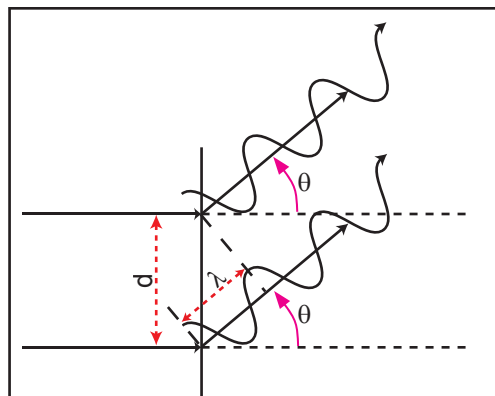
$$n\lambda = d \sin\theta$$

The picture on the right illustrates the geometry of a diffraction grating. Two (of the thousands) of slits in the grating allow light to pass through. The separation between the slits is d . The angle at which we observe the waves is θ . The wavelength of the light is λ .

You can see that the waves are in the same relative position (the same phase) along their direction of travel, because one wave has exactly one wavelength farther to travel than the other one, which gives rise to constructive interference and which produces light which can be seen on a screen or in the eye.

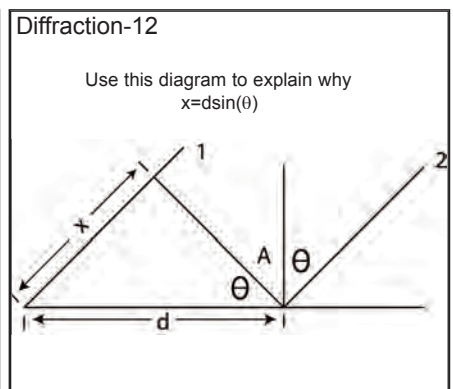
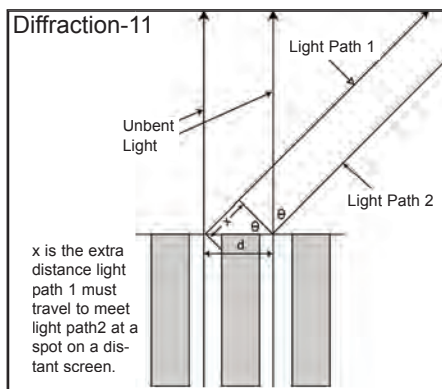
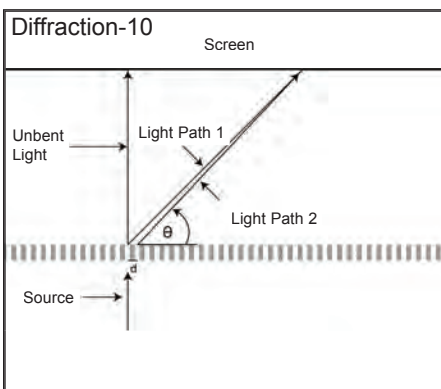
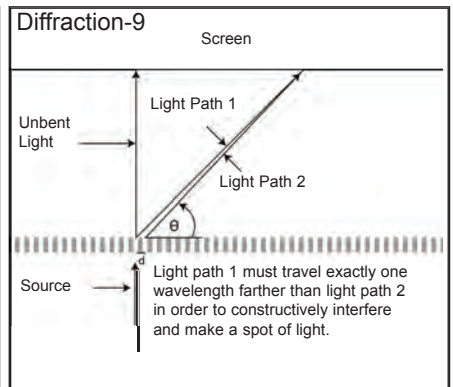
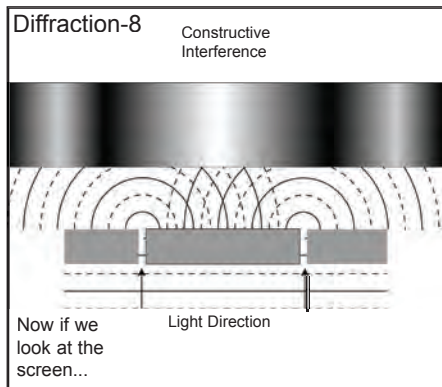
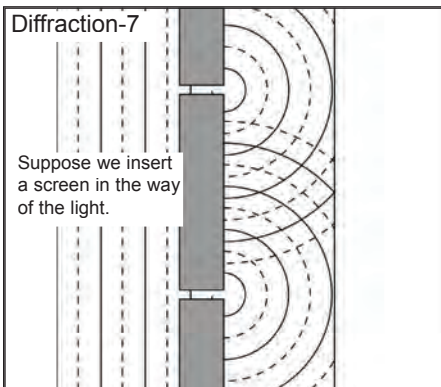
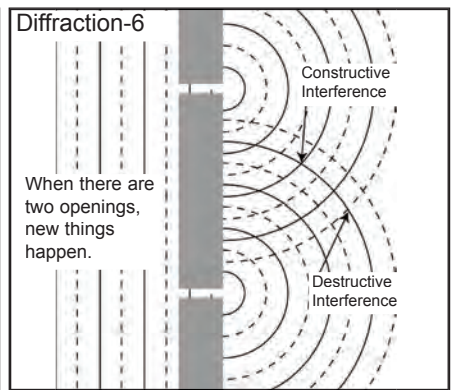
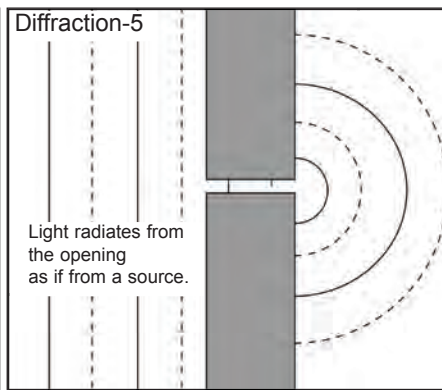
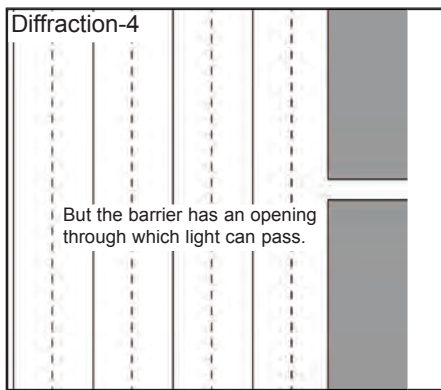
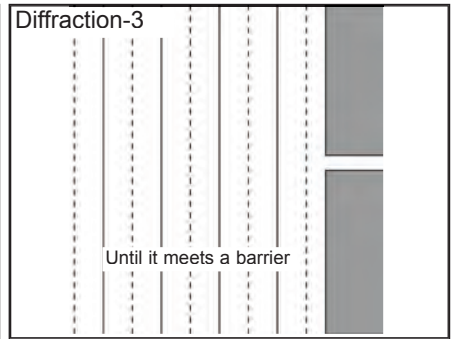
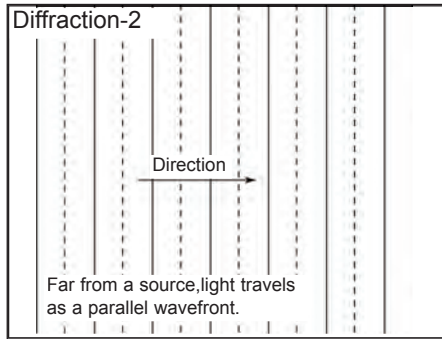
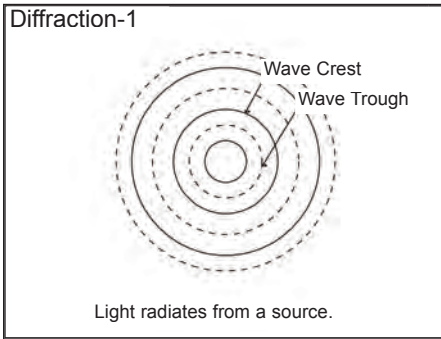
By trigonometry you can see (Picture number 12 on the NEXT page may help) that $\lambda = d \sin\theta$.

You would also have constructive interference if one wave traveled exactly two wavelengths, or any integral number n , further than the other one, which is how we obtain the general equation $n\lambda = d \sin\theta$.



FOUNDATIONS OF SPECTROSCOPY

DIFFRACTION

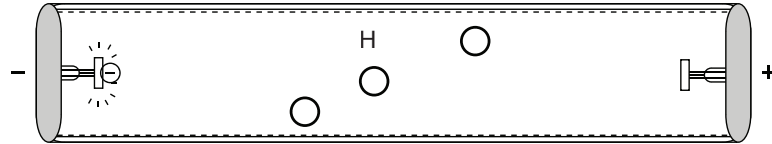


FOUNDATIONS OF SPECTROSCOPY

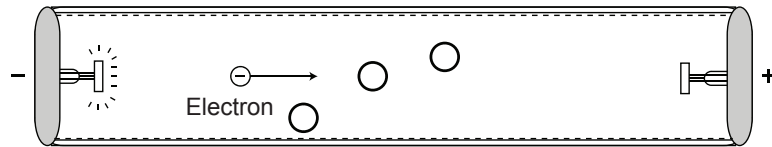
AN ATOMIC LINE EMISSION SPECTRUM FROM A DISCHARGE TUBE

A high voltage supply produces a 2000 V difference across the tube.

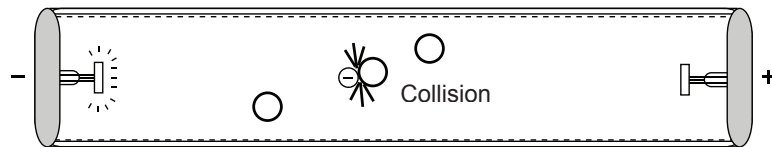
The cathode is heated to drive electrons off into the tube.



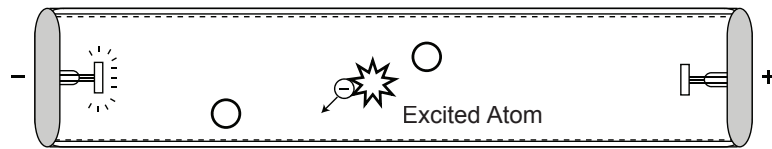
Electrons gain kinetic energy as they are pulled toward the anode.



The electron hits a hydrogen (H) atom.



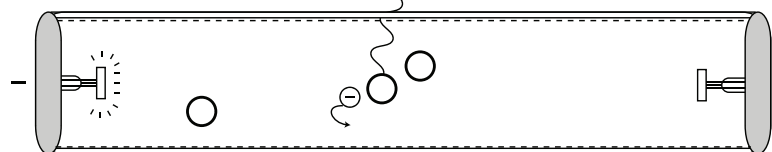
The electron will use its kinetic energy to excite the H atom.



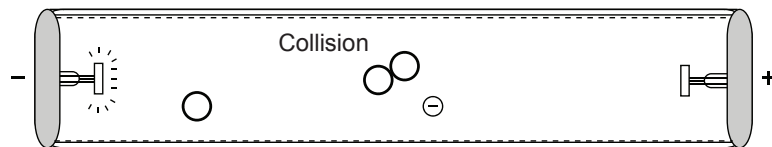
A line spectrum is emitted.



The H atom will emit visible light at different wavelengths. The visible light escapes.



If the atoms had collided before emission of radiation, then the energy would have been dissipated into motion.



Why does collision with an electron excite an atom but collision with another atom does not?

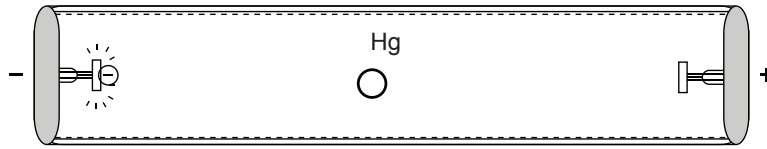
In a gas, what factors control the time interval between atomic collisions?

Line emission and absorption spectra come from low pressure gases containing atoms.

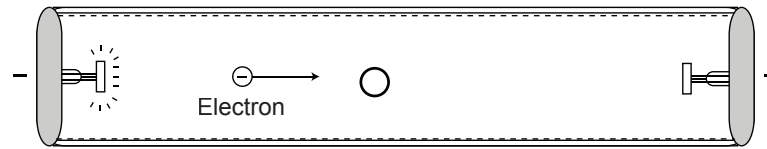
FOUNDATIONS OF SPECTROSCOPY

FLUORESCENT LIGHTS

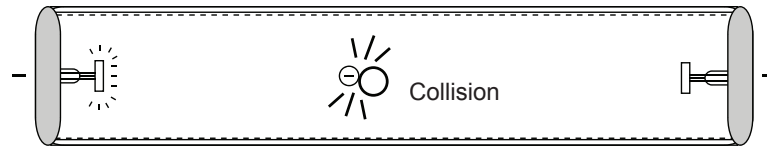
The cathode is heated to drive electrons off into the tube.



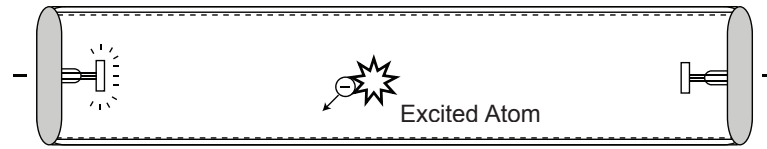
Electrons gain kinetic energy as they are pulled toward the anode.



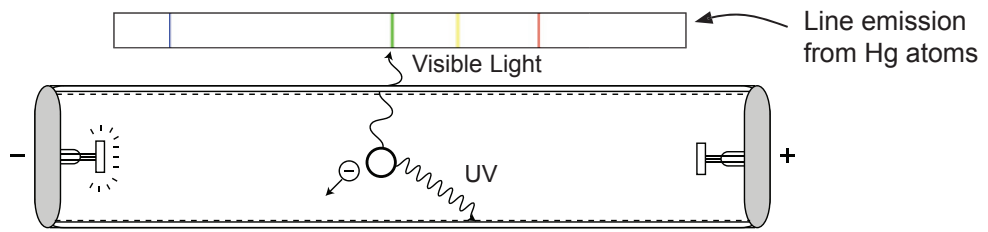
The electron hits a mercury (Hg) atom.



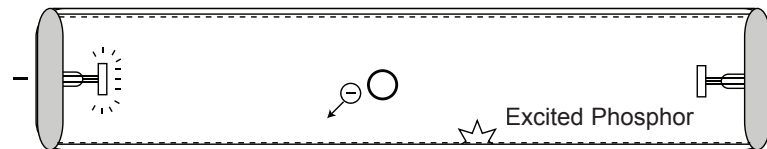
The electron will use its kinetic energy to excite the Hg atom.



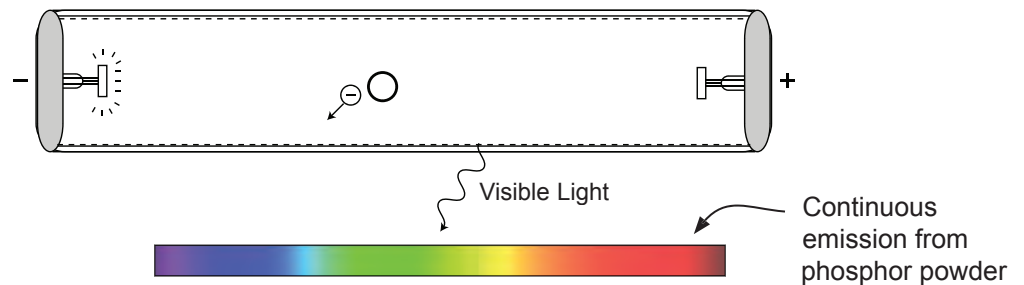
The Hg atom will emit visible or ultraviolet light or both. The visible light escapes.



The UV photon will excite the phosphors on the inside of the tube.



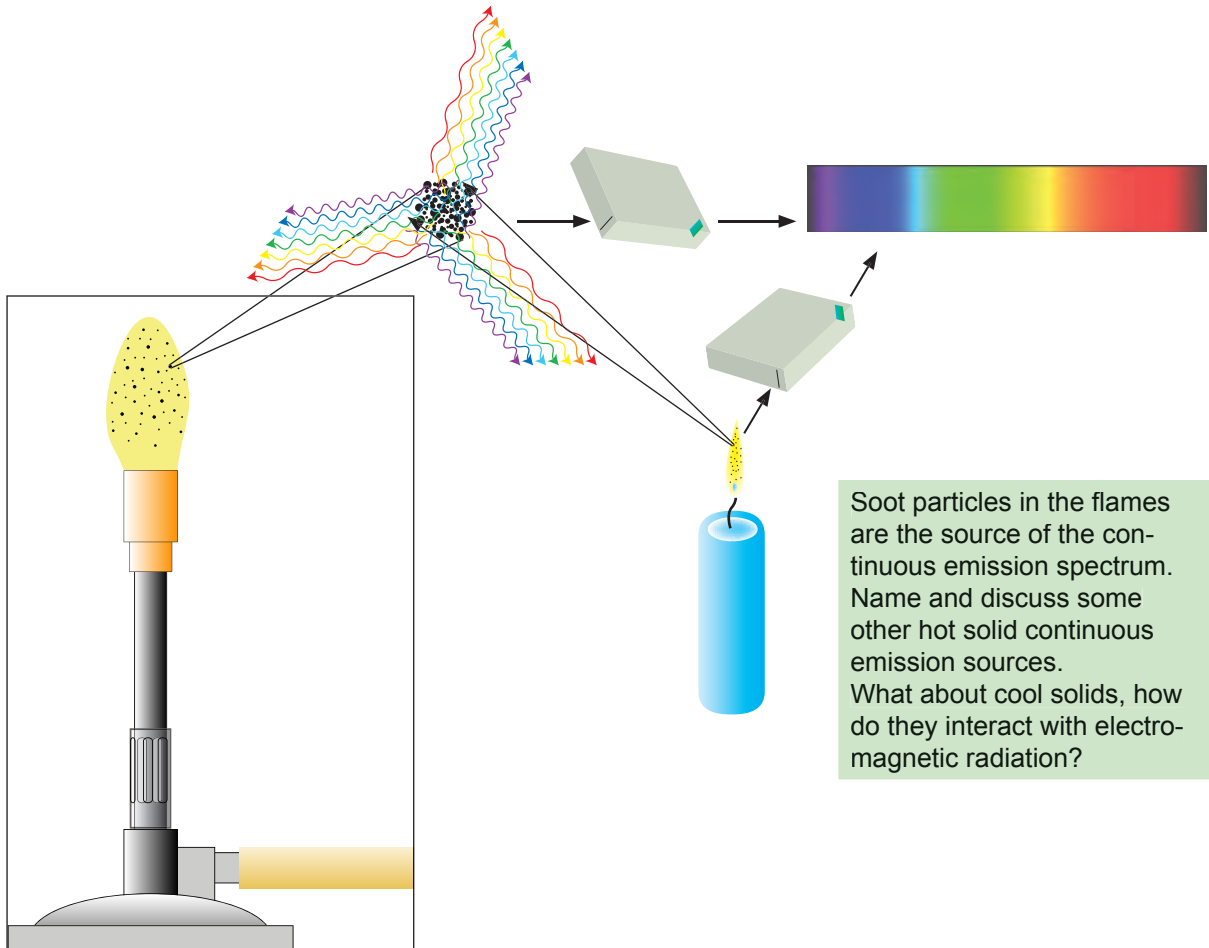
The phosphors will fall back to their original state and emit visible light.



Spectrum of 'Warm' Fluorescent Light Bulb

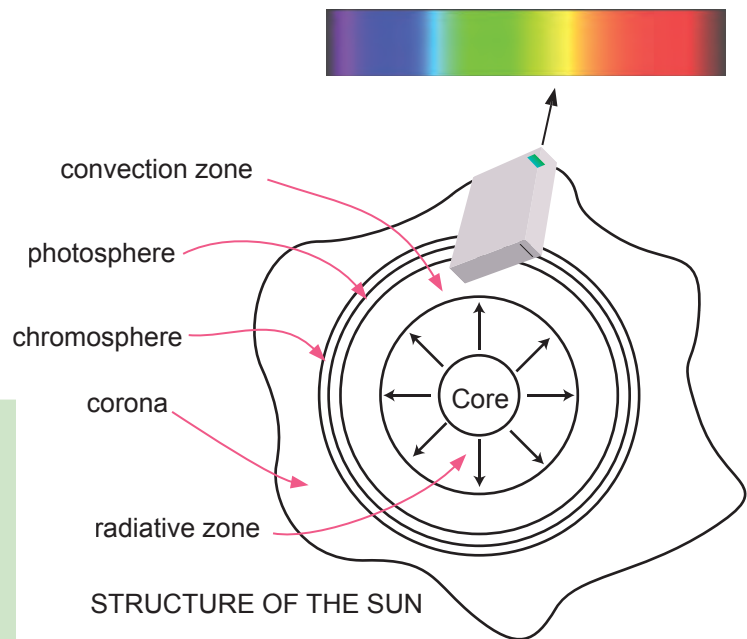
FOUNDATIONS OF SPECTROSCOPY

CONTINUOUS EMISSION



In the part of the sun where the continuous spectrum is produced, called the photosphere, atoms are entirely ionized, giving rise to a gas of free protons and electrons called a plasma. Because they are not bound to an atom, these particles can have any energy state.

The sun is powered by nuclear reactions in the core. Eventually the energy works its way upward through the radiative zone until it reaches the photosphere, from where it escapes into space (and to earth). What frequency range of radiation would you expect to occur in the radiative zone and what sort of effects would that radiation have if it could reach the earth directly?



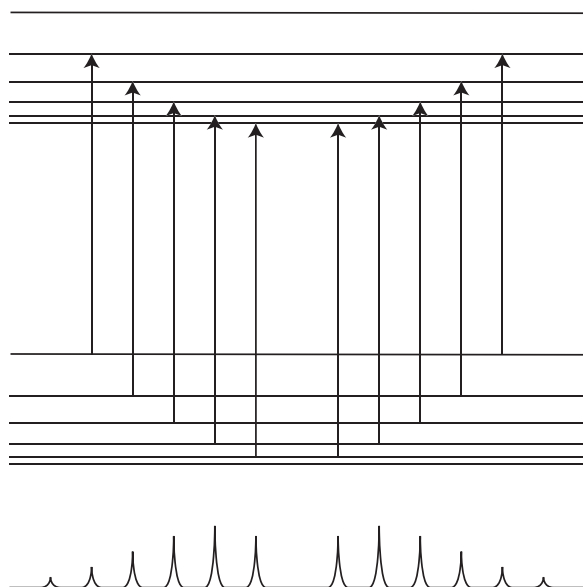
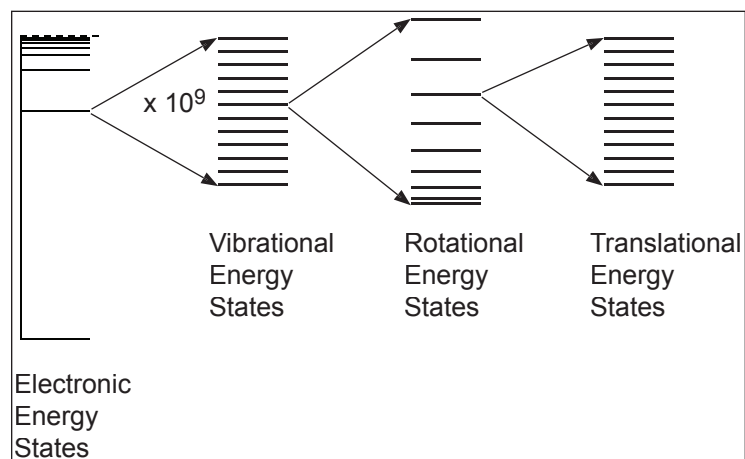
FOUNDATIONS OF SPECTROSCOPY

THE ORIGINS OF BAND SPECTRA

Atoms are spherically symmetric but molecules have shapes which permit them to vibrate and rotate. These vibrations and rotations provide new energy LEVELS which are also quantized.

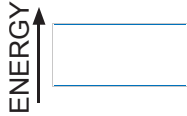
Explain why the spherical symmetry of atoms prevents them from having vibrational and rotational energy levels.

MOLECULAR ENERGY LEVELS

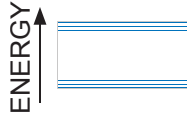


FOUNDATIONS OF SPECTROSCOPY

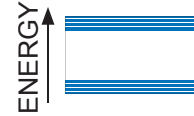
ORIGINS OF BAND SPECTRA



As we know, electrons can occupy different electronic energy states.

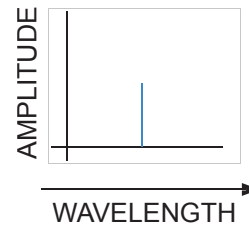
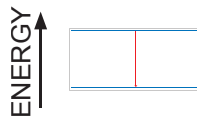


In molecules the electronic states are subdivided into vibrational states.

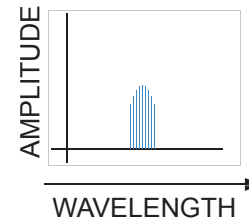
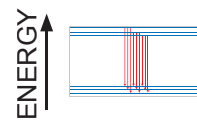


The electronic-vibrational states are also subdivided into rotational states.

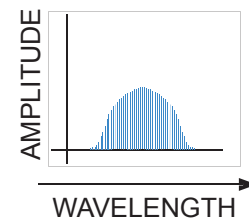
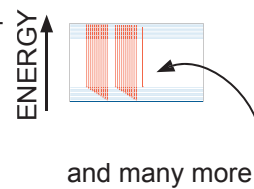
Transitions between electronic levels give line spectra.



Transitions between vibrational-electronic states give more complex spectra.



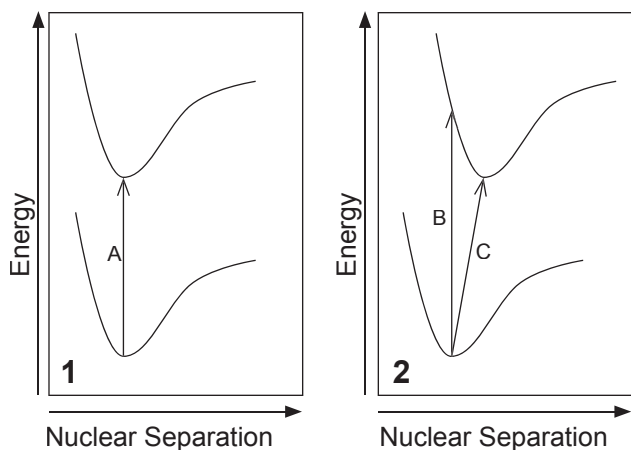
Transitions between electronic-vibrational-rotational states give rise to spectra that appear to have bands.



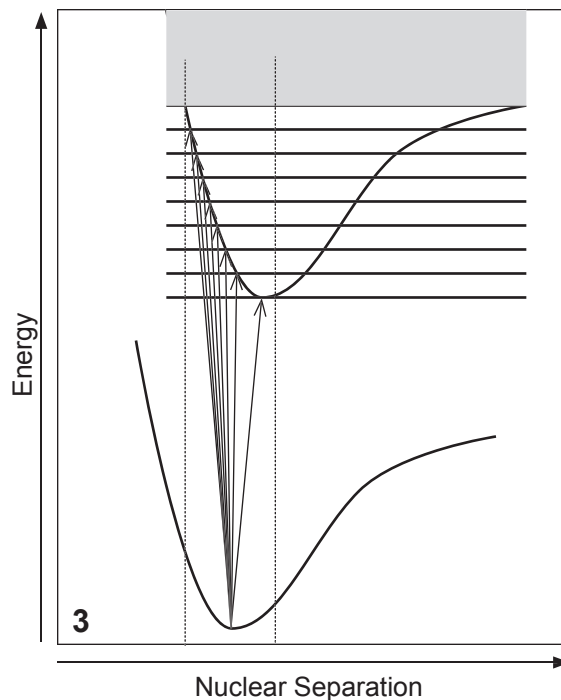
FOUNDATIONS OF SPECTROSCOPY

THE FRANK-CONDON PRINCIPLE

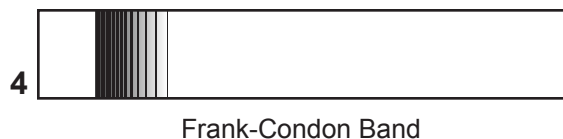
It can be established from the Uncertainty Principle of quantum mechanics that high energy transitions in atoms or molecules tend to be very fast. Also, as atomic nuclei are very heavy compared to electrons, the nuclei move much slower than the electrons. Therefore the FRANK-CONDON PRINCIPLE states that during electronic transitions in a molecule, the nuclei can be assumed to be in the same place before and after the transition. This has significant effects upon the appearance of band spectra.



Pictures 1 and 2 show molecular electronic transitions. In picture 1 we see a transition between two states with the same nuclear separation. In picture 2 we see two transitions between states with different nuclear separations. Transition B, however, still involves no nuclear movement and is allowed by the Frank-Condon Principle. Transition C would require nuclear motion and is thus disfavored by the Frank-Condon Principle.



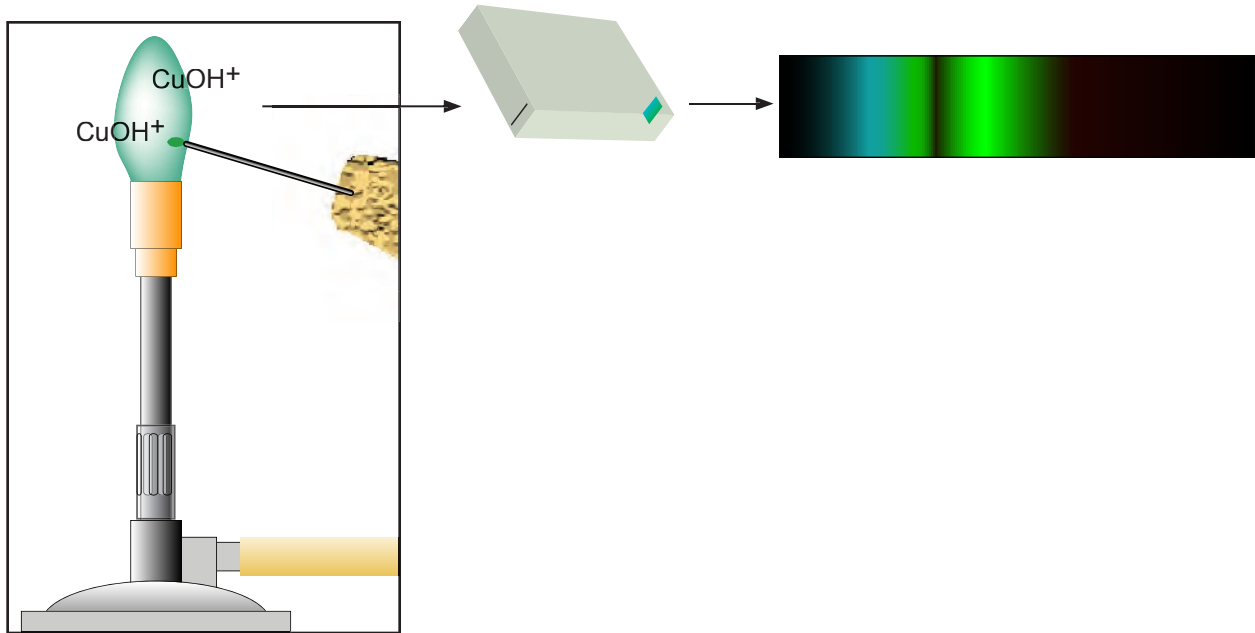
Picture 3 is similar to picture 2 with some changes. The vibrational states of the upper electronic state have been added and dashed lines show the region in which appreciable transitions can actually occur. We have also added the arrows for the transitions which would occur.



Explain how the transitions shown in picture 3 can be correlated to the spectral lines in picture 4. Explain why the lines appearing in picture 4 cluster to the left of the spectral band.

FOUNDATIONS OF SPECTROSCOPY

BAND SPECTRA



Molecules produce band spectra.

Suppose you see bands in the spectrum of an interstellar cloud. What can you deduce about the nature and condition of the cloud?

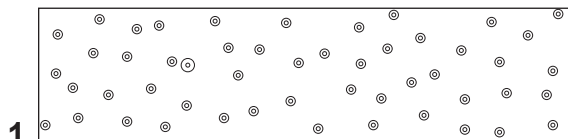
FOUNDATIONS OF SPECTROSCOPY

LASERS

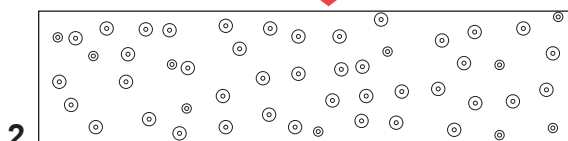
Light Amplification by Stimulated Emission of Radiation.
What does that mean?



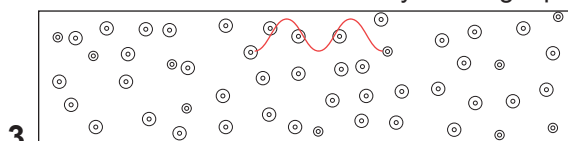
We begin with a system of molecules.



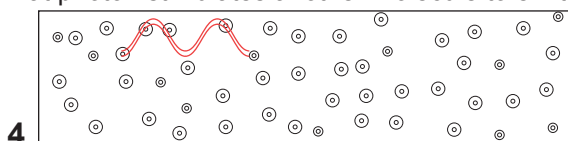
Energy is pumped into the system, exciting the molecules



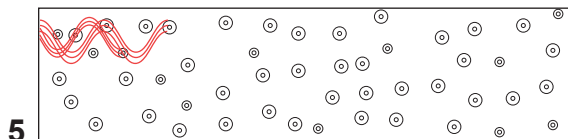
One of the molecules de-excites by emitting a photon.



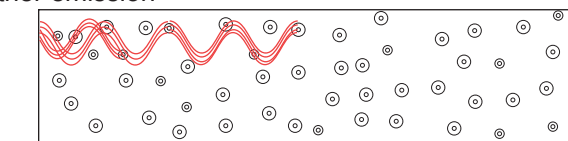
That photon stimulates another molecule to emit.



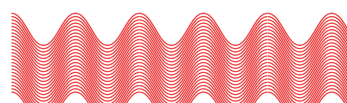
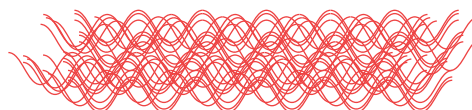
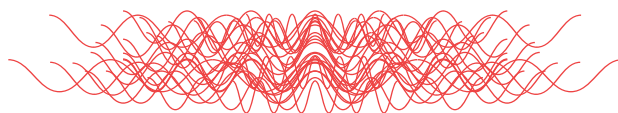
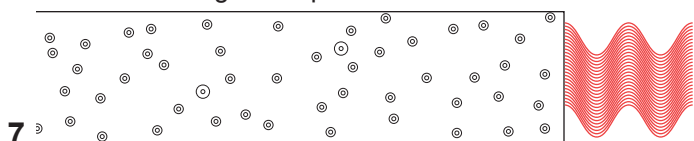
...and so on...



The photons are reflected by the mirrored surface on the left of the system. They continue to stimulate further emission



Resulting in an intense beam of photons of the same wavelength and phase.



Compare and Contrast pictures 8, 9 and 10. Describe the relationship between the different waves. What are possible sources for each of the wave patterns pictured?

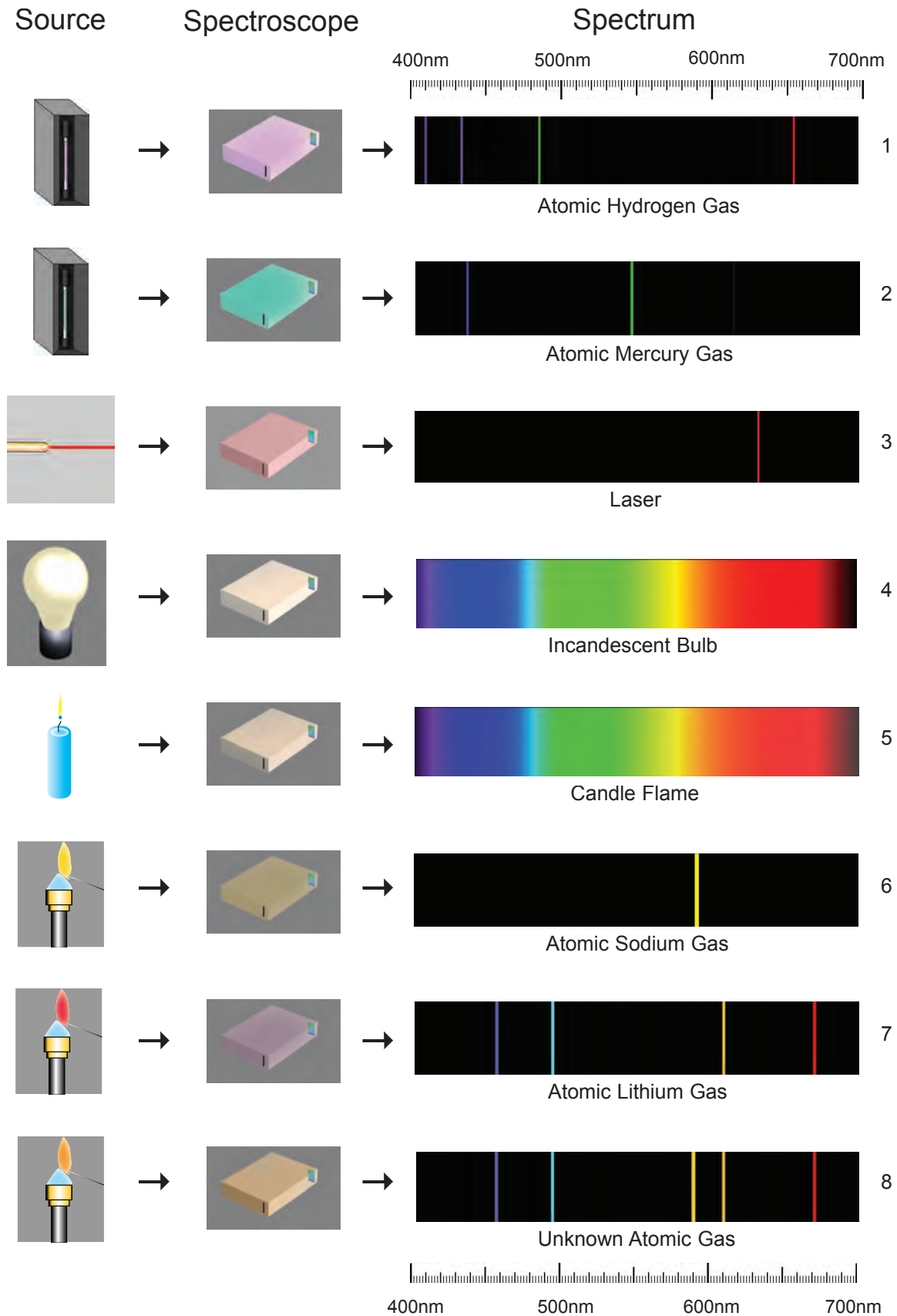
Using an internet search engine, such as www.google.com, perform an advanced search for 'chemical lasers'. Describe the chemistry of at least two kinds of chemical laser. What is the most powerful laser owned by the United States and what is its power range?

Describe a half dozen different uses of lasers in everyday life. What kind of lasers are used?

The original development work which led to the laser was carried out in the interest of microwave spectroscopy.

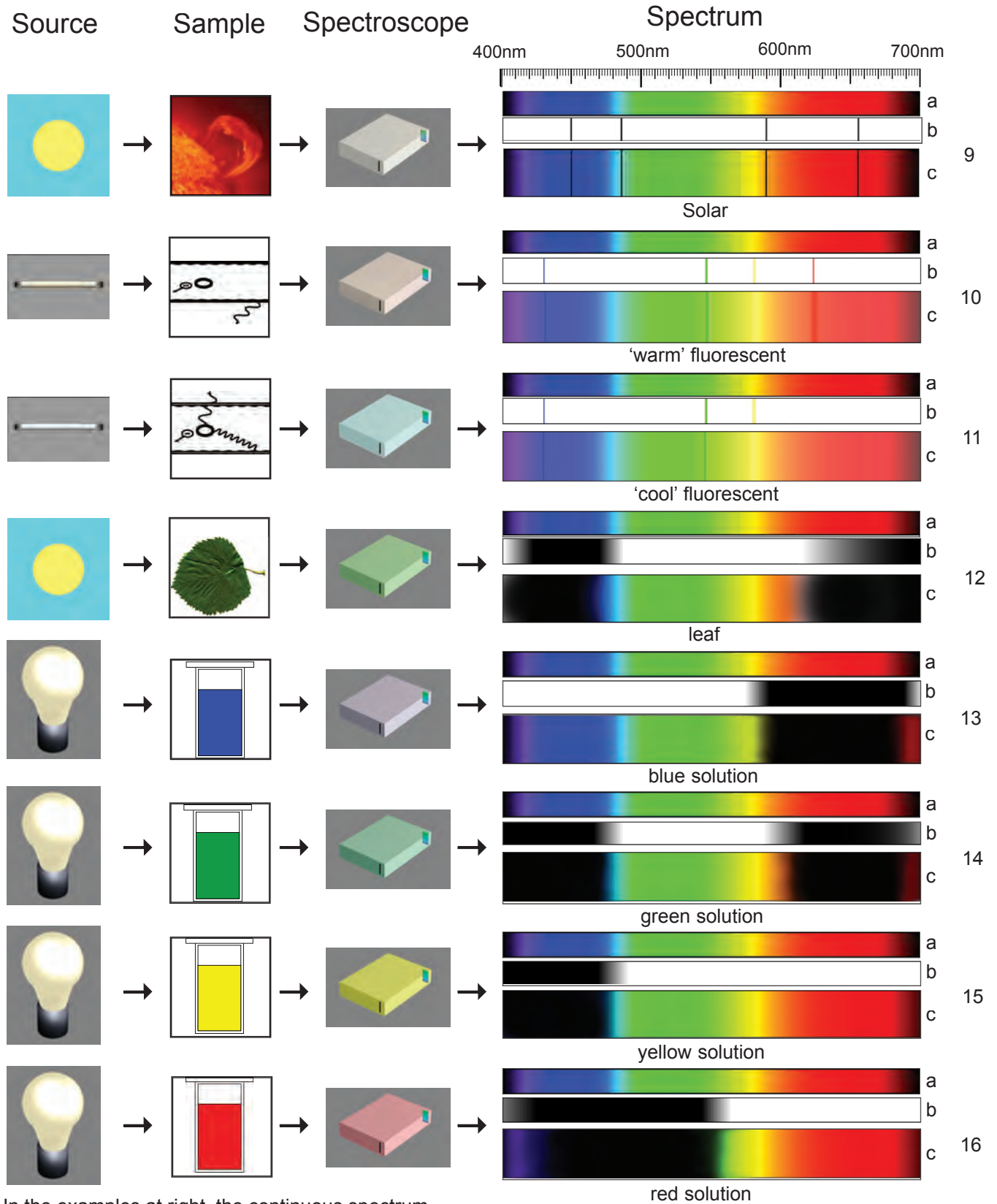
FOUNDATIONS OF SPECTROSCOPY

SIMPLE SPECTRA



FOUNDATIONS OF SPECTROSCOPY

COMPLEX SPECTRA



In the examples at right, the continuous spectrum a is reduced by the absorption pattern b to give the resulting spectrum c.



FOUNDATIONS OF SPECTROSCOPY

SPECTRAL QUESTIONS

The following questions refer to the sixteen spectra on the last two pages.

1. In spectrum number 1, measure the wavelength of the four visible lines.
2. In spectrum number 2, what is the frequency of the green line?
3. Referring to spectrum number 3, what is the wavelength of the light emitted by the laser?
4. Describe the origin of the light which produces spectrum number 4.
5. Describe the origin of the light which produces spectrum number 5.
6. What is the energy of the photons which produce the sodium yellow line?
7. List the four visible lines of lithium gas in decreasing order of frequency.
8. Using a chart of known spectra, determine the nature of the unknown gas in spectrum number 8.
9. Describe the source of the black lines which appear in spectrum number 9.
10. Referring to the fluorescent light description page which appears later in this module, explain why spectrum number 10 has both a continuum and discrete lines.
11. Why doesn't the red line appear in spectrum number 11?
12. Referring to spectrum number 12, what colors of light are absorbed by the green leaf?
13. What happens to the light which is absorbed by the blue solution?
14. How would spectrum number 14 change if fluorescent light replaced the incandescent bulb as the light source?
15. What would spectrum number 15 look like if blue dye were added to the yellow dye?
16. Find a good question to ask about spectrum number 16.
17. The yellow flame in the Bunsen burner is given by the sodium from sodium chloride. How do sodium ions get to be sodium atoms? See the Bonding Module.
18. Why is the yellow part of the continuous spectrum narrower than the green or red parts?
19. What might be responsible for the variations in thickness of the atomic emission lines?
20. Draw the combined spectrum of H, Li, Hg and Na.
21. Using the solution absorption spectra, explain how you could make black ink?
22. What do you find unusual about the spectrum of a leaf?
23. What do you think the spectrum of an autumn leaf would look like?

GENERAL EQUILIBRIUM



by

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Mr. Joe Staley

Ms. Mary Peacock

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

GENERAL EQUILIBRIUM

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GENERAL EQUILIBRIUM

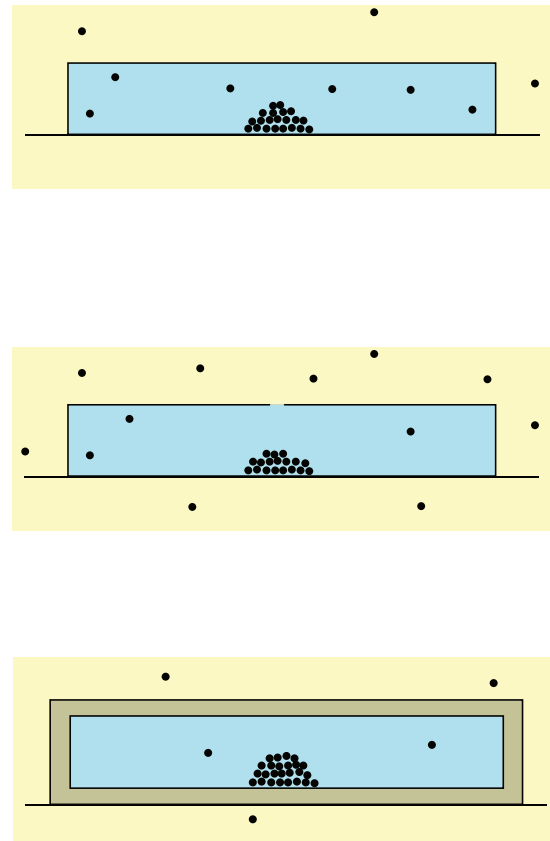
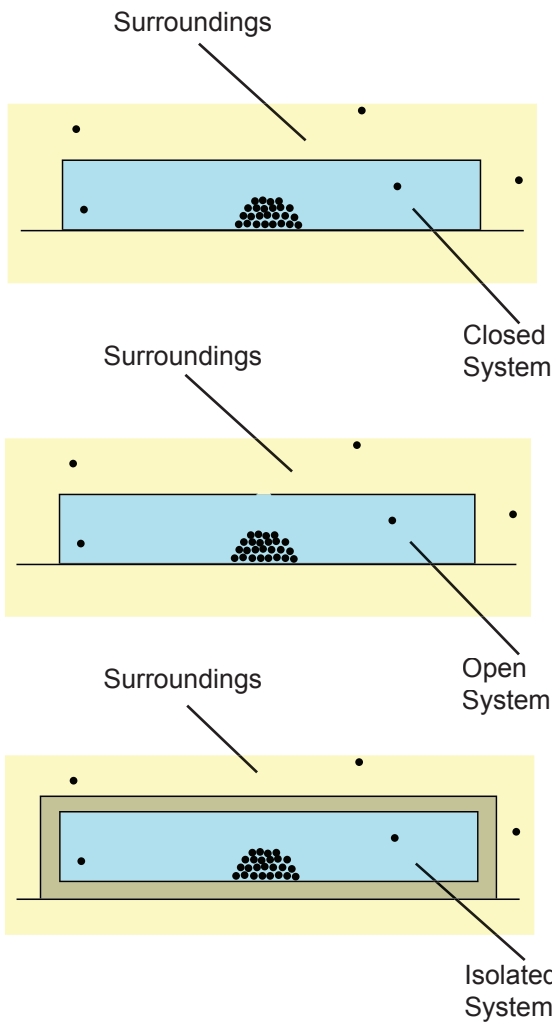
SYSTEM AND SURROUNDINGS

A system is the part of the world we want to study. The surroundings are everything outside the system. The system must be chosen carefully, and the ways the surroundings affect the system must always be considered.

Let's take a look at the petri dish with a drop of water that we've studied in other modules. The drop of water in the dish is the system, everything else is the surroundings.

System and surroundings at equilibrium.

The same system and surroundings at a higher temperature, also at equilibrium.



Is energy transfer alone allowed in
 a.) an open system
 b.) a closed system
 c.) an isolated system

Is transfer of energy and matter allowed in
 a.) an open system
 b.) a closed system
 c.) an isolated system

Neither energy nor matter is transferred in
 a.) an open system
 b.) a closed system
 c.) an isolated system

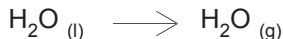
State whether each of the following is an open, closed, or isolated system:

- a.) the human body
- b.) an electric battery
- c.) a burning candle

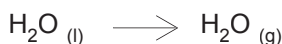
GENERAL EQUILIBRIUM

VAPOR PRESSURE EQUILIBRIUM

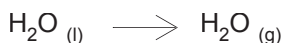
The simple experiment that follows reaches equilibrium over time. Try to define equilibrium as you study the experiment.



► A drop of water is placed in a petri dish and covered. Notice the blue water molecules in the air. This is water vapor. At this time in the experiment (after placing a drop of water in a petri dish and covering it), would there be more or less water vapor if the experiment were done on a lake or in the desert?



► As time proceeds more water molecules evaporate from the drop. What happens to the size of the drop?



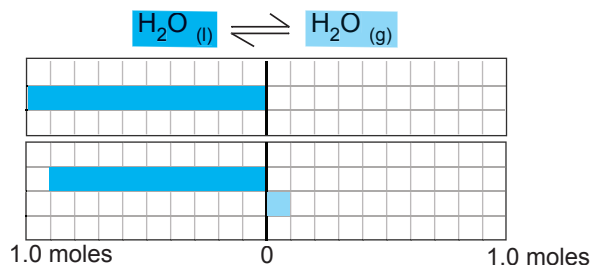
► Still more molecules evaporate, shrinking the drop still further. Is the amount of total water in this petri dish the same as at the start?



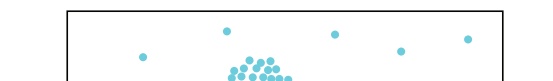
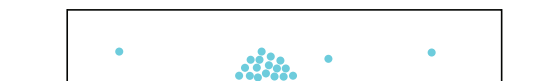
Eventually the number of water molecules in the air and the size of the drop become constant. At this point, we have reached **EQUILIBRIUM**.

Equilibrium is reached when the rate of the forward reaction (water evaporating from the drop) equals the rate of the backward reaction (water condensing into the liquid state). More precisely, it is called dynamic equilibrium.

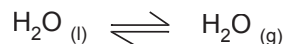
ChemLog shows the process much more quantitatively. Show your understanding of this equilibrium by explaining the ChemLog before and after equilibrium has been reached.



Water ●



In equilibrium reactions, we combine the forward and reverse reactions and use a different arrow. The above reactions, where liquid is going to gas and gas is going to liquid is shown as follows:

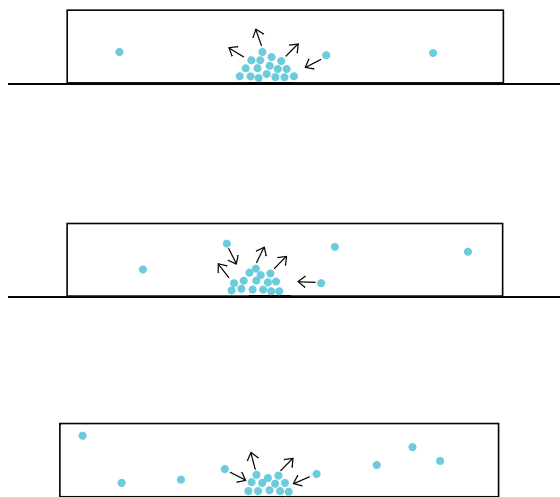
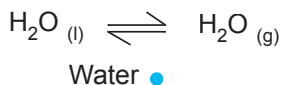


► Can the reaction $\text{H}_2\text{O}_{(g)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ also be used to describe the above experiment?

GENERAL EQUILIBRIUM

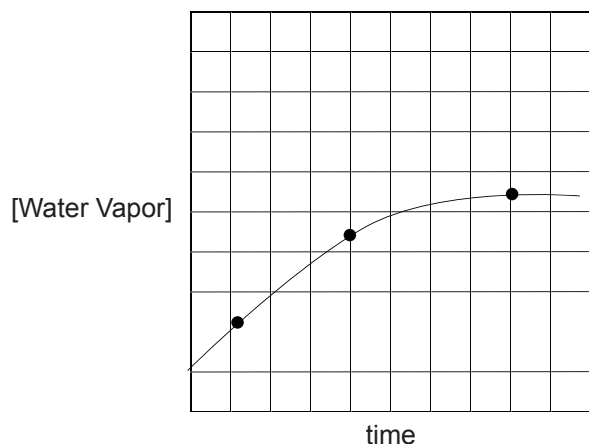
REACHING EQUILIBRIUM

It is important to remember that in DYNAMIC EQUILIBRIUM, the rate of the forward reaction (liquid going to vapor) is equal to the rate of the backward reaction (vapor going to liquid), but that the molecules do not stop at that point. The water molecules are constantly moving in both the liquid and vapor phases.



There are billions of molecules in a single drop of water. There may be small fluctuations in the numbers of molecules leaving the liquid phase vs. the number of molecules entering the liquid phase even at equilibrium. For example, 2 billion molecules might leave the liquid phase, while 2 billion and 2 enter the liquid phase. So the rate of the forward reaction is not equal to the reverse reaction, correct? However, because there are so many molecules, small variations do not matter. These slight fluctuations happen in every chemical reaction, and because we work with so many molecules at one time, we say that at equilibrium, the rate of the forward reaction equals the rate of the reverse reaction despite these fluctuations.

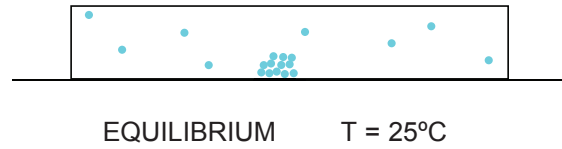
► Each of the three points marked on the graph correspond to one of the pictures above. Match each picture with the point it corresponds to.



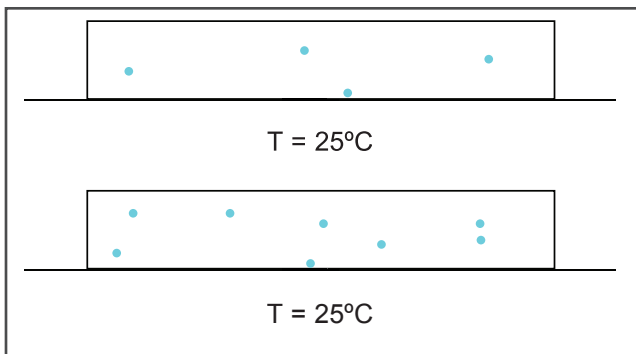
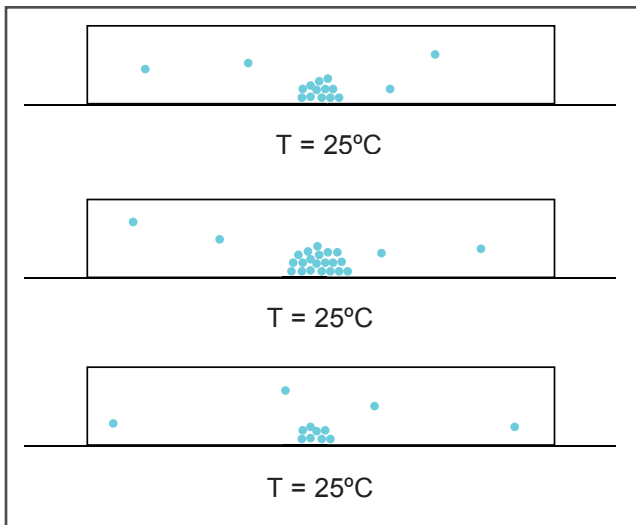
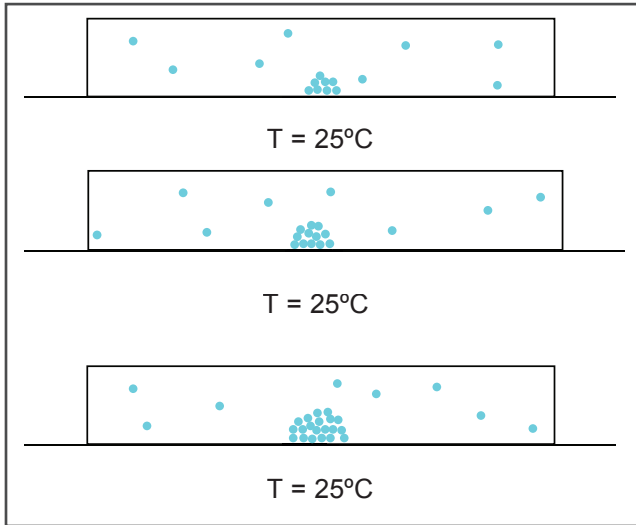
GENERAL EQUILIBRIUM

TO EQUILIBRIUM OR NOT!

The picture at the right shows an experiment that has reached equilibrium. It is a water drop with 12 molecules in the liquid state and 8 molecules in the vapor state. The temperature is 25 °C.



► Answer the questions at the right of the pictures by comparing them with the equilibrium picture above.



► The pictures at left are at equilibrium. Count the number of molecules in the liquid phase for each picture. How can each be at equilibrium when the number of molecules in the liquid phase is varying?

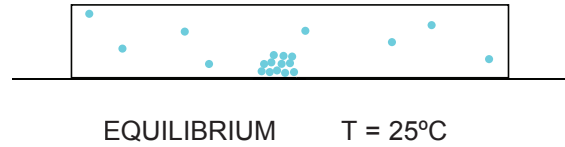
► The pictures at left are at equilibrium. Count the number of molecules in the vapor phase for each picture. Why is none of these pictures at equilibrium? Will these experiments ever reach equilibrium? Why or why not?

► Mark each of the pictures at left as either “at equilibrium”, “not at equilibrium”, or “not enough information given” and give the reasons for your answer.

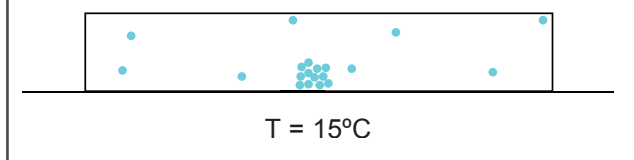
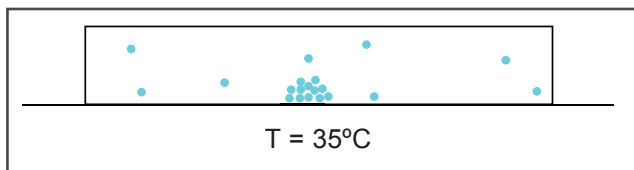
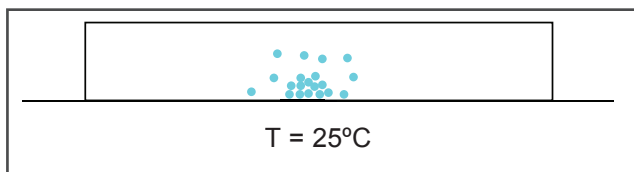
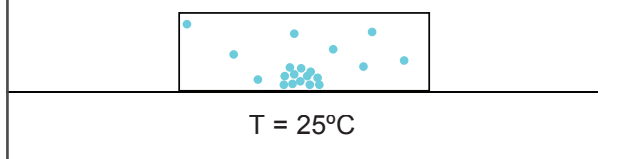
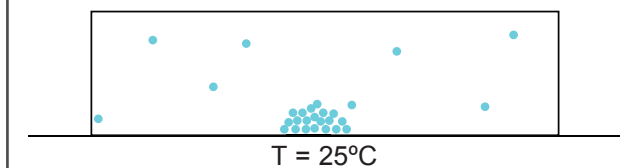
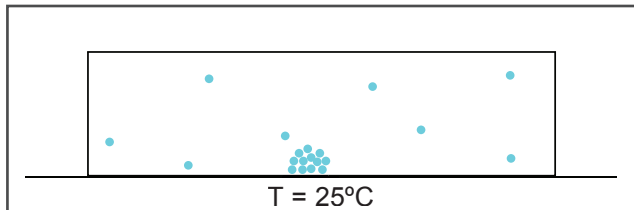
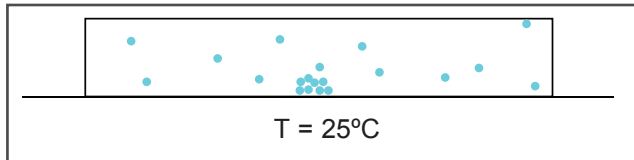
GENERAL EQUILIBRIUM

TO EQUILIBRIUM OR NOT!

The picture at the right shows an experiment that has reached equilibrium. It is a water drop with 12 molecules in the liquid state and 8 molecules in the vapor state. The temperature is 25 °C.



► Answer the questions at the right of the pictures by comparing them with the equilibrium picture.



► Is this experiment at equilibrium? Is this picture possible given the conditions? What will happen to the water vapor if this experiment was left alone for 10 minutes?

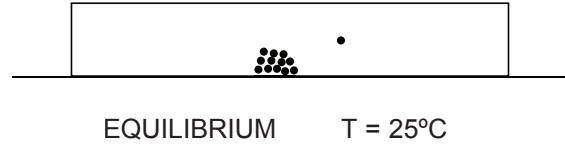
► Give 1 reason for each picture at the left for why it is not at equilibrium? Why does pressure affect equilibrium?

► This picture shows 8 molecules in the vapor phase; why is it NOT at equilibrium?

► Neither of these pictures at the left is at equilibrium. State whether there would be more than 8 molecules or less than 8 molecules in the vapor state at equilibrium for each picture. Give a reason for your answers.

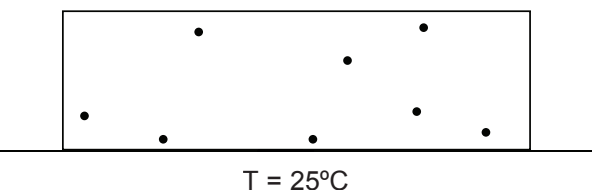
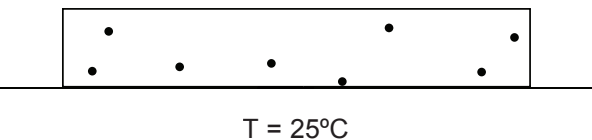
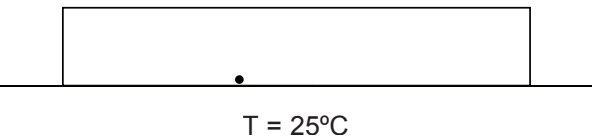
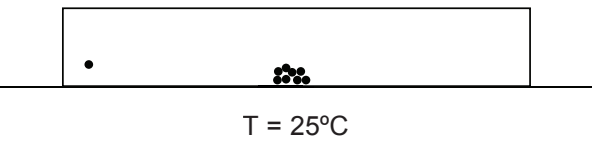
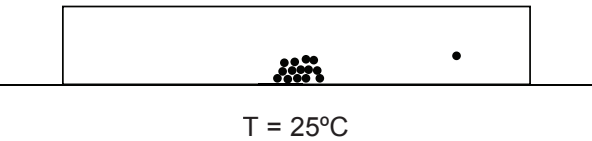
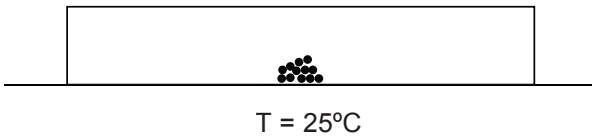
GENERAL EQUILIBRIUM TO EQUILIBRIUM OR NOT!

The picture at the right shows an experiment that has reached equilibrium. It is a liquid drop with 12 molecules in the liquid state and 1 molecule in the vapor state. The temperature is 25 °C.



► Compare each of the following pictures with the equilibrium state. Mark each picture to show whether it is at equilibrium (E), not at equilibrium (NE), or whether you need more information (NMI). Give one reason for your answer for each picture.

► Could this liquid be water?

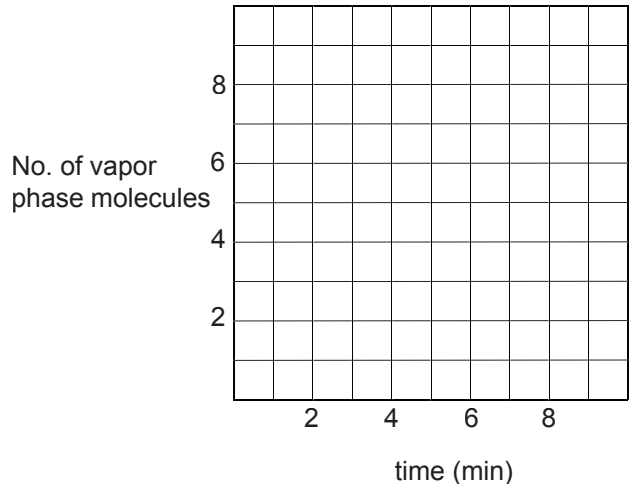
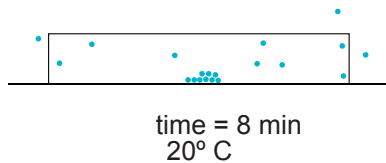
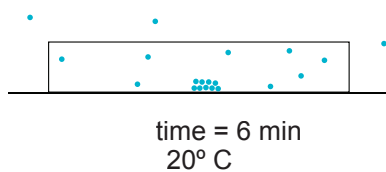
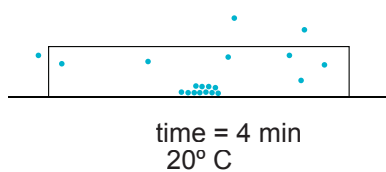
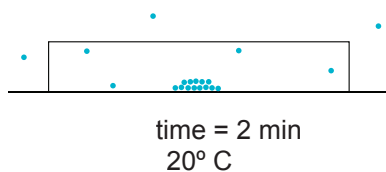
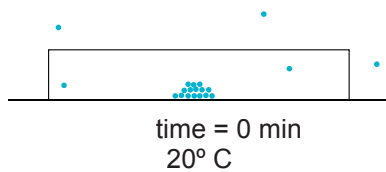


GENERAL EQUILIBRIUM

EVAPORATIVE EQUILIBRIUM

Let's look again at the same experiment. This time, count the number of water molecules in the vapor phase and plot them on the graph.

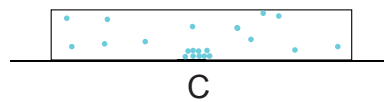
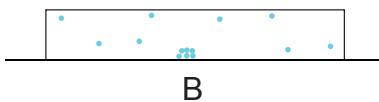
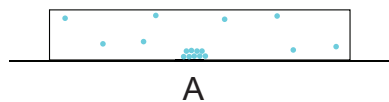
► Do you think you should include the vapor phase molecules outside the petri dish?



► At which point does the experiment reach equilibrium? Mark this point on the graph.

► Write two equilibrium reactions to describe this experiment.

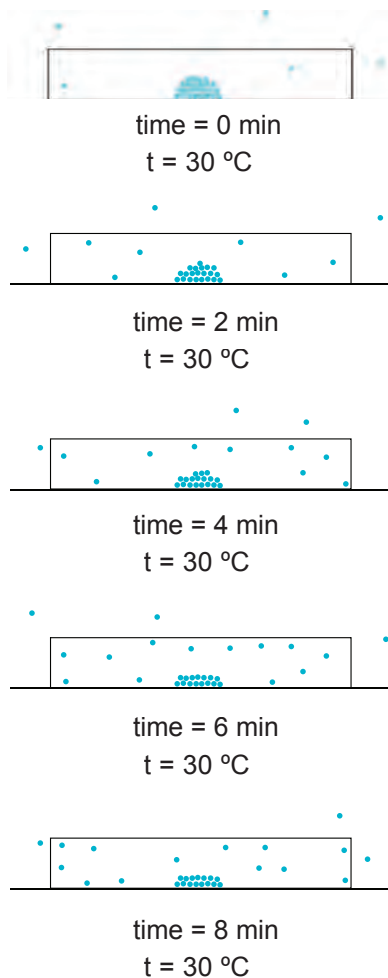
► Choose the correct picture that represents the state of the above experiment after 10 minutes at equilibrium and explain why it is the correct answer?



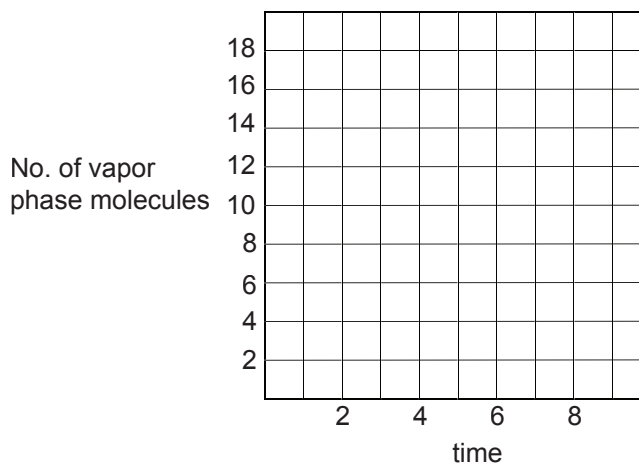
GENERAL EQUILIBRIUM

EVAPORATIVE EQUILIBRIUM

In this experiment, the temperature of the container is raised.

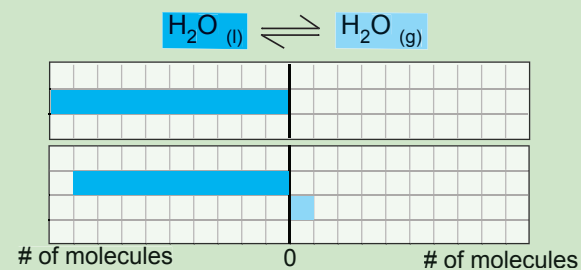


► Again, plot the number of molecules in the vapor phase vs. time.

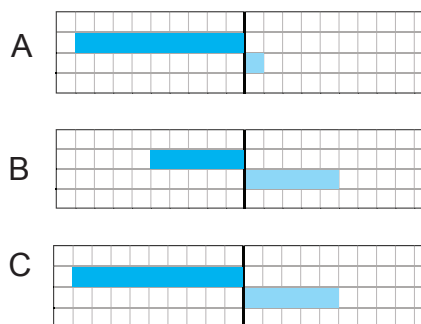


► Compare the graph above with the previous graph. What effect does increasing the temperature have on equilibrium?

► Starting with the following equilibrium shown in this ChemLog:



Choose the ChemLog that most accurately represents the number of water molecules in each phase when the original drop reaches equilibrium at a higher temperature. Explain the reasons for your choice.

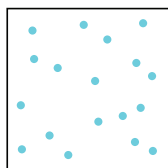


GENERAL EQUILIBRIUM

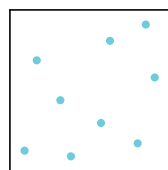
HUMIDITY

Humidity refers to the amount of moisture in the air. The relative humidity is a measure of how much water the air is holding compared to how much it could hold (the saturation) at a certain temperature.

The following picture shows one liter of air that is saturated with water at 25 °C. Each blue dot equals one 1 gram of water.



The following picture shows one liter of air at 25 °C.



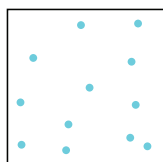
Let's calculate the relative humidity.

$$\frac{\text{Humidity at } 25\text{ }^{\circ}\text{C}}{\text{Water saturation at } 25\text{ }^{\circ}\text{C}} \times 100 =$$

$$\frac{[\text{H}_2\text{O}_{(g)}]}{[\text{H}_2\text{O}_{(g)}]} \times 100 =$$

$$\frac{0.5\text{ mol L}^{-1}}{1\text{ mol L}^{-1}} \times 100 = 50\%$$

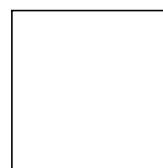
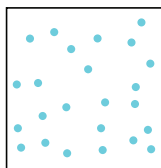
► Calculate the relative humidity for this picture at 25 °C.



► Will the saturation of water increase or decrease when the temperature is raised?

► If the temperature of air at 50% relative humidity is raised 10 °C, will the relative humidity increase or decrease?

► The following picture on the left shows a saturation vapor pressure. Draw a 25% relative humidity in the blank box.



► Is the box on the left at a temperature greater than or lesser than 25 °C? Explain your answer.

The equilibrium constant, K_c , is a measure of the composition of a reaction mixture at equilibrium. It is defined as the concentration of products raised to their stoichiometric coefficients, divided by the concentration of reactants raised to their stoichiometric coefficients.

So what is the equilibrium constant for this reaction?

$$K_c = \frac{[\text{H}_2\text{O}_{(g)}]}{[\text{H}_2\text{O}_{(l)}]}$$

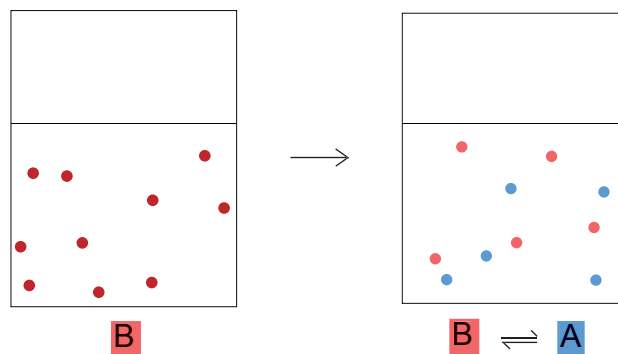
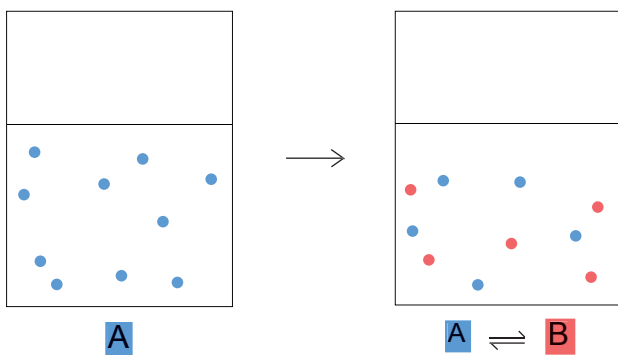
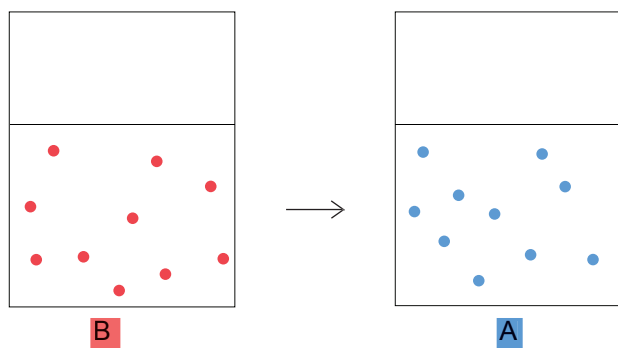
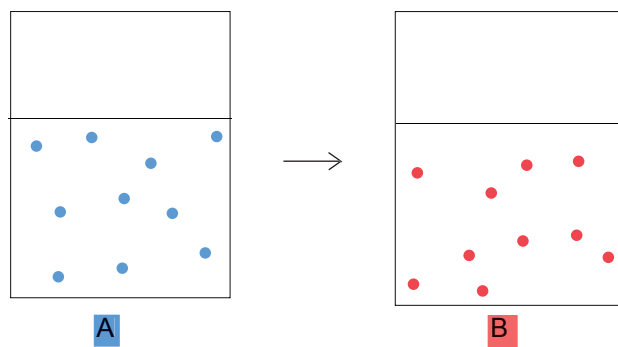
Yikes! The molarity of water? Uh oh! Actually, it's not as bad as it seems. The molarity of pure water is a constant - 55.6 M. So,

$$55.6\text{ M} \times K_c = [\text{H}_2\text{O}_{(g)}]$$

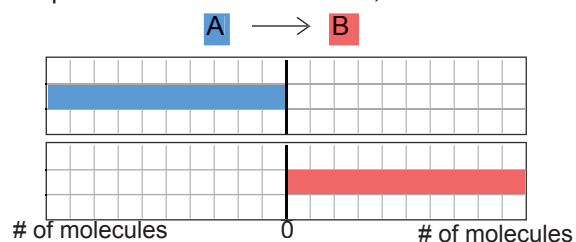
GENERAL EQUILIBRIUM

REACTANTS AND PRODUCTS

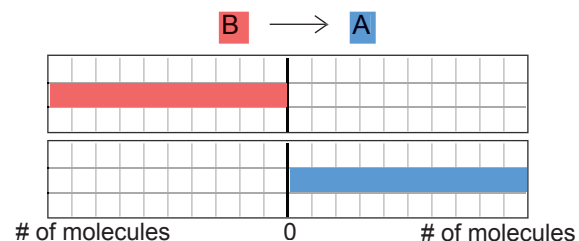
In an equilibrium reaction involving compounds A and B, A goes to B at the same rate that B goes to A. In general, the things on the left side of the arrow are termed "reactants" while the items on the right side of the arrow are termed "products".



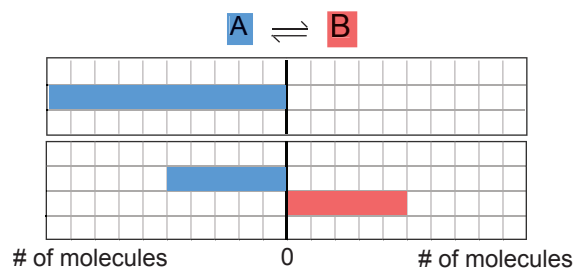
The reactant of this reaction is A, the blue dots. The product of this reaction is B, the red dots.



► What is the reactant in this reaction?
What is the product of this reaction?

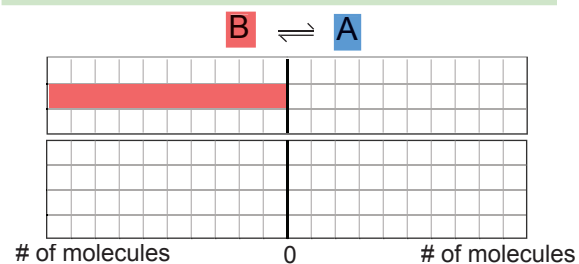


The reactant of this equilibrium reaction is A, the blue dots. The product of this equilibrium reaction is B, the red dots.



► What is the reactant in this reaction?
What is the product of this reaction?

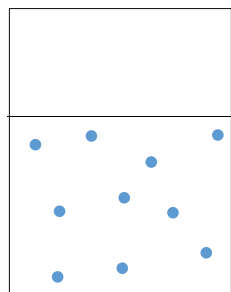
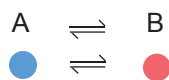
► Complete the ChemLog.



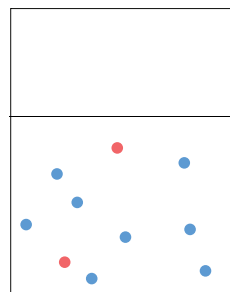
GENERAL EQUILIBRIUM

PLOTTING EQUILIBRIUM CONSTANTS

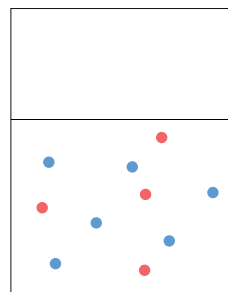
► Assume each circle below is 0.1 mole and that each box contains 1 liter of solvent. Plot the concentration of A versus time on the graph directly below the pictures. Then plot the concentration of B versus time on the same graph. Label each line as [A] or [B].



1



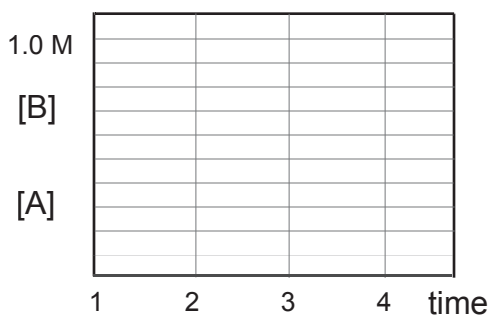
2



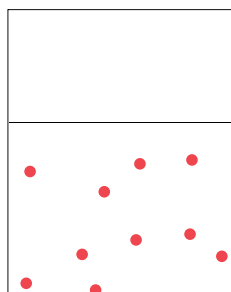
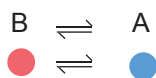
3



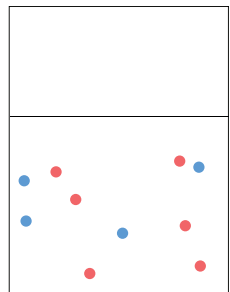
4



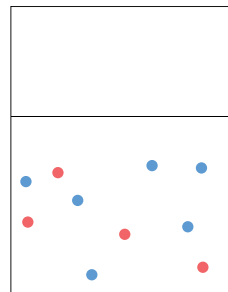
► Mark the point at which equilibrium is reached.



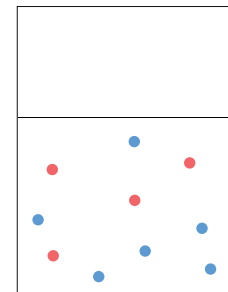
1



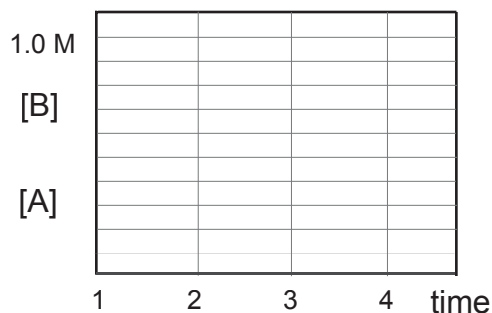
2



3



4



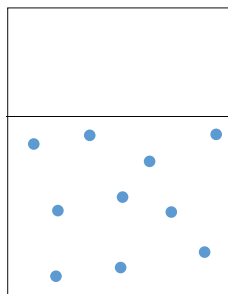
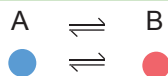
► Mark the point at which equilibrium is reached.

► Define equilibrium in terms of the rates of the forward and reverse reactions.

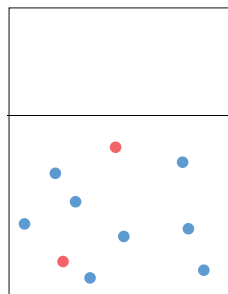
GENERAL EQUILIBRIUM

PLOTTING EQUILIBRIUM CONSTANTS

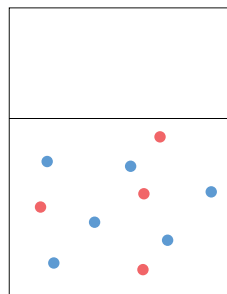
► Assume each circle below is 0.1 mole and that each box contains 1 liter of solvent. Plot the concentration of A versus time on the graph directly below the pictures. Then plot the concentration of B versus time on the same graph. Label each line as [A] or [B].



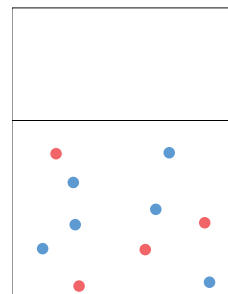
1



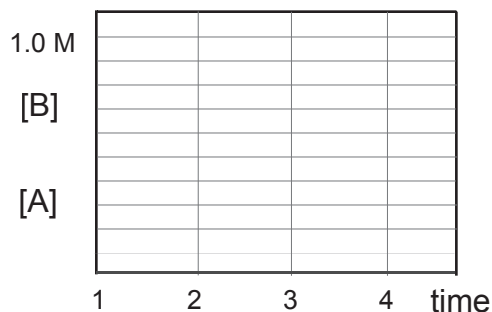
2



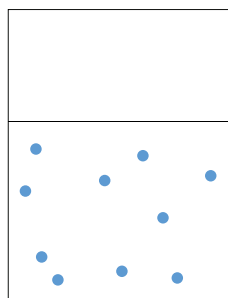
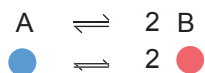
3



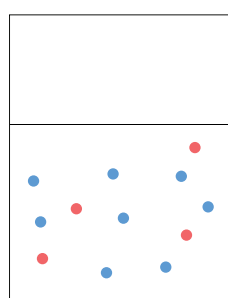
4



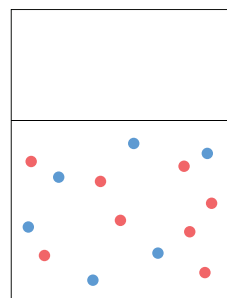
► Mark the point at which equilibrium is reached.



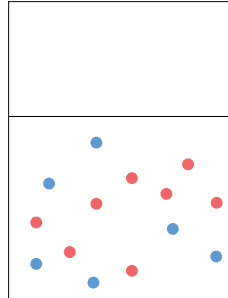
1



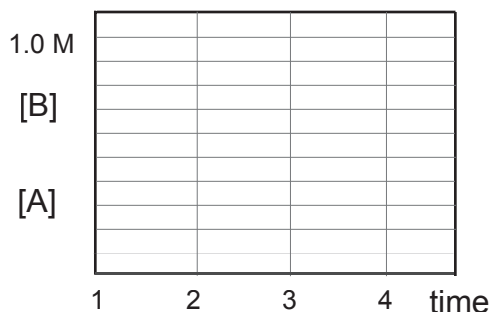
2



3



4



► Mark the point at which equilibrium is reached.

► Explain any differences or similarities you see in each graph.

GENERAL EQUILIBRIUM

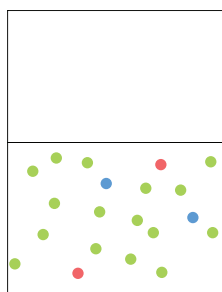
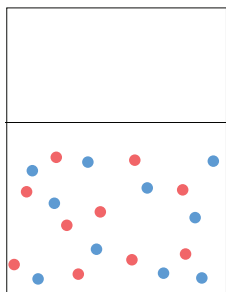
CALCULATING EQUILIBRIUM CONSTANTS

As stated earlier, the equilibrium constant, K_c , is a measure of the composition of a reaction mixture at equilibrium. It is defined as the concentration of products raised to their stoichiometric coefficients, divided by the concentration of reactants raised to their stoichiometric coefficients.

► For the following pictures, give the equilibrium equation and calculate K_c . The first one is done for you.

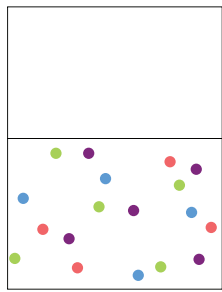
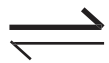
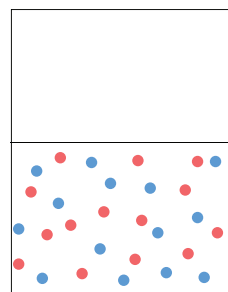
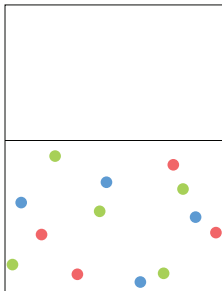
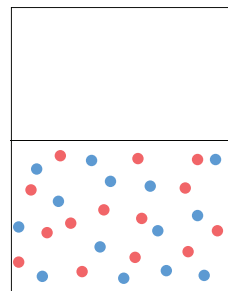
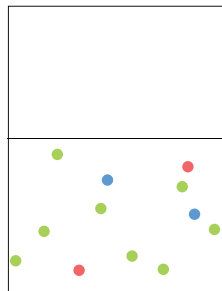
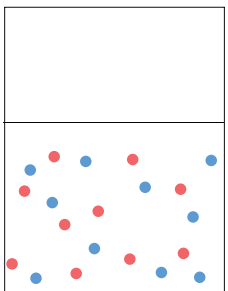
Reactants

Equilibrium



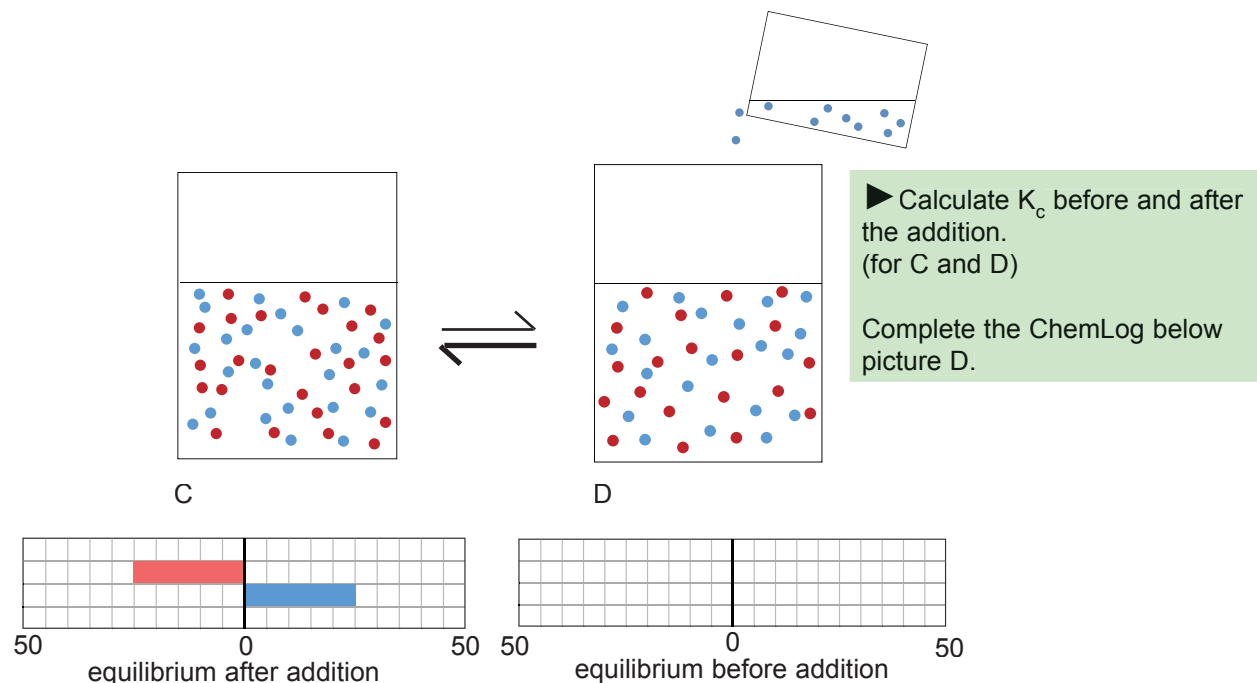
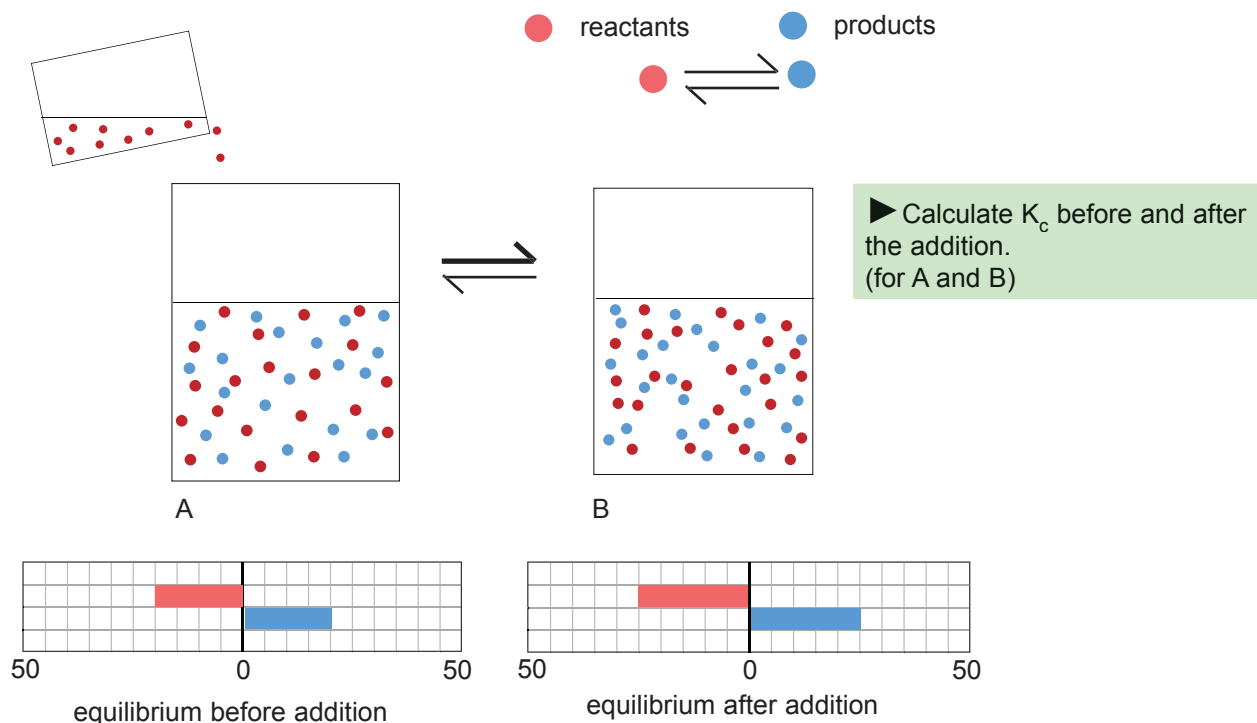
$$K_c = \frac{[C]^2}{[A][B]} = \frac{[16]^2}{[2][2]} = \frac{256}{4}$$

$$K_c = 64$$



GENERAL EQUILIBRIUM

LE CHATELIER'S PRINCIPLE

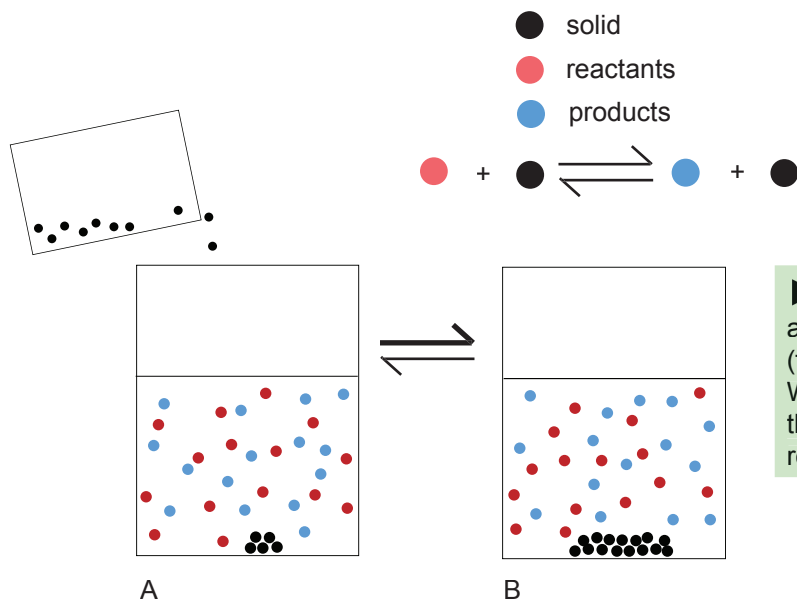


► How would removing products from D affect the equilibrium?

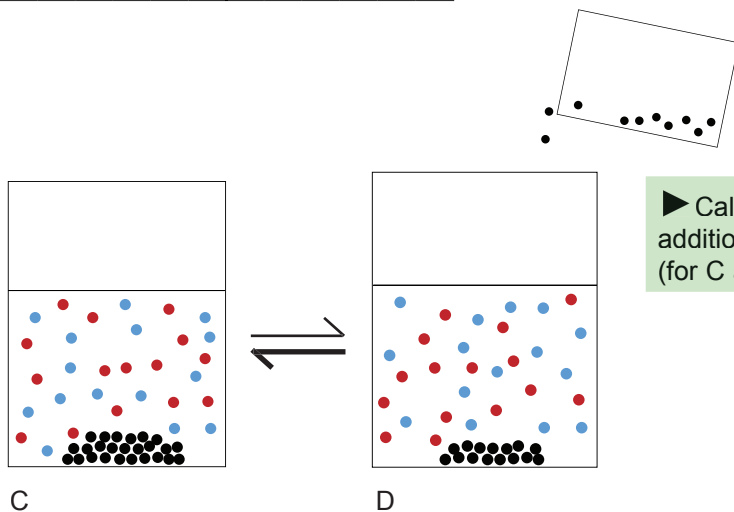
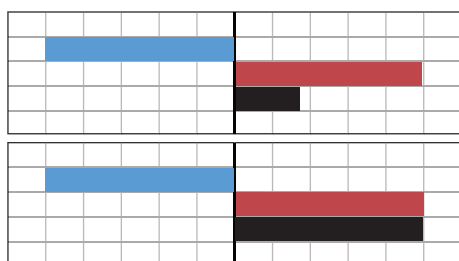
► Is the reaction at equilibrium in A when more reactants have been added, but have not yet made products?

GENERAL EQUILIBRIUM

LE CHATELIER'S PRINCIPLE



► Calculate K_c before and after the addition.
 (for A and B)
 What does this addition tell you about the effect of solids in an equilibrium reaction?



► Calculate K_c before and after the addition.
 (for C and D)

► How would removing black circles from D affect the equilibrium?

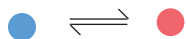
► Is the reaction at equilibrium in A when more reactants have been added, but have not yet made products?

► If you worked in the chemical industry, where obtaining the maximum product in the most cost efficient way is the primary goal, how would you use Le Chatelier's principle to maximize products in equilibrium reactions without adding more reactants?

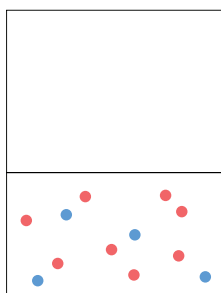
GENERAL EQUILIBRIUM

TEMPERATURE AND EQUILIBRIUM

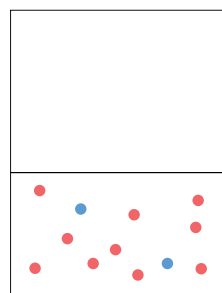
For an endothermic reaction



$$T_1 < T_2$$



Equilibrium at T_1

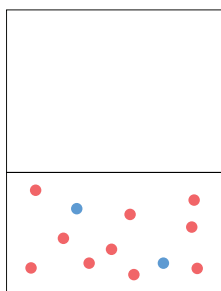


Equilibrium at T_2

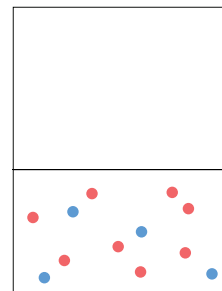
For an exothermic reaction



$$T_1 < T_2$$



Equilibrium at T_1



Equilibrium at T_2

► Explain why an increase in temperature would shift an endothermic reaction towards products.

► Explain why an increase in temperature would shift an exothermic reaction towards reactants.

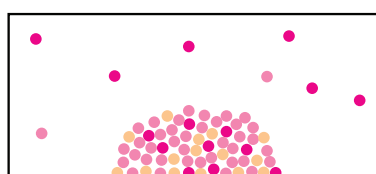
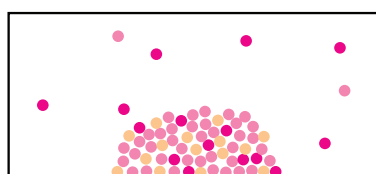
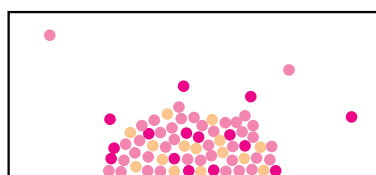
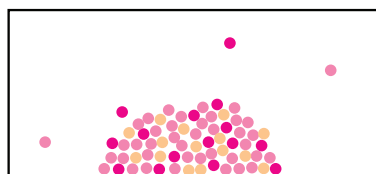
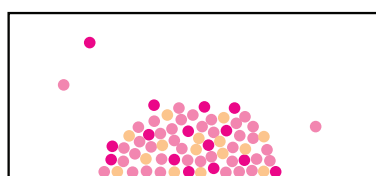
► For endothermic and exothermic reactions, state whether an increase in temperature will increase or decrease the value of K_c . You may calculate K_c for each beaker to determine the answer.

► For endothermic and exothermic reactions, state whether a decrease in temperature will increase or decrease the value of K_c . You may calculate K_c for each beaker to determine the answer.

GENERAL EQUILIBRIUM

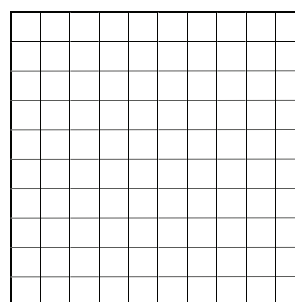
VAPOR PRESSURE EQUILIBRIUM

Back to vapor pressure equilibrium that we discussed as an introduction to equilibrium. Notice that in this drop of water, the molecules are colored differently. Each color represents a molecule of a different energy. Of course, the drop is at a certain temperature, but the molecules that make up the drop can vary in their speed.



► Plot the number in the gas phase molecules versus time and mark on the graph where equilibrium is reached.

no. in
gas
phase



time

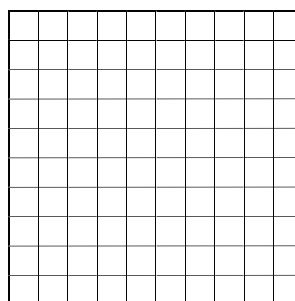
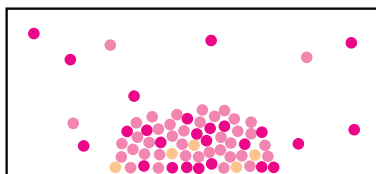
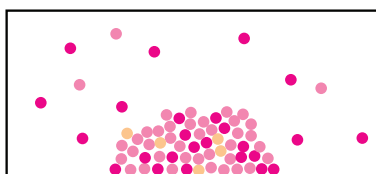
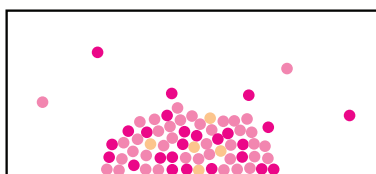
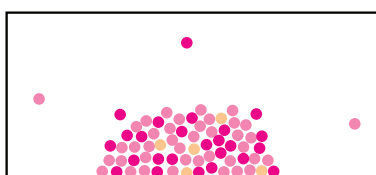
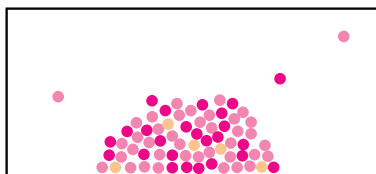
► Which water molecules do you think are at the highest energy? Which are moving the slowest?

GENERAL EQUILIBRIUM

EQUILIBRIUM DEPENDENCE ON TEMPERATURE

Now we've increased the temperature of the water drop. This is evident from the fact that there are more dark pink molecules in the container.

► What effect do you think this will have on the equilibrium? Plot the equilibrium and compare it to the equilibrium curve in the previous example. Describe the effect that raising the temperature has on this equilibrium.

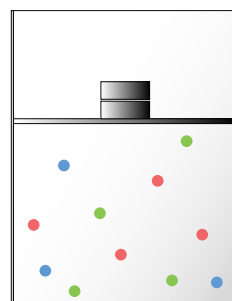
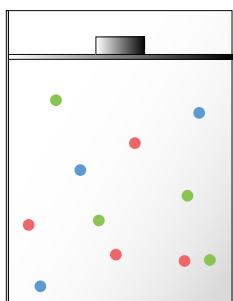
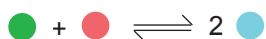
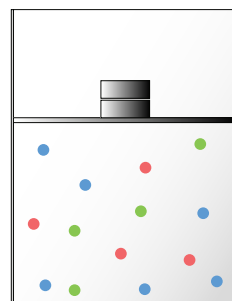
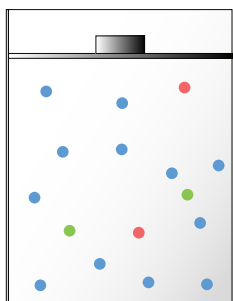
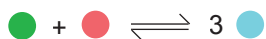
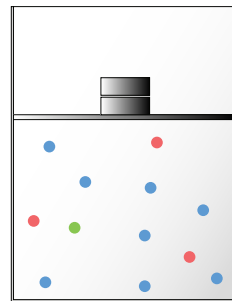
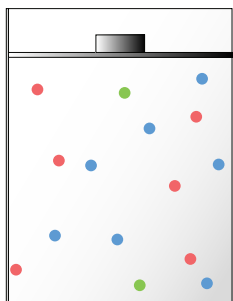


GENERAL EQUILIBRIUM

PRESSURE AND EQUILIBRIUM

Increases in pressure tend to minimize the number of moles in an equilibrium reaction.

► In each of the following examples, count the number of products. State why the equilibrium shifted in the direction it did.

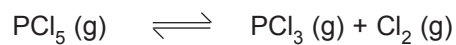


► In which direction would the equilibrium shift if we lowered the pressure for the systems in the left column?

GENERAL EQUILIBRIUM

EQUILIBRIUM SHIFTS

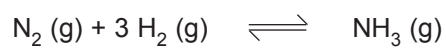
In the following reactions, state whether the equilibrium will shift towards products or reactants upon the change stated.



Addition of $\text{PCl}_5(\text{g})$?

Addition of $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$?

Increase in pressure?



Addition of $\text{N}_2(\text{g})$?

Removal of $\text{NH}_3(\text{g})$?

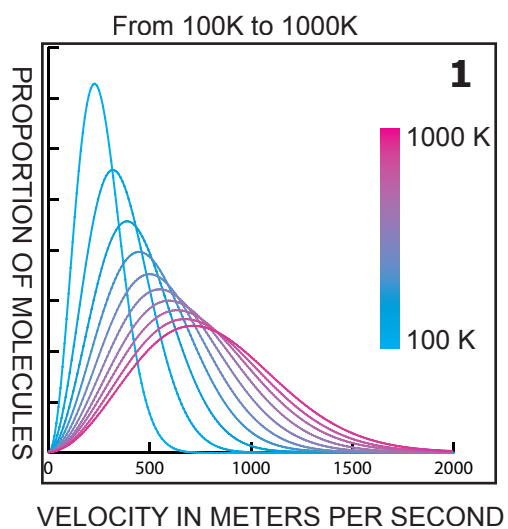
Removal of $\text{H}_2(\text{g})$?

Decrease in pressure?

Why does the equilibrium shift?

In other words, why is Le Chatelier's Principle correct?

KINETICS



by
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MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

KINETICS

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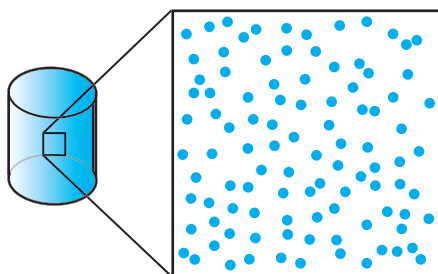
KINETICS

RATE OF A REACTION



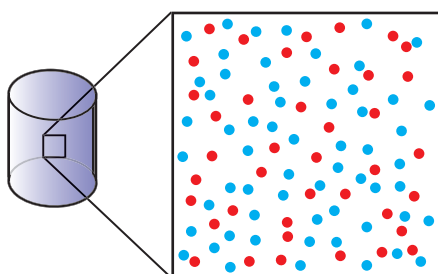
t = time

t = 0 minutes



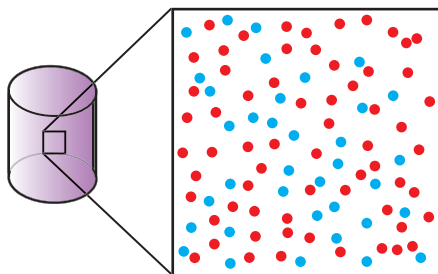
100 blue

t = 1 minute



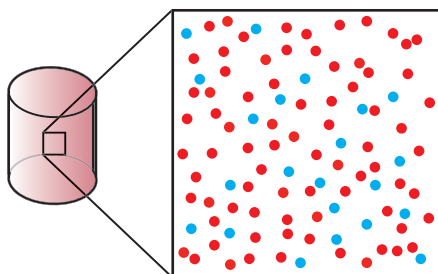
60 blue, 40 red

t = 2 minutes



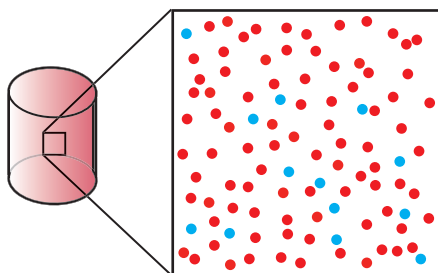
36 blue, 64 red

t = 3 minutes



22 blue, 78 red

t = 4 minutes



13 blue, 87 red

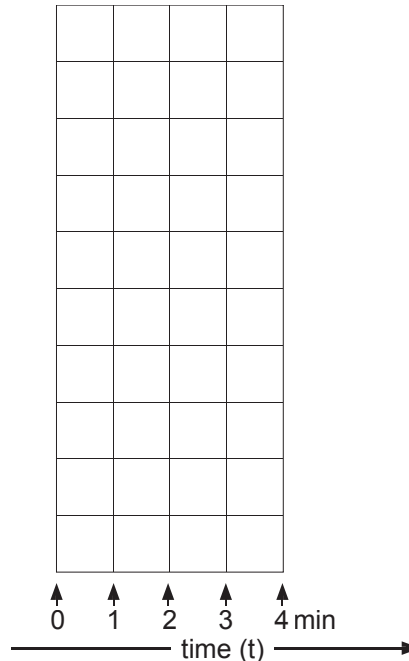
What is happening to the number of blue dots as time proceeds?

What is happening to the number of red dots as time proceeds?

Is the total number of dots changing?

If each dot represents a molecule, what is the stoichiometry of the reaction?

Forty blue dots disappeared during the first minute (between t = 0 minutes and t = 1 minute). How many blue dots disappeared between t = 1 minute and t = 2 minutes? Between t = 2 minutes and t = 3 minutes? Between t = 3 minutes and t = 4 minutes? What does this tell you about the rate at which blue dots are disappearing?



KINETICS

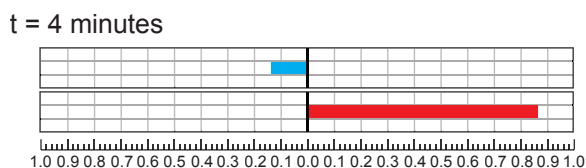
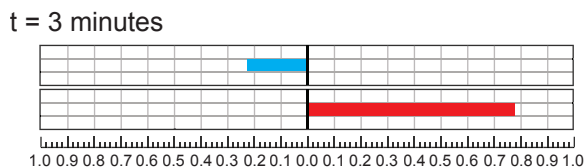
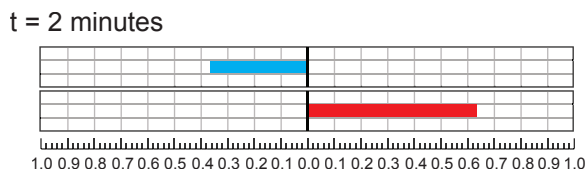
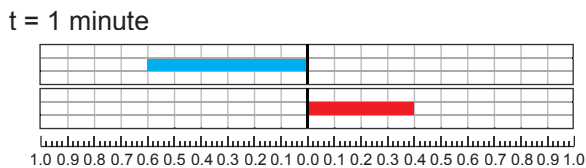
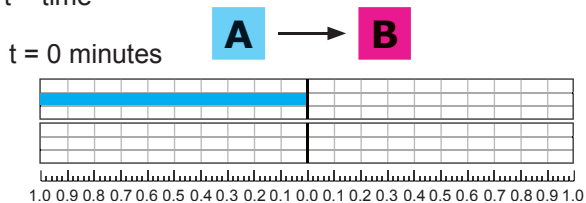
RATE OF A REACTION

On the previous page we show a molecular representation of a reaction $A \rightarrow B$ where A is represented by blue circles and B by red circles. Actual chemical concentrations are measured in moles per liter, which has the units mol L^{-1} .

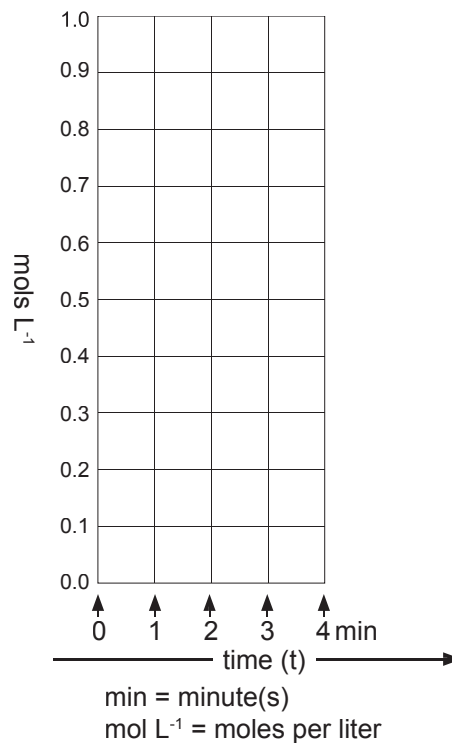
Now we will give the original concentration of A as 1 mol L^{-1} .

This is shown by the width of the blue stripe on the ChemLog for $t = 0$ just below.

$t = \text{time}$



Using the ChemLogs at left, measure the concentration of A (blue) at times 0 through 4 minutes. Plot those concentrations on the chart below, then draw a curve through the five points. Do the same for B (red).



Now calculate the change in A at one minute intervals.

For example, 40 A's change to B during the interval between $t = 0$ minutes and $t = 1$ minute. Now we can say that the average rate at which A changed to B during the first minute was 40 A's per minute.

Do this for the intervals from $t = 1$ minute to $t = 2$ minutes, then from $t = 2$ minutes to $t = 3$ minutes, then from $t = 3$ minutes to $t = 4$ minutes.

Compare and contrast the average rates for each of the four 1 minute intervals. What do you notice and why do you think this is happening?

Using the graph you made above, find the time at which the original concentration of A (1.0 mol L^{-1}) had been reduced to half (0.5 mol L^{-1}), then find the time at which the concentration of A was 0.25 mol L^{-1} .

The time it takes to reduce a substance to one half of its original concentration is called its half life.

What can you deduce about this reaction by comparing its half life from 1.0 mol L^{-1} to 0.5 mol L^{-1} , with the half life from 0.5 mol L^{-1} to 0.25 mol L^{-1} ?

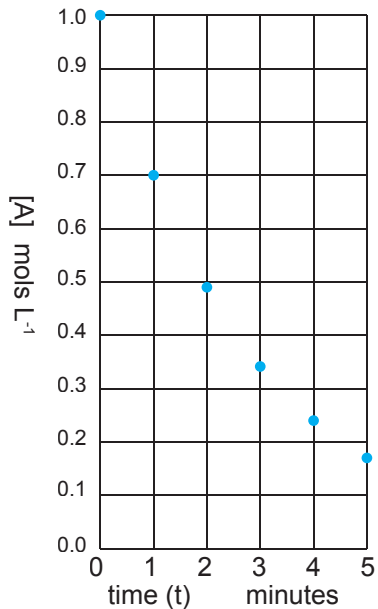
KINETICS

RATE OF A REACTION

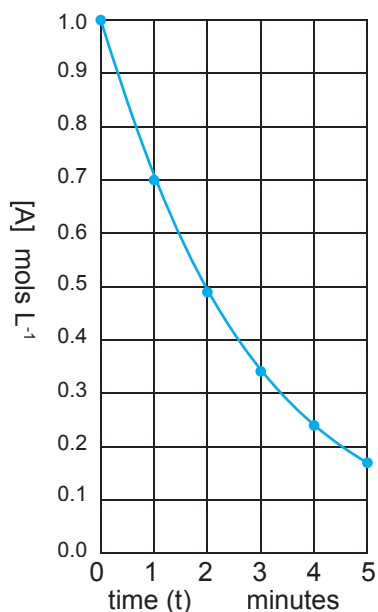
Suppose we have an $A \rightarrow B$ reaction and we experimentally measure the concentrations at different times, which are given in the following table:

time	[A]
0 minutes	1.00 mol L ⁻¹
1 minute	0.70 mol L ⁻¹
2 minutes	0.50 mol L ⁻¹
3 minutes	0.34 mol L ⁻¹
4 minutes	0.24 mol L ⁻¹

We can plot the data on a graph:

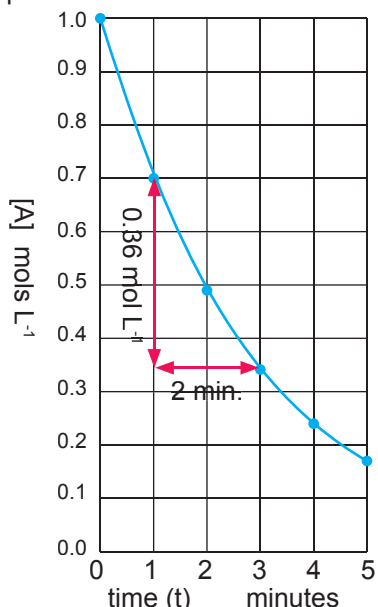


The next step is to connect the data with a curve:



The last graph gives the concentration of A in moles per liter, [A], at any time between $t = 0$ minutes and $t = 5$ minutes but we want to know the rate at which [A] is changing.

The definition of the rate is how many moles per liter of A is lost per unit of time. We will determine this from our graph.

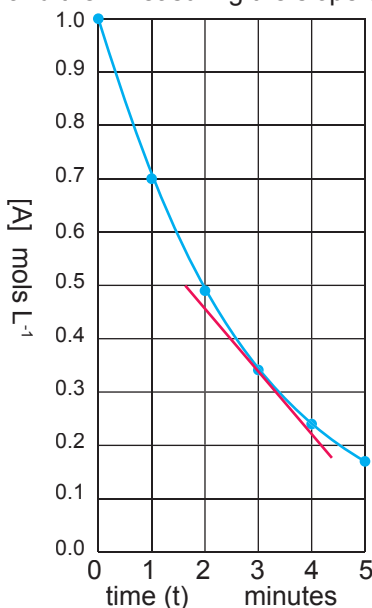


From our graph we can see that [A] decreased by 0.36 moles per liter over the two minute interval between $t = 1$ minute and $t = 3$ minutes. We can calculate the average rate at which [A] changes by

$$\text{rate} = \frac{-0.36 \text{ moles L}^{-1}}{2 \text{ min}} = -0.18 \text{ mol L}^{-1} \text{ min}^{-1}$$

By definition, the change in the vertical dimension of a curve divided by the change in the horizontal dimension of the curve is the average slope of that curve over that interval. You may recall from trigonometry that this is also the definition of the tangent.

We can, in fact, measure the instantaneous rate of change by drawing a tangent to the curve at any point and then measuring the slope of that tangent.



Find the instantaneous change in the rate of decrease of [A] at $t = 3$ min. by measuring the slope of the tangent drawn on the graph. Draw a tangent to the curve at $t = 1$ min and use that tangent to determine the rate of decrease of [A] at that time. Compare the rates at $t = 1$ min and $t = 3$ min.

KINETICS

ORDER OF A REACTION

On the previous page we introduced a set of experimental measurements of the concentration of a reactant, A, at successive times. From that we could graphically determine the rate of decrease in the concentration of A at any intermediate time. But what determines the varying rates? In fact, the only aspect of the situation which differs at the various times is the concentration of A itself. So we can try to find a rate law which shows how the rate of change in the concentration of A depends upon the concentration of A.

A simple possibility would be:

$$\text{rate} = k[A]^n$$

where k is some constant, [A] is the concentration of A (in moles per liter) and n is some exponent of [A].

If we can determine k and n from the data then we have found the rate law.

Using our last graph we can find the rate at t = 2 minutes to be

$$\text{rate}_2 = -0.18 \text{ mols L}^{-1} \text{ min}^{-1}$$

and at t = 4 minutes we find

$$\text{rate}_4 = -0.09 \text{ mols L}^{-1} \text{ min}^{-1}$$

Next we divide the rates

$$\frac{\text{rate}_2}{\text{rate}_4} = \frac{-0.18 \text{ mols L}^{-1} \text{ min}^{-1}}{-0.09 \text{ mols L}^{-1} \text{ min}^{-1}} = 2$$

but also

$$\frac{\text{rate}_2}{\text{rate}_4} = \frac{k[A_2]^n}{k[A_4]^n} = \left(\frac{A_2}{A_4}\right)^n = \left(\frac{0.48 \text{ mols L}^{-1}}{0.24 \text{ mols L}^{-1}}\right)^n = 2.0^n$$

from which we can reasonably conclude, within the limits of our measurements, that n = 1 and

$$\text{rate} = k[A]^1 = k[A]$$

We can then find k by substituting data from any of our measurements, for example, at t = 2 minutes we have

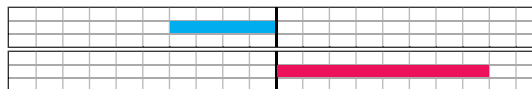
$$\text{rate} = -0.18 \text{ mols L}^{-1} \text{ min}^{-1} = k(0.49 \text{ mols L}^{-1})$$

giving

$$k = -0.37 \text{ min}^{-1}$$

And so we can write the rate law as

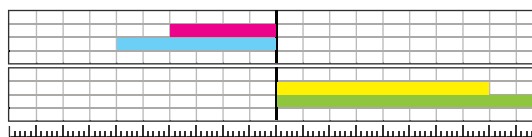
$$\text{rate} = k[A] = (-0.37 \text{ min}^{-1})[A]$$



If M reacts at a rate of $0.5 \text{ mol L}^{-1} \text{ min}^{-1}$, at what rate does N appear?

$$0.5 \text{ mol L}^{-1} \text{ min}^{-1} \times \frac{\text{red bar}}{\text{blue bar}} =$$

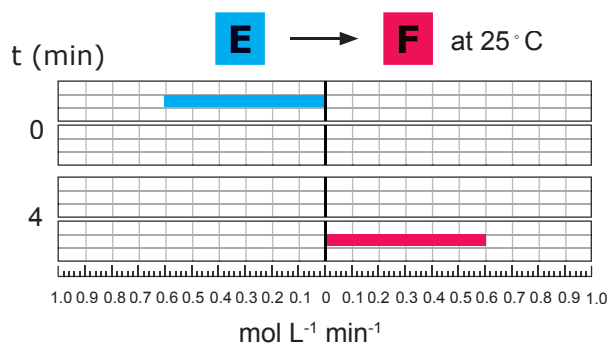
$$0.5 \text{ mol L}^{-1} \text{ min}^{-1} \times \frac{2}{1} = 1.0 \text{ mol L}^{-1} \text{ min}^{-1}$$



Calculate the rate of disappearance of B and the rate of appearance of C and D if A reacts at a rate of $1.25 \times 10^{-5} \text{ mol}^{-1} \text{ L}^{-1} \text{ min}$.

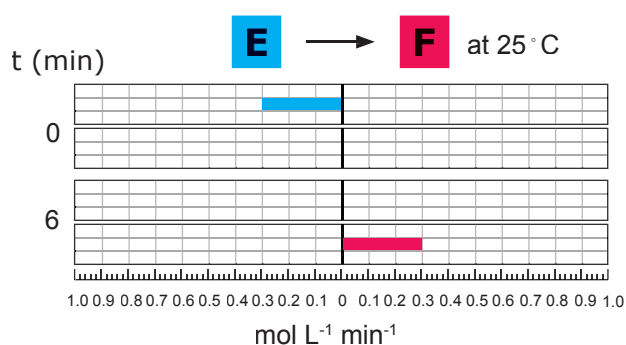
KINETICS

FACTORS THAT AFFECT RATE



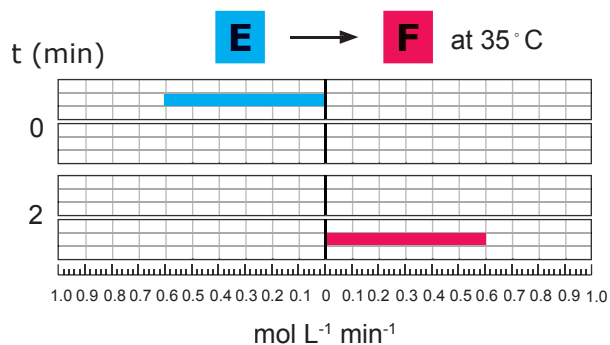
The ChemLog shows the reaction of E → F. Each subsequent ChemLog shows the same reaction and how it is affected by certain changes. Compare the different ChemLogs in order to answer the following question for each factor - concentration change, temperature change, and the presence of a catalyst.

Concentration Change

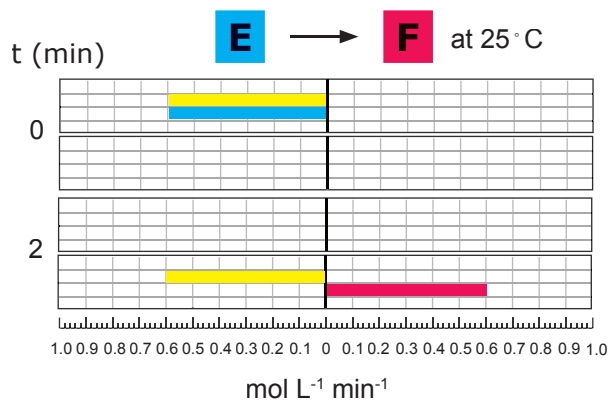


Show your understanding of each ChemLog by stating how the changing factor affects the rate of the reaction and why the change affects the rate in the way it does?

Temperature Change



Presence of a Catalyst



KINETICS

A FIRST ORDER REACTION

The process is radioactive decay of Plutonium to Americium. The formula is $\text{Pu} \rightarrow \text{Am} + e$. In the boxes below we show the Plutonium and the Americium

1

2

3

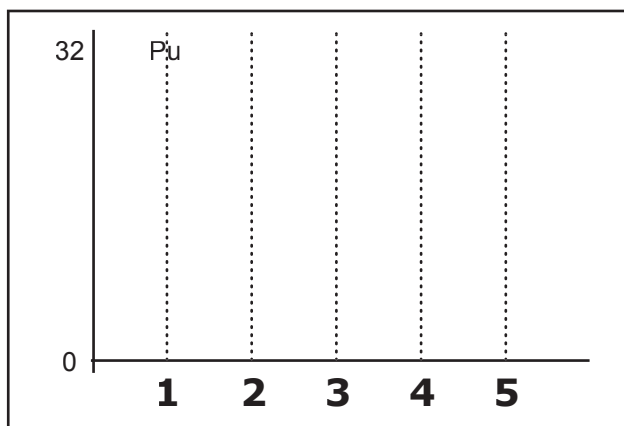
4

5

Count the number of Plutonium atoms and the number of Americium atoms in each box.

BOX	#Pu	#Am
1	_____	_____
2	_____	_____
3	_____	_____
4	_____	_____
5	_____	_____

Plot the number of each kind of atom on the graph below.



Radioactive decay is an important example of a first order reaction. Since the chances of a nucleus decaying is unaffected by any normal external influence, the rate of decay clearly depends only upon the number of nuclei (atoms) present. Thus the rate law is first order and we have:

$$\text{rate} = k[A]$$

The HALF LIFE of a reaction is defined as the time required for half of the reactants to disappear. First order reactions (and only first order reactions) the half life does not depend upon the concentration or amount of the reactant and so we can measure the half life or specify it (from previous measurement) without referring to the amount or concentration of the reactant.

Given that the half life of the decay, $\text{Pu} \rightarrow \text{Am} + e$, is 14.4 years, how long does it take to get from the situation in box 1 to the situation in box 2? box 3? box 4? box 5?

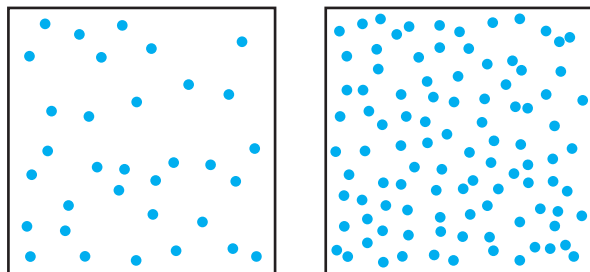
If a certain first order reaction has a half life of one year, how long will it take before one mole of the reactant becomes one half mole? one thirty-second of a mole? one atom?

Why can the last answer (for one atom) only be an approximation?

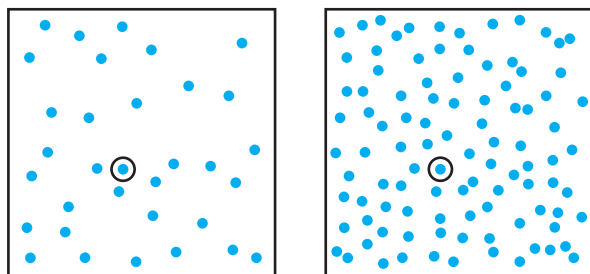
KINETICS

SECOND ORDER REACTIONS

Suppose we have a situation in which two molecules of A combine to give one molecule of B. We write the stoichiometry as $2A \rightarrow B$. How does the concentration of A affect the rate of the reaction?



The pictures above show two different initial conditions. The concentration of A on the right is three times the concentration of A on the left. In a real chemical reaction the A molecules are moving at various velocities and when they collide they sometimes interact to form a B molecule.



Now we have isolated one molecule in each of the two situations. The circled molecule on the right will collide with one of the other molecules three times as often as the circled molecule on the left because the one on the right has three times as many molecules to collide with. This effect causes the rate of collisions to be multiplied by a factor of three. But notice also that we could have circled three times as many different molecules on the right as on the left, which means the rate of collisions will be multiplied by another factor of three. So we have three times as many molecules colliding three times as often. For this reaction the rate of collisions and thus of the reaction depends on the product of the concentration with itself and we can write the rate law as:

$$\text{rate} = k[A][A] = k[A]^2$$

This is called a second order reaction.

The discussion in the left hand column is valid if we are picturing a direct molecular interaction between the blue molecules. This is called an elementary step.

Why would the discussion not be valid if $2A \rightarrow B$ were still the chemical formula for the reaction but not an elementary step?

Look a little closer at the rate law. Suppose we write the rate for the smaller concentration on the left side as $\text{rate}_L = k[A_L][A_L]$ and we can write the rate for the right hand boxes as $\text{rate}_R = k[A_R][A_R]$

From the pictures we know that

$$[A_R] = 3x[A_L]$$

So we have

$$\text{rate}_R = k(3x[A_L])(3x[A_L])$$

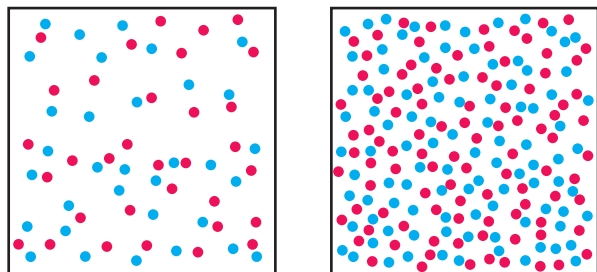
3 times as many molecules to collide with

3 times as many molecules

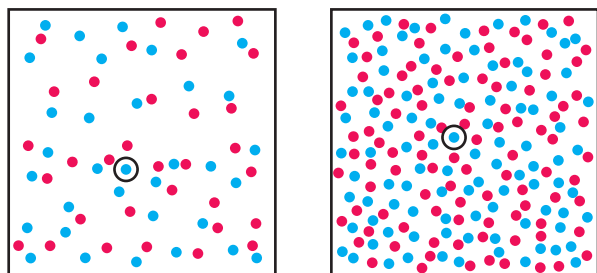
KINETICS



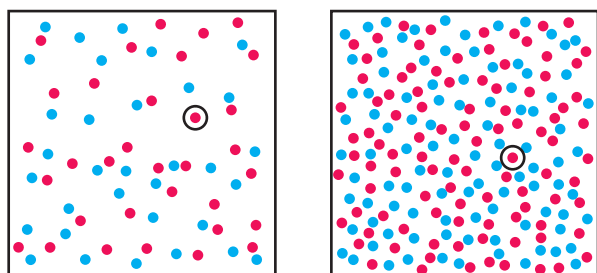
There are chemical reactions where the collision of two different molecules sometimes produces a third kind of molecule. We can write this as $A + B \rightarrow C$.



The left picture above shows initial conditions for the reaction containing 33 blue and 33 red dots, representing molecules. The picture on the right has 99 blue and 99 red dots.



We have isolated one blue molecule in each of these pictures. Assuming that the average speed of the molecules is the same (same temperature) the blue dot on the right will collide with a red dot three times as often as the blue dot on the left.



The circled red dot on the right has three times as many blue dots to collide with as the circled dot on the left.

Assuming that we are describing an elementary step, what order is the reaction described on this page?
Write the rate law.

How will the half life of A relate to the half life of B?

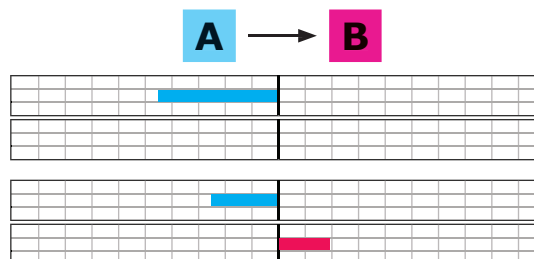
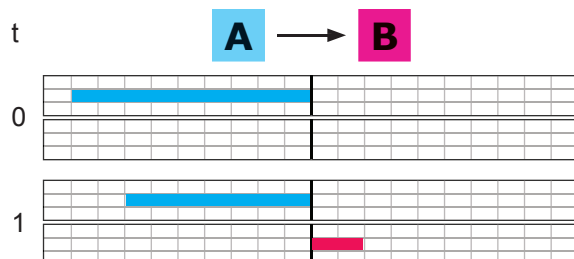
Does your answer to the last question depend upon the fact that we have shown A and B having the same initial concentration in our examples?

KINETICS

CHEMLOGS OF THE ORDERS

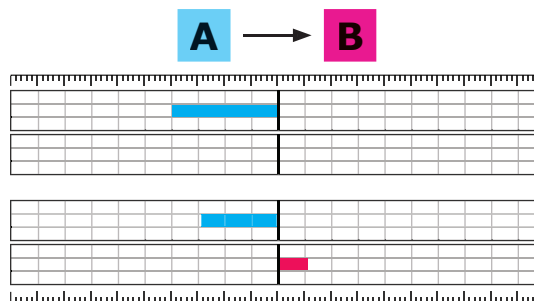
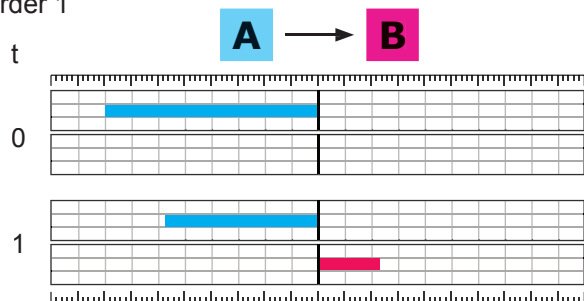
A → B

Order 0



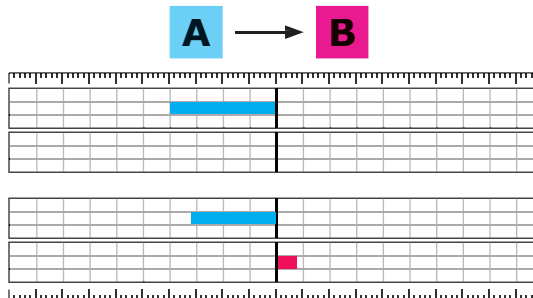
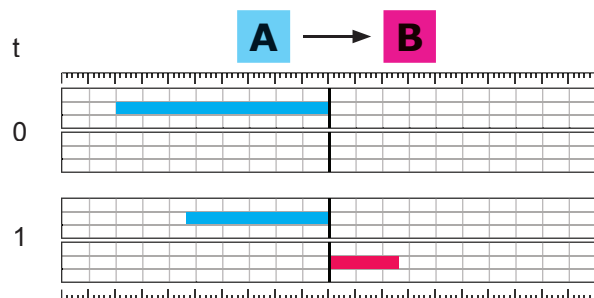
A → B

Order 1



A → B

Order 2

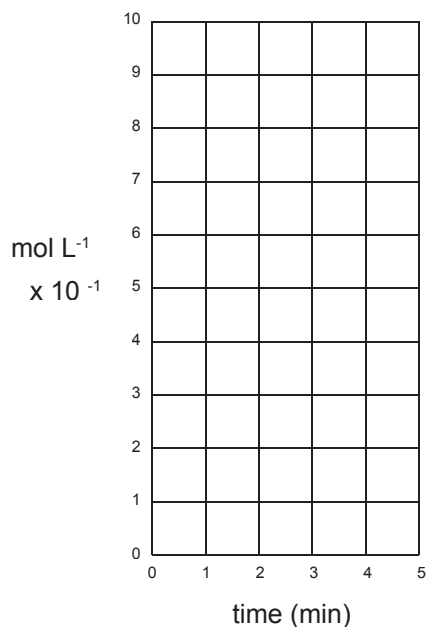
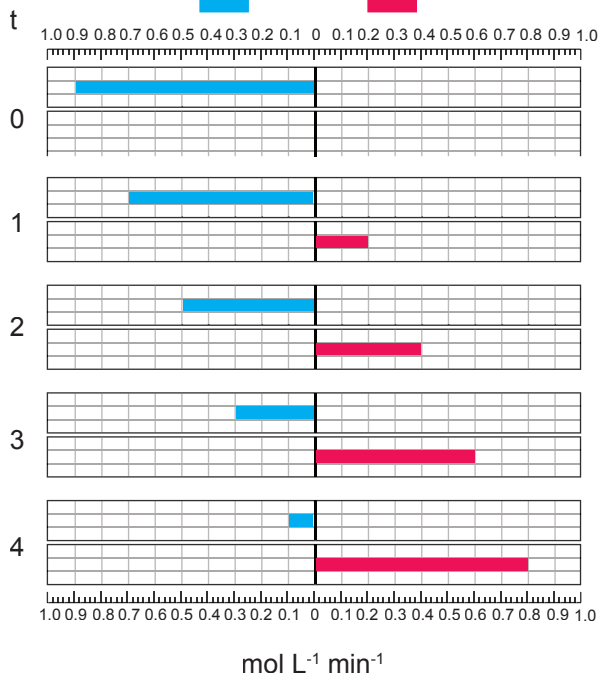


KINETICS

CHEMLOGS OF THE ORDERS

C → D

Order 0



Plot [C] vs. time on the graph.
Plot [D] vs. time on the graph.

This is strange! Remember A → B (page 8) where the rate got smaller and smaller with time?

What happens to the rate here?
How did you determine what happens to the rate?

In this reaction, rate DOES NOT depend on [C]!!

$$\begin{aligned} \text{rate} &= k [\text{C}]^0 \\ \text{rate} &= k \times 1 \\ \text{rate} &= k \end{aligned}$$

This is called a zero order reaction.

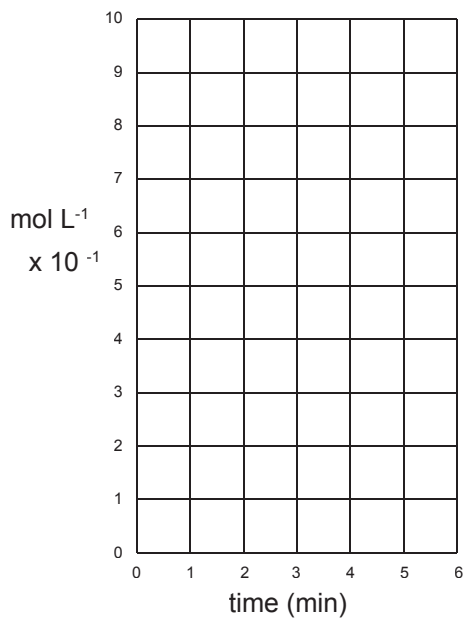
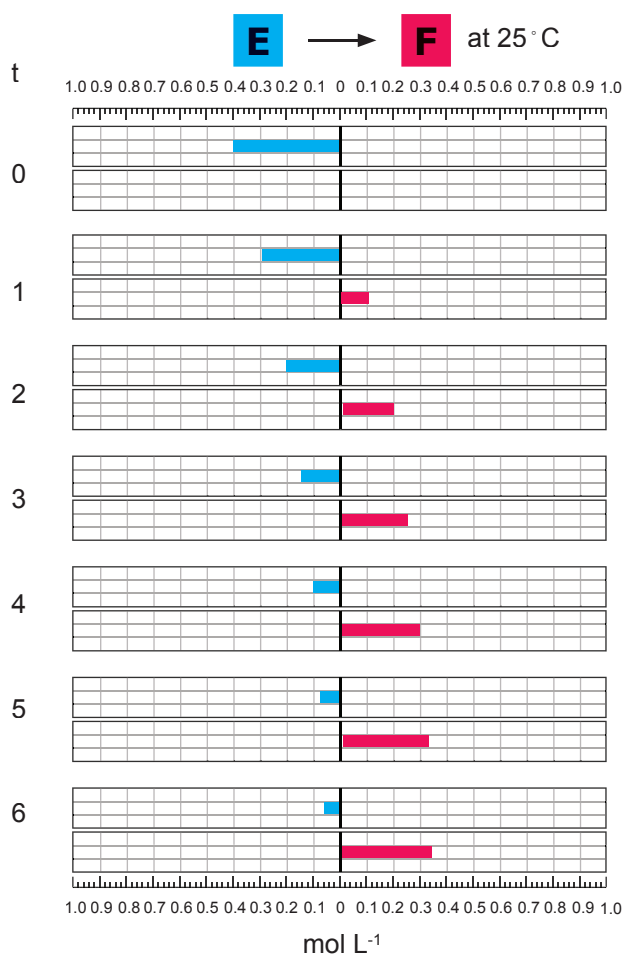
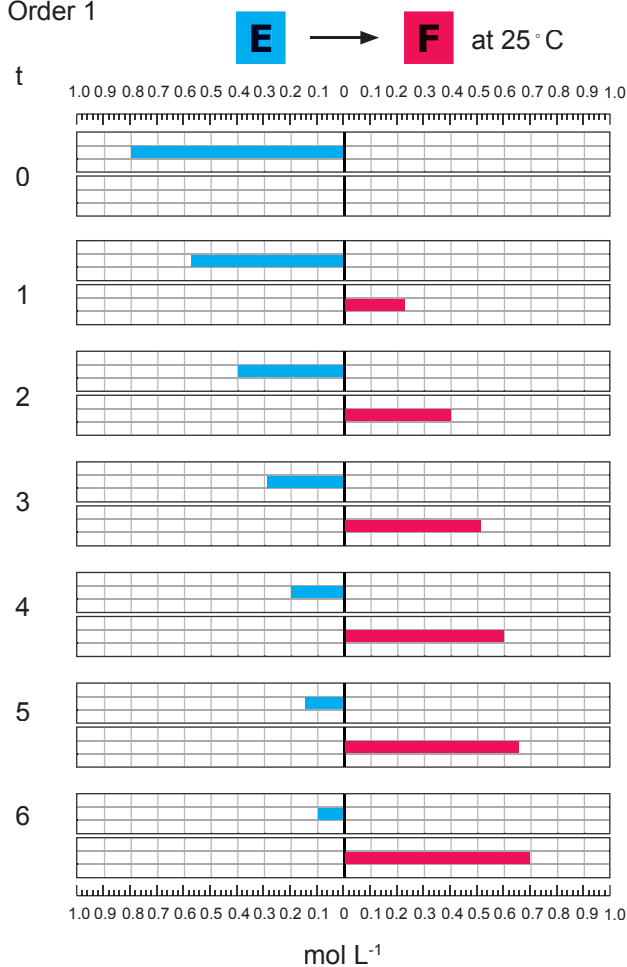
What is the value of k?

KINETICS

CHEMLOGS OF THE ORDERS



Order 1



Using the method described earlier, we have determined the initial rates for you. They are:

[E]	initial rates (mol L ⁻¹ min ⁻¹)
0.8	5×10^{-5}
0.4	2.5×10^{-5}

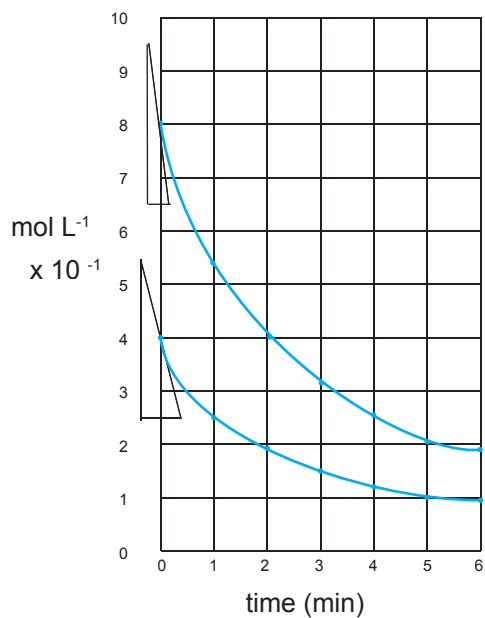
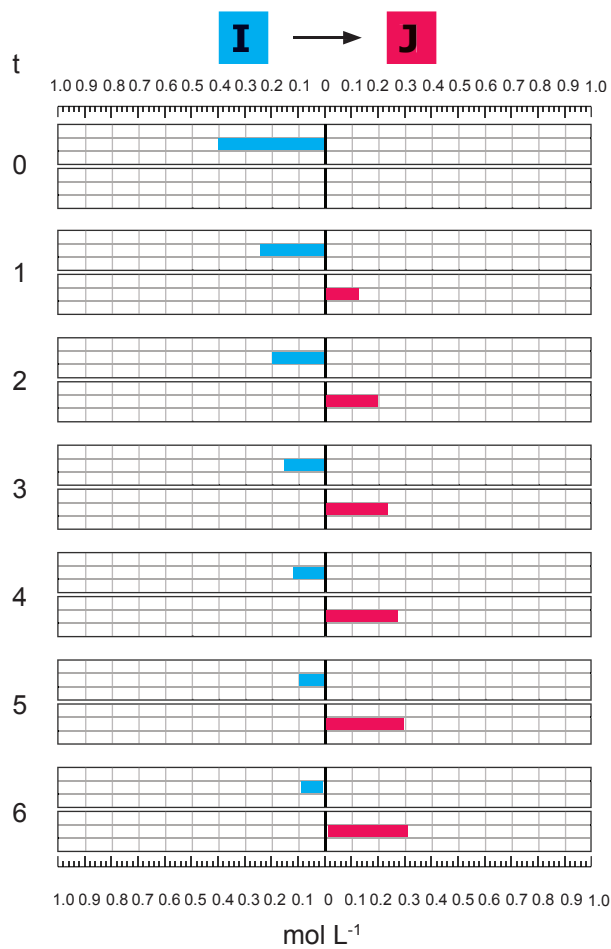
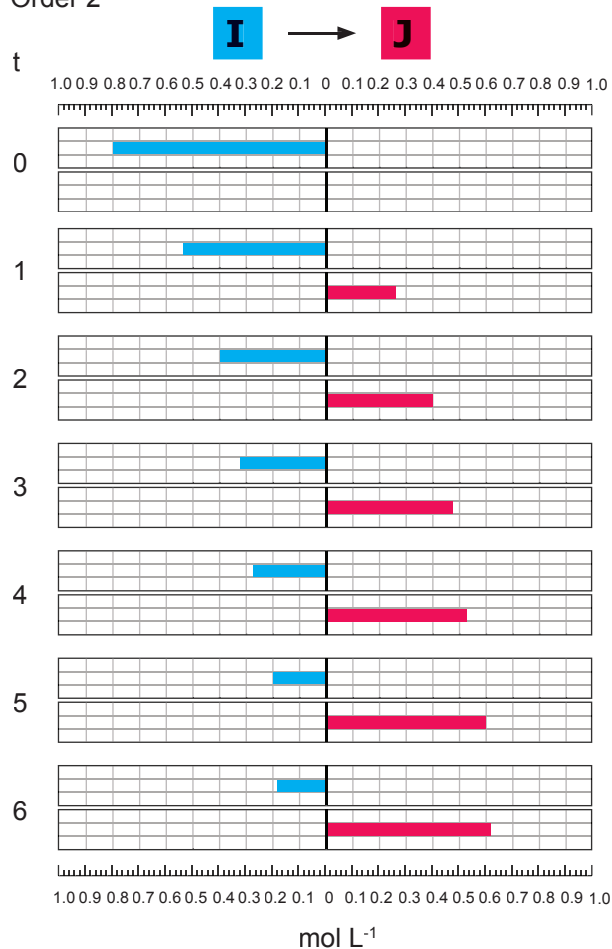
Determine the rate law and calculate k for this reaction.

KINETICS

CHEMLOGS OF THE ORDERS



Order 2



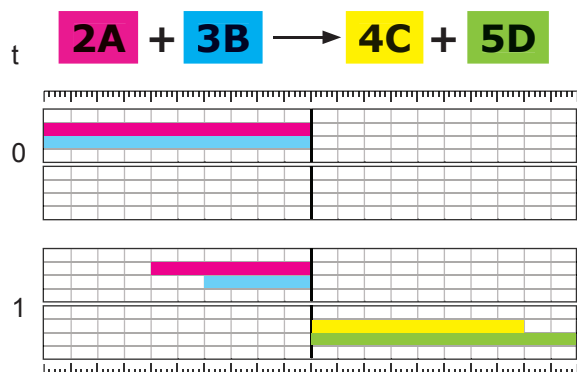
Using the method described earlier, we have determined the initial rates for you. They are:

[I]	initial rates (mol L ⁻¹ min ⁻¹)
0.8	5 × 10 ⁻⁵
0.4	1.25 × 10 ⁻⁵

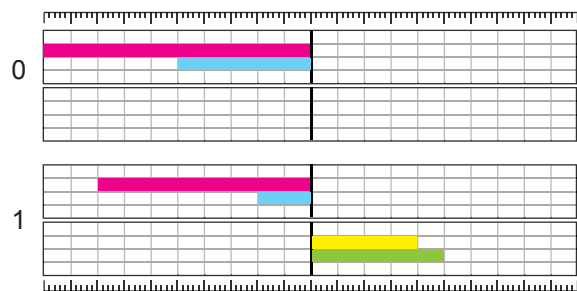
Determine the rate law and calculate k for this reaction.

KINETICS

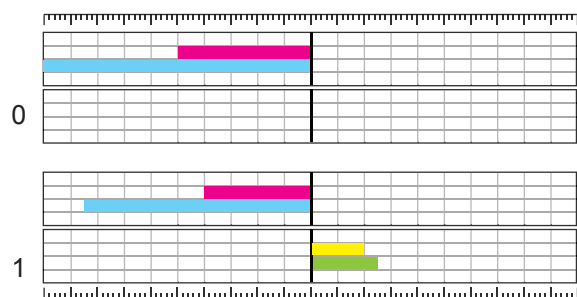
CHEMLOGS OF THE ORDERS



These three sets of ChemLogs involve the same reaction over the same interval of time, but with different initial concentrations of the reactants. The first set establishes a reaction rate. Find the reaction rate.



In the ChemLog at left the initial concentration of reactant B has been halved. Compare the reaction rate to the first case above. Determine the order of the reaction in [B].



In the ChemLog at left the initial concentration of reactant A has been halved. Compare the reaction rate to the first case above. Determine the order of the reaction in [A].

KINETICS

REACTION RATES: THE COLLISION THEORY

The *rate* of any reaction is defined as the number of molecules reacting in a given period of time. This is normally measured in terms of the *variation in concentration, c, of either reactants or products with time, t.*

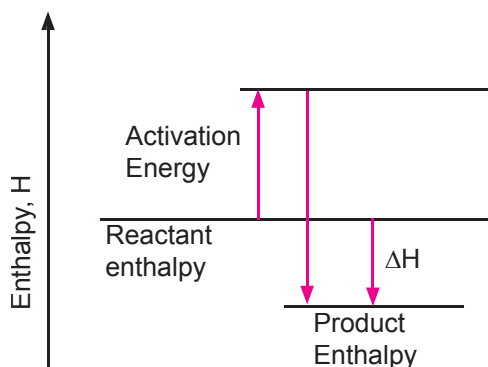
$$\text{Rate of Reaction} = \frac{\text{change in concentration}}{\text{change in time}}$$

$$\text{Rate of Reaction} = \frac{\Delta c}{\Delta t} = \frac{c_2 - c_1}{t_2 - t_1}$$

A Tentative Hypothesis

$$\text{Reaction rate} \propto \text{total number of collisions per unit time per unit volume}$$

The problem is not quite so simple. Just because two molecules collide does not mean that they will necessarily react. The rate of reaction depends not only upon the *collision frequency* but also on the *collision efficiency*. The collision must be an effective one, in that the molecules must collide with sufficient *energy* to bring about reaction. The minimum energy required to bring about a reaction is known as the *activation energy*.

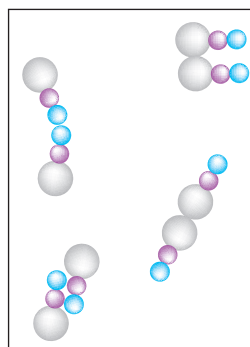
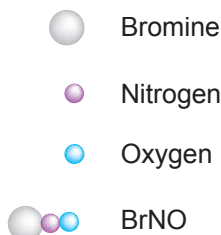


Is the reaction, whose enthalpies are shown in the picture above, exothermic or endothermic? Would it be thermodynamically spontaneous or nonspontaneous?

A Modified Tentative Hypothesis

$$\text{Reaction rate} \propto \text{Collision frequency} \times \text{Frequency of collisions having sufficient energy}$$

There is still another factor. Molecules have shape and the occurrence of a reaction often depends upon which parts of the reactant molecules collide.



When two BrNO molecules collide, they will react according to $2\text{BrNO} \rightarrow \text{Br}_2 + 2\text{NO}$ if the bromine atoms collide but will just bounce off of each other otherwise. In the picture above, circle which of the collisions will cause a reaction.

The effect of molecular orientation upon reaction rates is called the steric factor. Is the steric factor larger or smaller than one?

A Final Hypothesis – The Collision Theory

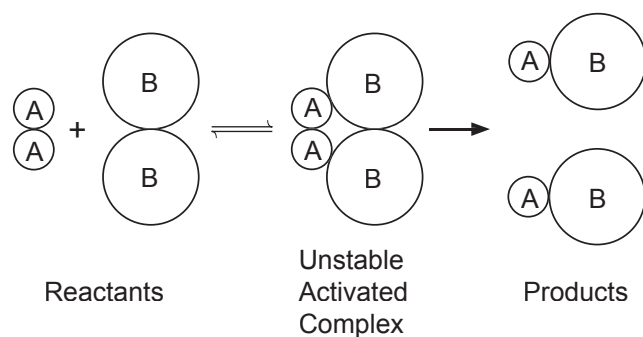
$$\text{Reaction rate} \propto \text{Collision frequency} \times \text{Fraction of collisions having sufficient energy} \times \text{Fraction of collisions with correct geometry}$$

$$\text{Reaction rate} \propto \text{Collision frequency factor} \times \text{Collision energy factor} \times \text{Collision geometry factor}$$

KINETICS

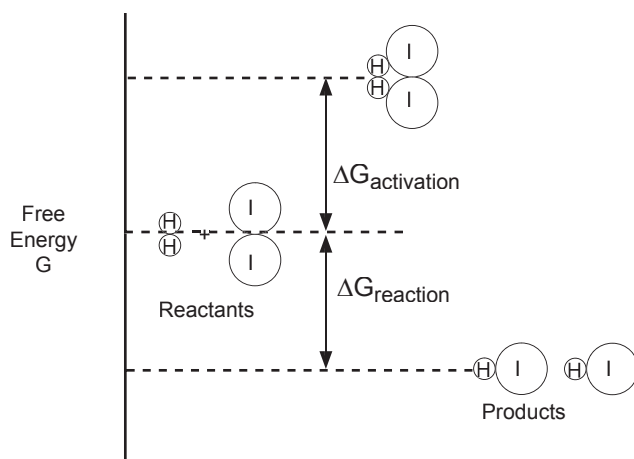
REACTION RATES: THE TRANSITION STATE THEORY

When molecules collide with at least the minimum energy necessary for reaction and the right geometry, or orientation, it seems reasonable that they may unite momentarily to produce an unstable species, which can be called the *activated complex* or *transition state*. This activated product can then break apart to give the new reaction products, or it can break up to yield the original reactants. It is also assumed that *the activated complex is in equilibrium with the original reactants*.



Assumptions of the Transition State Theory

1. An unstable transition state, called the activated complex, is formed.
2. The activated complex is in equilibrium with the original reactants.



Free Energy Diagram for the Reaction of H_2 and I_2 to form 2HI .

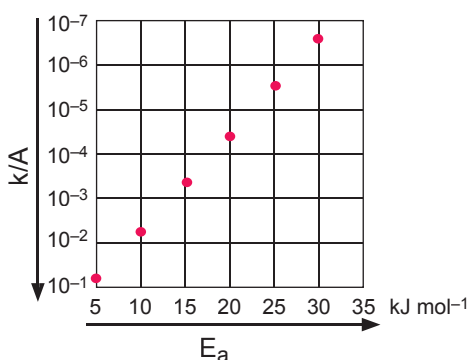
KINETICS

THE ARRHENIUS EQUATION

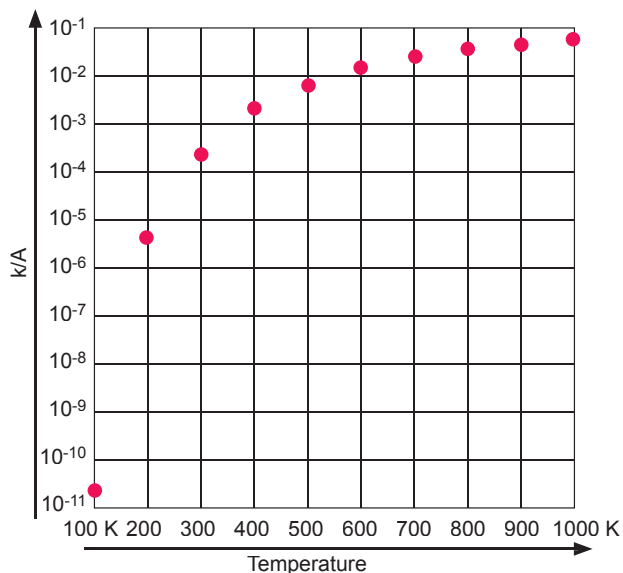
In 1897 Gustave Arrhenius introduced an equation to fit the data relating reaction rate to activation energy and temperature. The equation, which is known by his name, is:

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

k is the reaction rate in moles per second.
 A is a constant depending upon the types of molecules.
 e is the basis for the natural logarithms.
 E_a is the activation energy in kilojoules per mole.
 R is the gas constant = 8.314 Joules per mole-Kelvin.
 T is the temperature in Kelvin.



The graph above shows the influence of E_a on reaction rate. Actual reactions will also depend upon A . What is the approximate value of k/A for $E_a = 20 \text{ kJ mol}^{-1}$? Extrapolate the graph to find the approximate value of k/A for $E_a = 35 \text{ kJ mol}^{-1}$.



The graph above shows the influence of temperature on reaction rate, for an activation energy: $E_a = 20 \text{ kJ mol}^{-1}$. Discuss the influence of entropy on the change of reaction rates at high temperatures.

Your chemistry textbook shows you how to find the activation energy from the Arrhenius equation, by graphing a series of measurements of the reaction rate versus the temperature. It begins by taking the natural logarithm of the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

When $\ln k$ is chosen as the y-axis and $1/T$ is chosen as the x-axis, this is a linear equation with slope $-E_a/R$. For additional insight we will show a similar method using algebra on two measurements: k_1 at T_1 and k_2 at T_2 .

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

If we subtract the second equation from the first we get:

$$\ln k_1 - \ln k_2 = \left(\frac{E_a}{R}\right) \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

solving for E_a , we get

$$E_a = RT_1T_2 \frac{\ln k_1 - \ln k_2}{T_1 - T_2}$$

knowing either k , we can easily find A from the Arrhenius equation:

$$A = k_1 e^{\left(\frac{E_a}{RT_1}\right)}$$

It may be better scientific practice to use the graphical method since it uses more data points (and is thus less susceptible to error) but this calculation may give you more insight into the graphical method.

We can summarize the affect of temperature on the rate of a reaction by stating that:

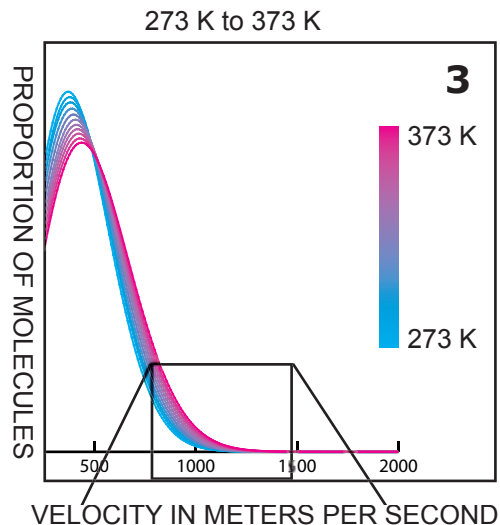
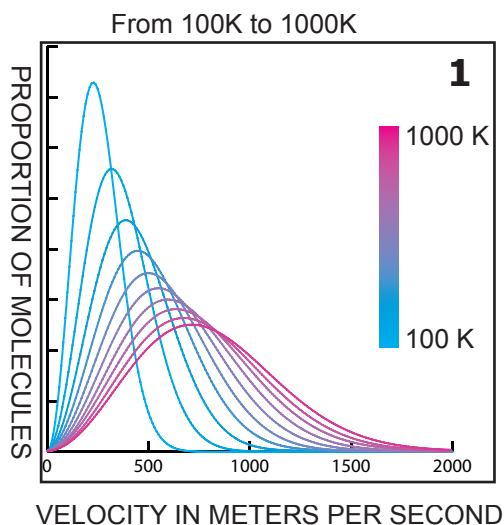
As temperature increases, rate increases because a larger proportion of molecules are moving faster, so a larger proportion of the colliding molecules have the minimum activation energy needed to react.

A good guide for affect of T on rate is that for a typical E_a , an increase in 10 K doubles the rate!

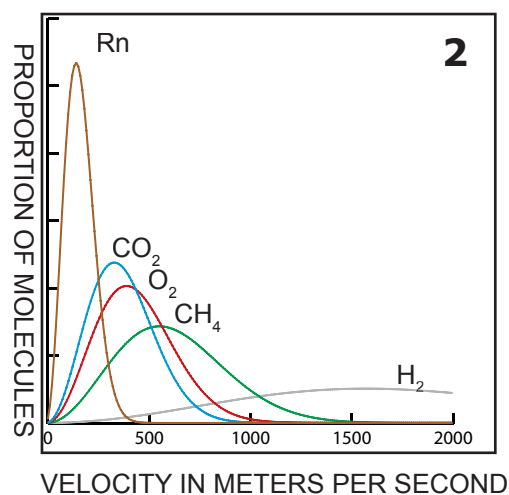
KINETICS

MAXWELL DISTRIBUTION OF MOLECULAR VELOCITIES

THE MAXWELL DISTRIBUTION FOR O₂ MOLECULES



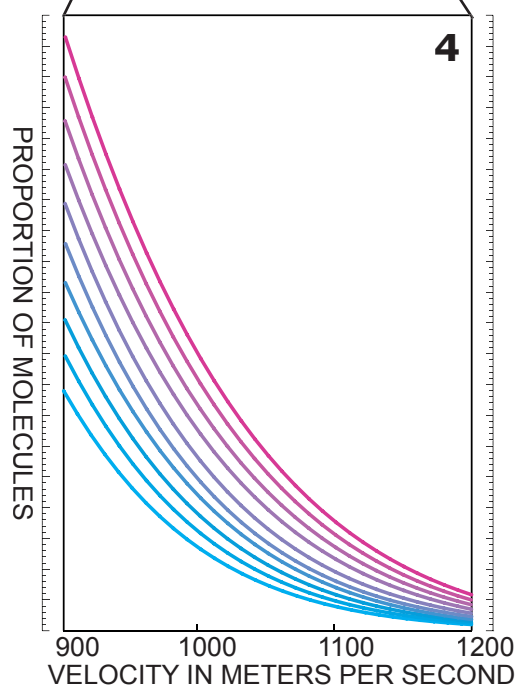
THE MAXWELL DISTRIBUTION FOR GASES OF DIFFERENT MASSES



The Maxwell distribution describes what proportion of the molecules in a gas or liquid are in a given velocity range. It depends on the temperature and on another factor.

Using Picture 2, deduce what other factor the Maxwell distribution depends on.

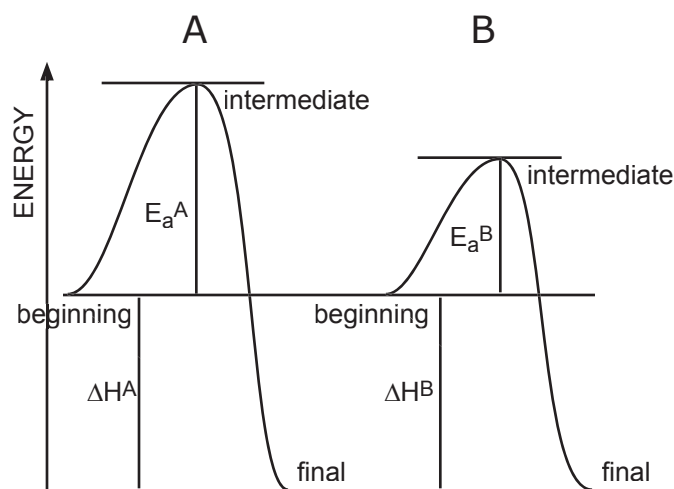
Using Picture 2, what is the most common velocity for radon? for carbon dioxide? for dioxygen? for methane? for dihydrogen?



In Picture 4, the bottom curve is for 283 K (not 273 K) and the top curve is for 373 K. If these molecules take part in a reaction where the rate at 283 K is 1.00 moles per liter, then what is the rate at 373 K?

KINETICS

ACTIVATION ENERGY

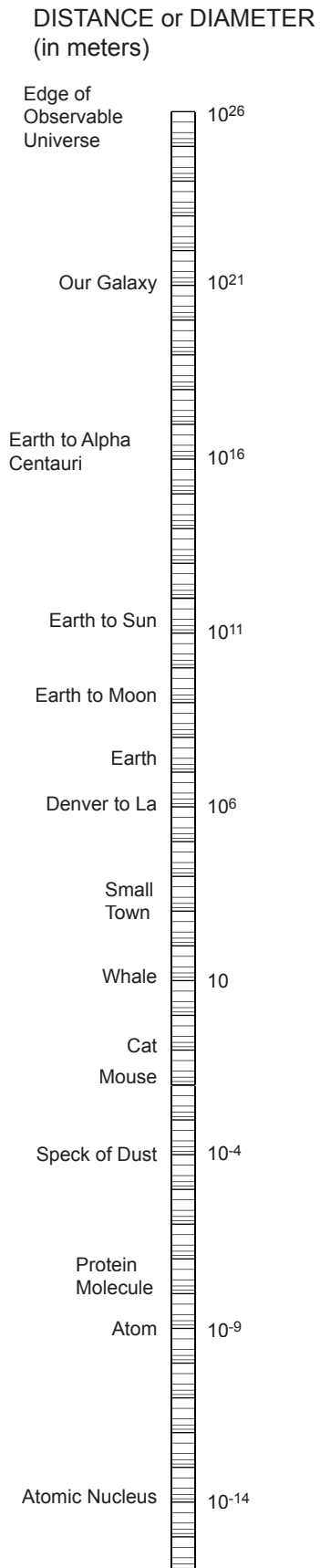


Since $\Delta H^A = \Delta H^B$ reactions A and B are thermodynamically equivalent. However, reaction B has a lower energy intermediate state than reaction A and thus requires less activation energy than A. In a collision driven reaction, more of the molecules will have a sufficient energy for B than for A and thus reaction B will proceed faster than reaction A.

Suppose you are working with a gas phase reaction. What factors would you change to speed it up?

KINETICS

DISTANCE SCALES

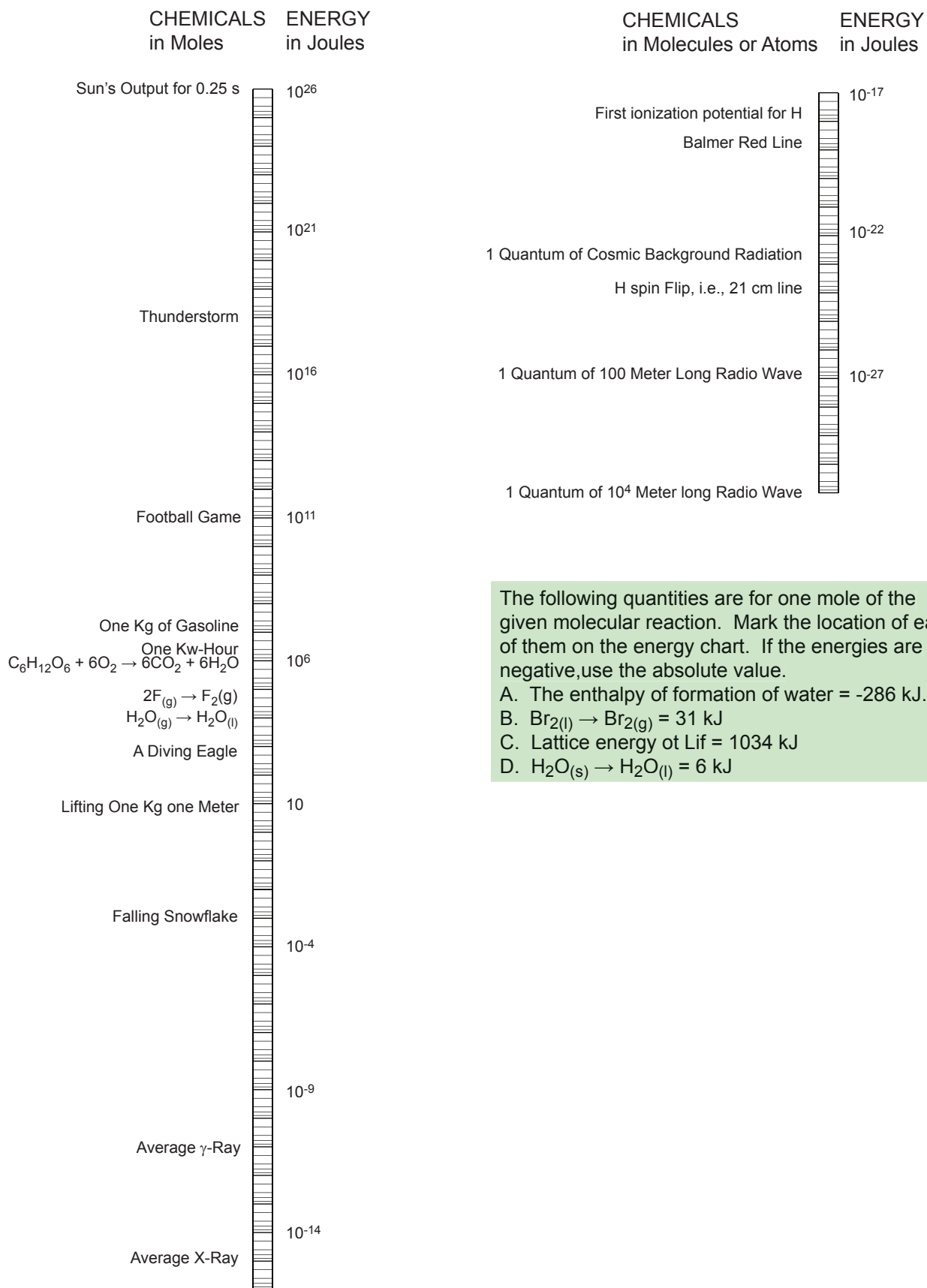


Draw an arrow from each of the following items to the location of its scale (size or distance) on the chart at left. You may need to look up or measure some of these. (hint: Consider using the Internet.)

- The distance to the galaxy Andromeda.
- The distance to Pluto.
- The diameter of Jupiter.
- The distance to your home.
- Your height.
- Your shoe size.
- The size of a dime.
- The thickness of a human hair.
- Amoeba Proteus
- Lacto bacillus acidophilis.
- A tobacco mosaic virus.
- A water molecule.

KINETICS

ENERGY SCALES

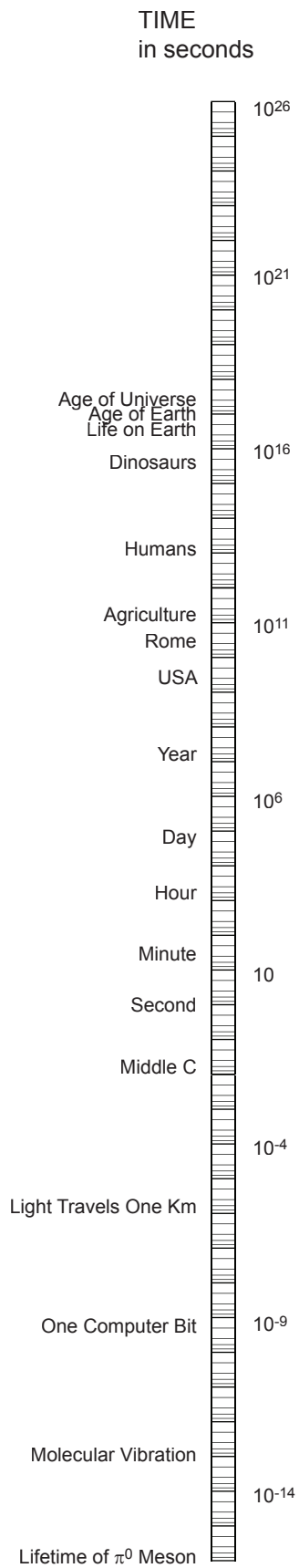


The following quantities are for one mole of the given molecular reaction. Mark the location of each of them on the energy chart. If the energies are negative, use the absolute value.

- A. The enthalpy of formation of water = -286 kJ.
- B. $Br_{2(l)} \rightarrow Br_{2(g)} = 31$ kJ
- C. Lattice energy of LiF = 1034 kJ
- D. $H_2O_{(s)} \rightarrow H_2O_{(l)} = 6$ kJ

KINETICS

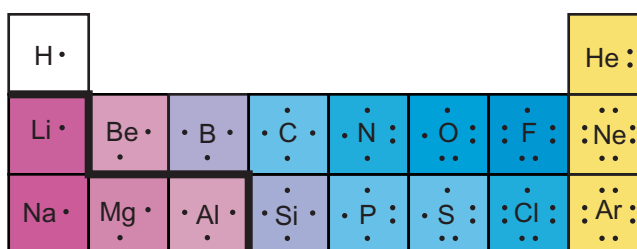
TIME SCALES



Draw an arrow from each of the following list of items to the position of its age or duration on the chart at left.

- The Permian-Triassic boundary.
- Cro-Magnon humans.
- Ur.
- The time since January 1, 1900.
- The time since January 1, 2000.
- A semester.
- A class period.
- A breath.
- A heartbeat.
- The time for sound to go one meter.

LEWIS DIAGRAMS



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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LEWIS DIAGRAMS

CONTENTS

2	Lewis Diagrams For Covalent Bonding
3	Lewis Diagrams For Covalent Bonding
4	Forming Lewis Diagrams
5	Resonance
6	Beyond The Steps
7	Beyond The Steps
7	Orbitals

LEWIS DIAGRAMS

LEWIS DIAGRAMS FOR COVALENT BONDING

In the figure below, the elements of the first three periods are shown with their valence electrons surrounding their symbols. It is only the valence electrons which may become involved in chemical bonding, because the inner electron shells are held too tightly to the atom to be either shared or given up in chemical bonding, although you can blast them off with X-rays.

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
H·							He :
Li·	Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
Na·	Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·

Electronegativity →

If we consider just the nonmetals, as shown below, the electronegativity differences between the elements is fairly small. For this reason a particular kind of bonding, called covalent bonding, occurs between the atoms. Because of the small electronegativity differences, none of the atoms in a covalent molecule pulls any electrons entirely away from any of the other atoms, but rather the atoms share some or all of the valence electrons.

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
H·							He :
	Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
			·Si·	·P·	·S·	·Cl·	·Ar·

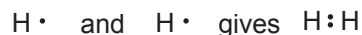
Electronegativity →

There is a particularly simple and convenient way of showing the connections between covalently bound atoms. We do this by forming what are called Lewis diagrams. In Lewis diagrams the atoms are shown by writing the atomic symbol surrounded by one dot for each of the valence electrons. In a covalently bound molecule the dots are arranged in pairs, with the bound pairs placed between the atoms which they connect and the lone pairs at different sides of the atomic symbol.

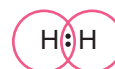
Later we will give the general rules for forming Lewis diagrams but first we will look at some simple examples beginning with the formation of a hydrogen molecule, H_2 , from two hydrogen atoms, H.

A GOOD DEFINITION OF A MOLECULE IS TWO OR MORE ATOMS COVALENTLY BONDED.

Lets form a covalent bond between two hydrogen atoms:



In covalent bonding electrons are always shared in pairs. In this example the pair of electrons (the two dots) are drawn in between the two H symbols in the H_2 molecule. The molecule H_2 has ONE covalent bond. Each atom in the H_2 molecule has, by sharing, a single pair of electrons. Each H atom now has the electron configuration of a helium atom. It is said to be isoelectronic (having the same number of electrons) with a helium atom. The helium atom electron configuration is very stable because it is a filled energy level. The red circles outline the structures isoelectronic to the helium atom.



In chemistry the covalent bond is often drawn as a single line.



Lets now take an example of an atom with more than one valence electron. The fluorine atom has seven valence electrons (F is in group 7A, 17).



The valence electrons are arranged in pairs around the atomic symbol. The seventh electron is drawn as a single dot and is called an unpaired electron. Two fluorine atoms can share their unpaired electrons and form a covalent bond. We can show this by means of a Lewis diagram as follows:



ATOMS OTHER THAN HYDROGEN SHARE ELECTRONS UNTIL THEY ARE SURROUNDED BY EIGHT VALENCE ELECTRONS. THIS IS CALLED THE OCTET RULE

Draw circles around each fluorine atom to show the octet rule.



What element is isoelectronic with each fluorine atom in the molecule F_2 ?

LEWIS DIAGRAMS

LEWIS DIAGRAMS FOR COVALENT BONDING

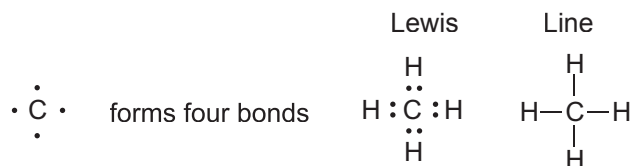
Yes, it is neon, the inert gas to the right of fluorine in the second period.

Note, the F atom is isoelectronic with neon but it is not neon because the F atom has 9 protons in the nucleus and neon has 10 protons in the nucleus.

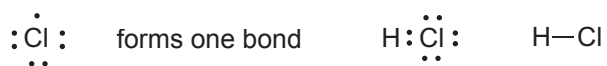
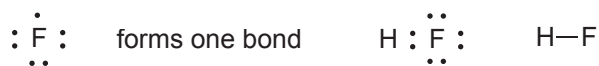
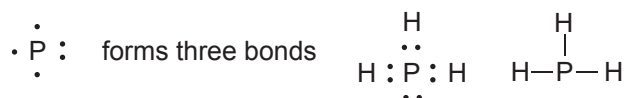
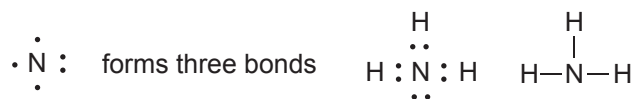
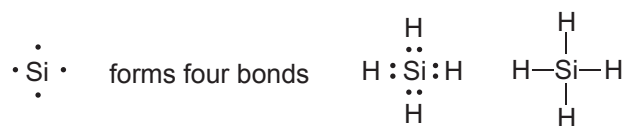
Looking at our section of the periodic table, notice how each element, as we move to the right, adds one more valence electron.

1 1A							18 8A
H·	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	He·
	Be·	B·	C·	N·	O·	F·	Ne·
			Si·	P·	S·	Cl·	Ar·

For example, carbon with four valence electrons (group 4A) can become isoelectronic with Ne (8 valence electrons, group 8A) by sharing 4 electrons from other non-metallic elements.



The octet rule provides a way to find out how many covalent bonds are formed by the representative non-metallic elements.



In the examples, draw circles to illustrate the duplet and octet rules and name the element to which the circled atom is isoelectronic.

So far we have only considered molecules which have single bonds between pairs of atoms. Molecules can have multiple bonds, e.g., double bonds O=O and triple bonds N≡N. Let's see if we can write a Lewis diagram for O₂, dioxygen.



See how in this case each oxygen atom shares two of its electrons with the other oxygen atom. So altogether there are four electrons shared between the two oxygen atoms, forming TWO covalent bonds. This is called a double bond.

Like fluorine in difluorine, each oxygen atom in dioxygen is isoelectronic to neon. Draw circles around each oxygen atom in the dioxygen Lewis diagram above to show the octet rule. The circles do not need to be drawn perfectly circular, but they do need to enclose the correct electrons.

Now you can predict the chemical formula for many molecules formed by combining different non-metallic elements. For example try to predict the formulas for compounds formed by combining:

- a) C and Cl b) F and O
c) N and I (hint: look at the periodic table on page 2).

So far we have introduced Lewis diagrams according to a few simple rules, which are sufficient to write the diagrams of the simple molecules we have been discussing. Lewis diagrams are also useful for more complex molecules. In order to use them for these more complex molecules we will need to use a definite procedure which we give on the next page.

LEWIS DIAGRAMS

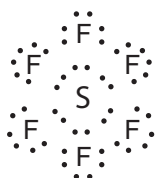
BEYOND THE STEPS

LARGE CENTRAL ATOMS

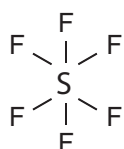
Some central atoms, in particular sulfur and phosphorus from the third period, are so large that it is possible to fit more than eight electrons in their valence shell. Examples are PCl_5 and SF_6 .

If we look at SF_6 we see that the only arrangement which allows each fluorine atom to have only one bond is that in which the sulfur atom is central and connected to each fluorine by a single bond. This is in fact what happens.

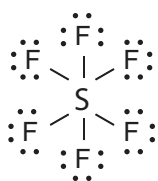
When we distribute the electrons according to our steps we arrive at:



We also have the line drawing:

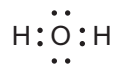


and the hybrid representation:

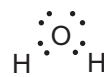


ORBITALS AND SHAPES

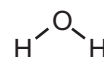
Lewis diagrams are electron dot pictures which give an excellent account of the number of valence electrons in a covalent molecule. The dot diagrams do NOT explain the reasons for covalent bonding - the 'glue' - nor do they explain the shapes of molecules. A good example is water. The Lewis diagram is:



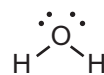
The overwhelming experimental evidence shows that water is a bent polar covalent molecule shaped something like:



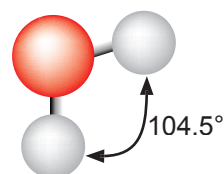
or



or

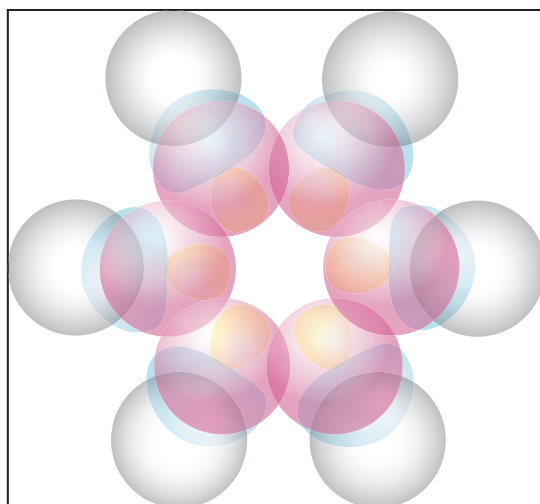


or



Explanations of shape, etc. require quantum theory and combinations of orbitals.

ORBITALS and MOLECULAR REPRESENTATION



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

ORBITALS AND MOLECULAR REPRESENTATION

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2	Atomic Orbitals ($n = 1$)
3	Atomic Orbitals ($n = 2$)
4	Atomic orbitals ($n = 3$)
5	Hybrid Atomic Orbitals (sp)
6	Hybrid Atomic orbitals (sp^2)
7	Hybrid Atomic Orbitals (sp^2)
8	Hybrid Atomic Orbitals (sp^3)
9	Overlapping Orbitals (Bonding And Antibonding)
10	Orbital Pictures For H And H_2
11	Difluorine
12	Carbon Orbitals (Methane And Ethane)
13	Carbon Orbitals (Ethene)
14	Carbon Orbitals (Ethene)
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19	Several Representations Of Molecules
20	Several Representations Of Benzene
21	Representations Of Molecules
22	Representations Of Molecules
23	Representations Of Molecules

ORBITALS AND MOLECULAR REPRESENTATION

ATOMIC ORBITALS

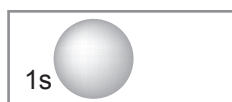
While Lewis diagrams and energy level structures can show connectivity and energy relationships of molecules, they do not show the shape of the molecules. For this we need to picture atomic and molecular orbitals.

$n = 1$

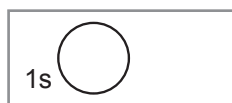
$l = 0$



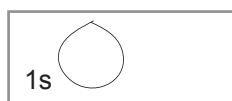
The picture above shows the spherically symmetric 1s orbital in the 'green' phase. Sometimes it is more convenient not to show the phase, in which case we can use a greyed representation, as shown below.



It is also possible to show the orbital as a simple loop.



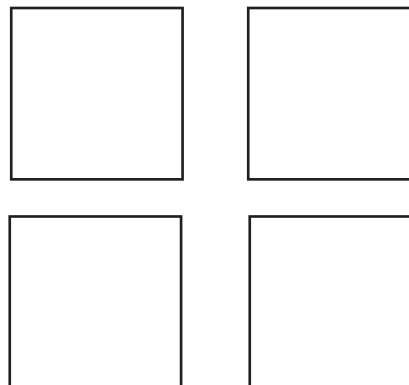
And if you are drawing this by hand, the loop does not have to be an exact circle.



As we proceed developing atomic and molecular orbitals we will show various forms of representation.

We denote the phase of the wave function by color, using light red for one phase and green for the opposite phase. Many books assign these phases plus or minus signs but the only real meaning is that they are opposite. Neither phase is plus or minus anything on its own but they are only opposite to each other. Sometimes when we are not concerned with phase we will draw the orbitals as a slightly reddish gray.

Here are some boxes for you to practice drawing s orbitals in, although you do not really need boxes.



$n = 2$

$l = 0$



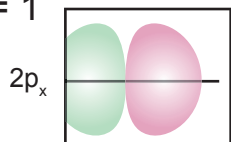
You can draw the two loops for 2s in the box below.

ORBITALS AND MOLECULAR REPRESENTATION

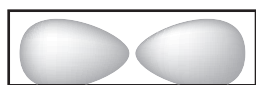
ATOMIC ORBITALS

$n = 2$

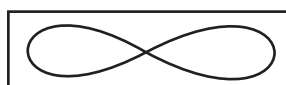
$l = 1$



This is an accurate representation of a $2p_x$ orbital.



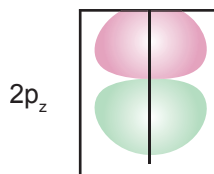
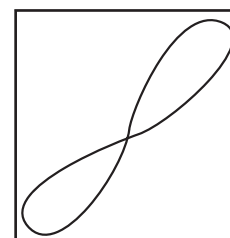
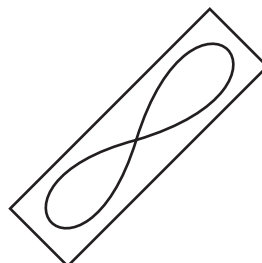
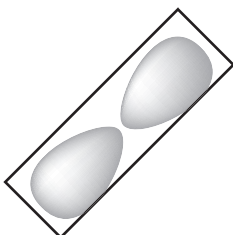
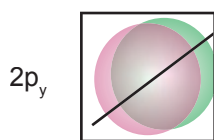
This is a common picture of a p_x orbital



This simplified p_x orbital is often useful.

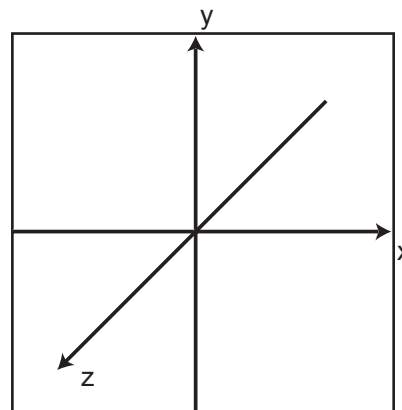
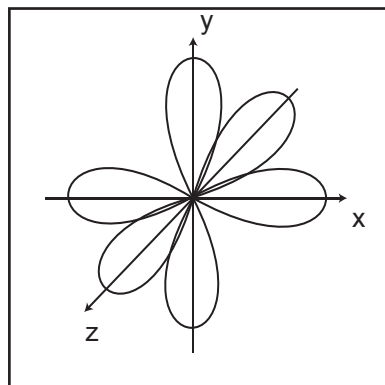
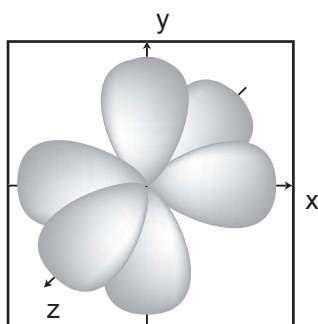


A hand drawn version does not have to be exact.



Use this box to draw a p_z orbital.

We can combine all three p orbitals in a three dimensional display.

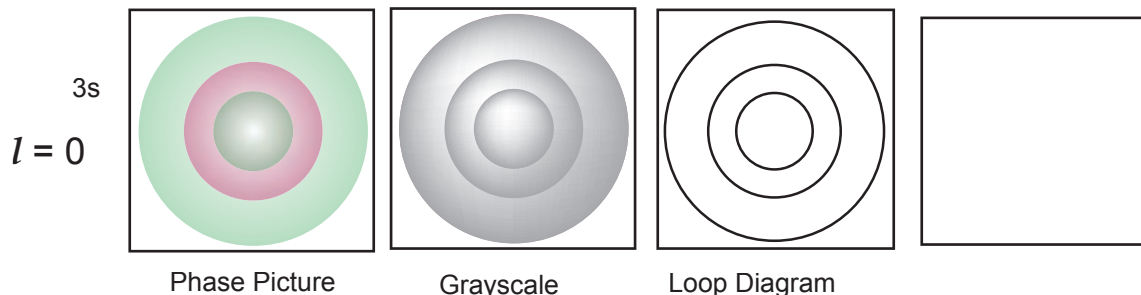


Use these axes to draw all three p orbitals.

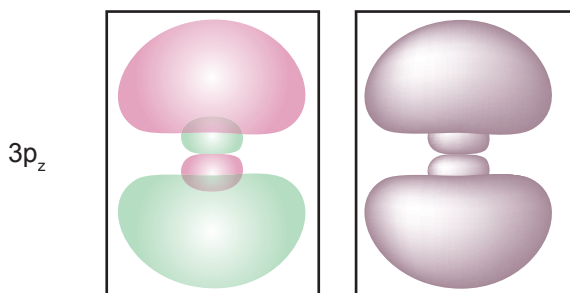
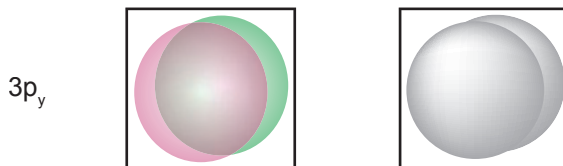
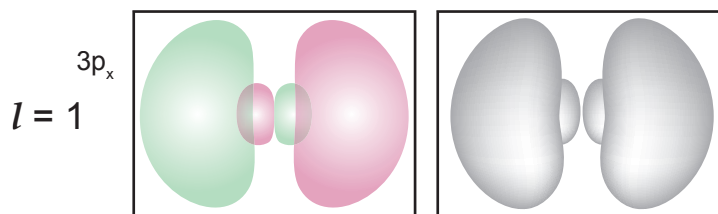
ORBITALS AND MOLECULAR REPRESENTATION

ATOMIC ORBITALS

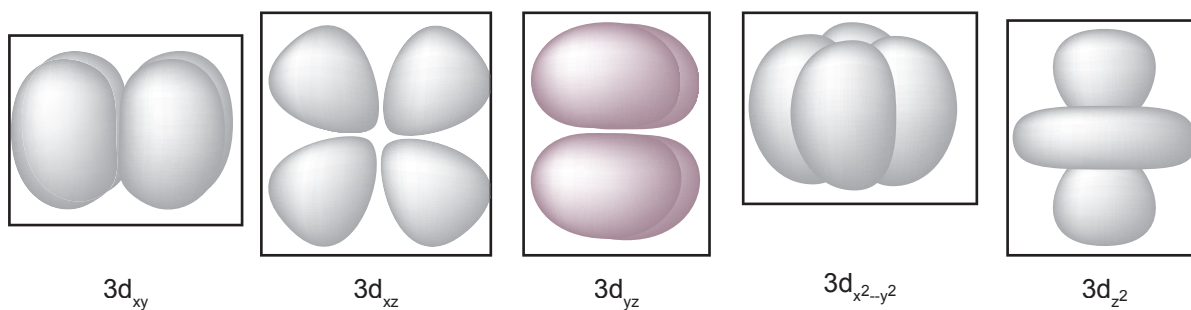
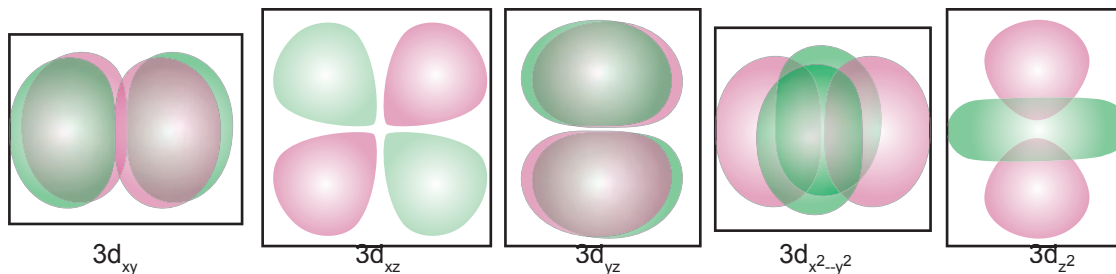
$n = 3$



Draw the
3s orbital
in the box
at left.



$l = 2$



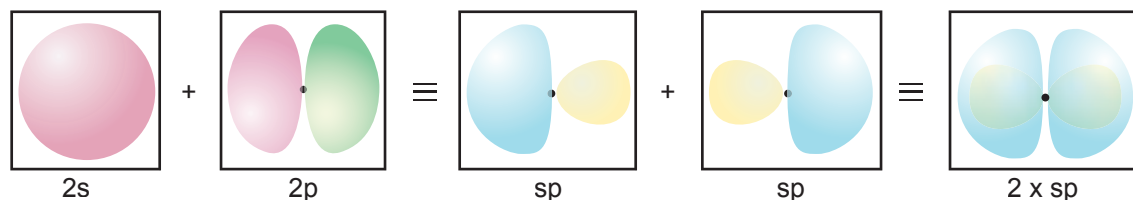
ORBITALS AND MOLECULAR REPRESENTATION

HYBRID ATOMIC ORBITALS

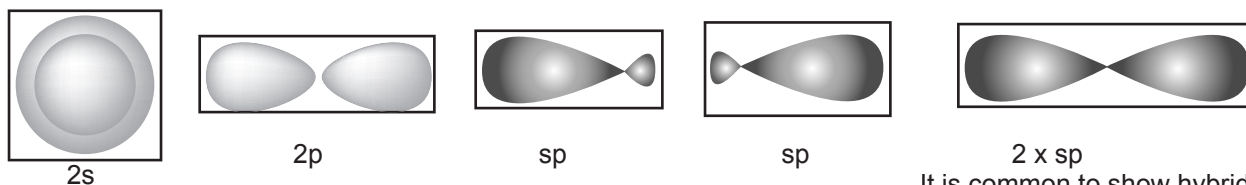
sp

sp orbitals are a combination, or hybrid, of an s and a p orbital. In addition there will be two remaining unhybridized p orbitals orthogonal to each other and to the line joining the two hybrid sp orbitals.

You will recall that our color convention is to show the phases of the atomic orbitals with red and green. We shall show the phases of hybrid orbitals in blue and yellow.

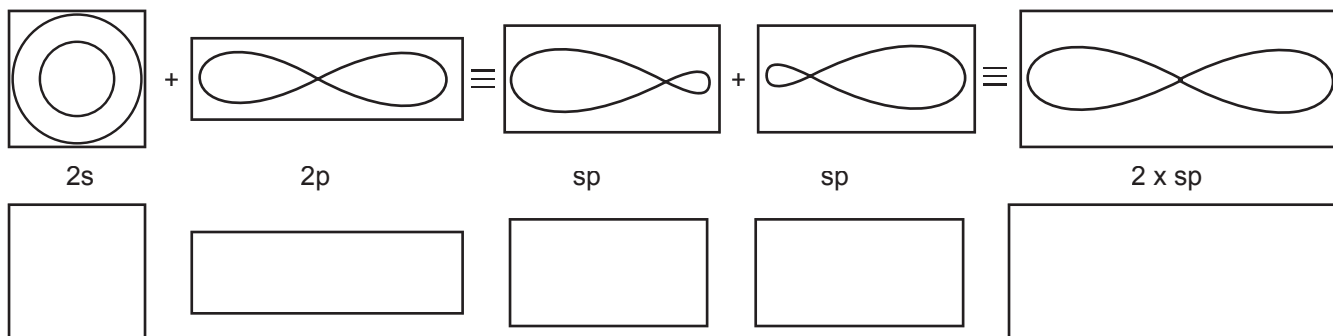


You will also see these orbitals in greyscale, without phases. We use reddish grey for unhybridized orbitals and plain grey for hybridized orbitals.



We can also draw these orbitals as simplified loops.

It is common to show hybrid orbitals without the small lobes.

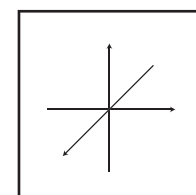
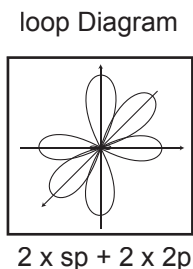
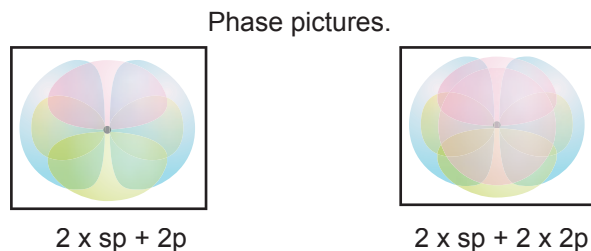


It is useful to draw the sp hybrid orbitals yourself.

An sp hybridized atom uses one s and one p orbital to make two sp hybrid orbitals; there are two remaining p orbitals.

Next we show the phase pictures of combining the sp hybrid orbitals with first one and then both of the remaining p orbitals.

Axes for you to draw the loop diagram.



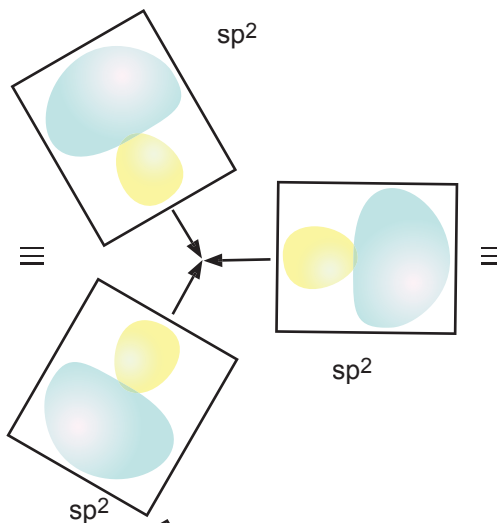
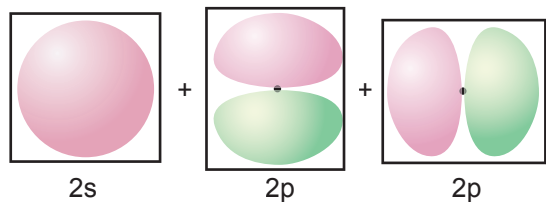
NOTE: When we write 2 x sp we mean two instances of sp and when we write 2p we mean one instance of a 2p orbital.

ORBITALS AND MOLECULAR REPRESENTATION

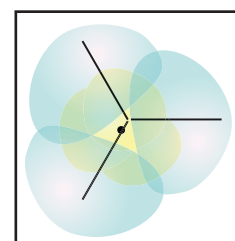
HYBRID ATOMIC ORBITALS

sp^2

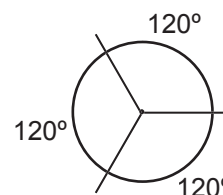
sp^2 hybrid orbitals are formed when one 2s orbital combines or hybridizes with two 2p orbitals in the shapes and arrangement shown.



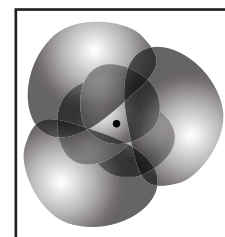
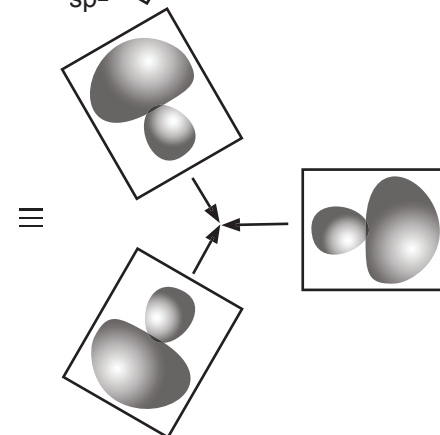
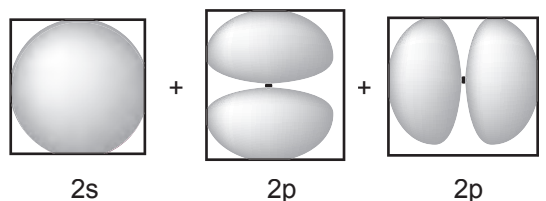
The pictures below are trigonal views of sp^2 . Trigonal means arranged in triangular form in a plane.



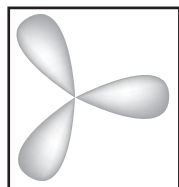
trigonal view of sp^2



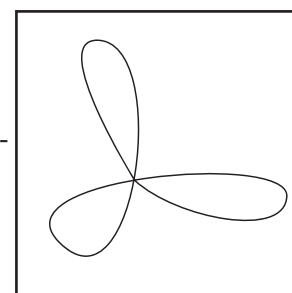
In greyscale:



You will often see a simple presentation of the sp^2 orbitals. The important points to know about are that the three bonds are in a plane and that they are 120° apart.



You can also draw the sp^2 hybrid orbital as simple loops.



Draw the loop version of the trigonal set of sp^2 orbitals in the box at right.



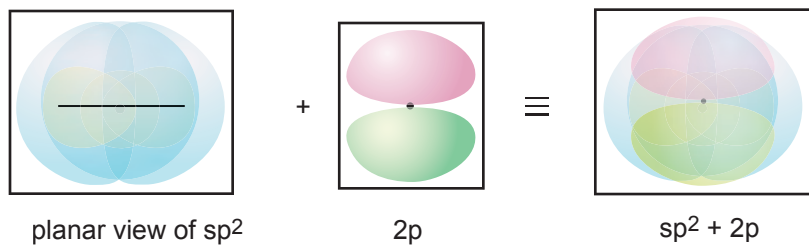
ORBITALS AND MOLECULAR REPRESENTATION

HYBRID ATOMIC ORBITALS

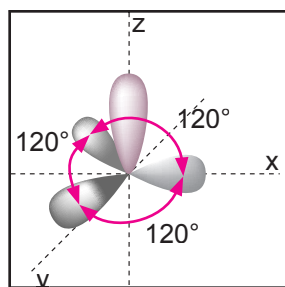
sp^2

In addition to the trigonal set of hybridized orbitals there is a remaining 2p orbital that will point above and below the trigonal plane.

First we show the phase orbitals.



Here we show the grayscale.

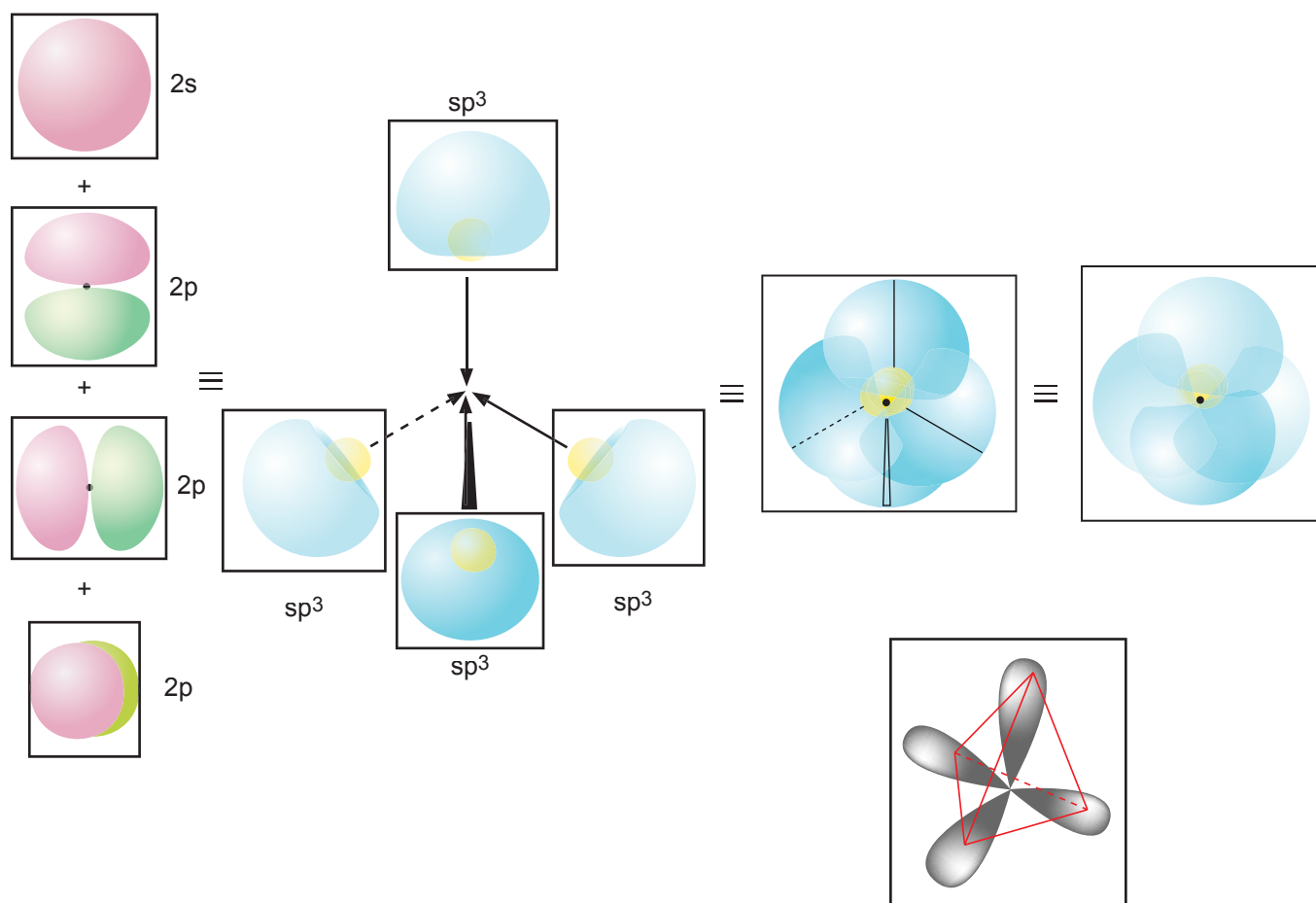


ORBITALS AND MOLECULAR REPRESENTATION

HYBRID ATOMIC ORBITALS

sp^3

sp^3 orbitals are formed by the hybridization of a 2s orbital and three 2p orbitals.



sp^3 orbitals have a tetrahedral structure.

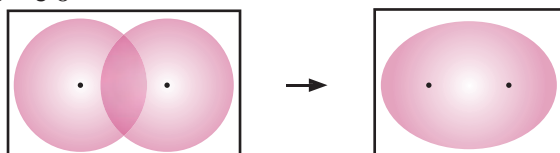
ORBITALS AND MOLECULAR REPRESENTATION

OVERLAPPING ORBITALS

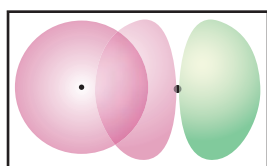
BONDING ORBITALS

Chemical bonds are formed from the overlapping of atomic orbitals having the same phase.

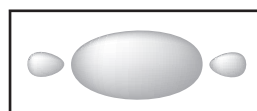
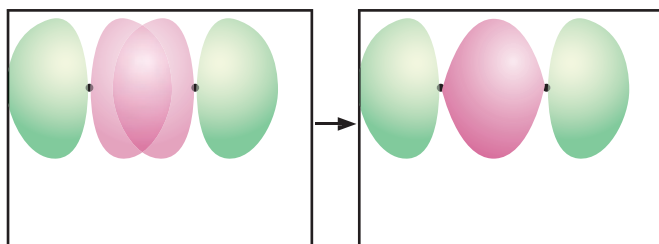
$s + s \sigma$



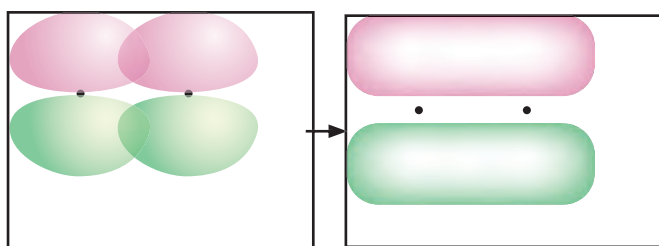
$s + p \sigma$



$p + p \sigma$



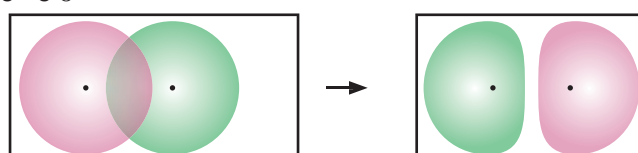
$p + p \pi$



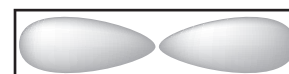
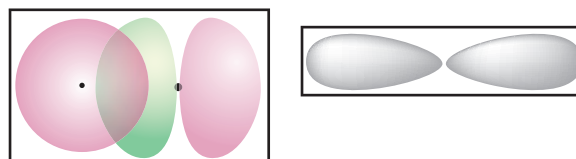
ANTIBONDING ORBITALS

Overlapping orbitals of opposite phase form antibonding orbitals.

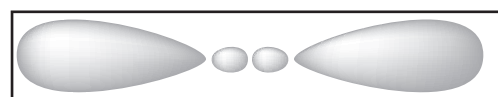
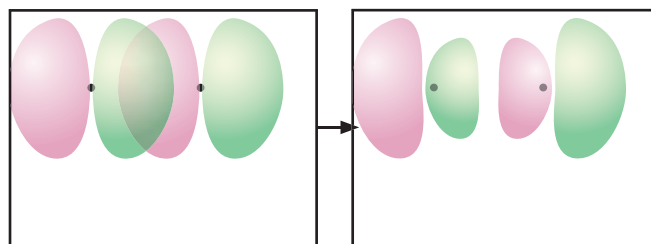
$s - s \sigma^*$



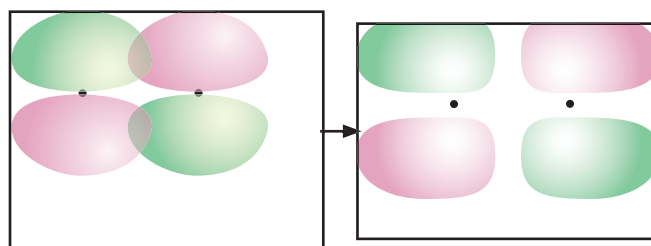
$s - p \sigma^*$



$p - p \sigma^*$



$p - p \pi^*$

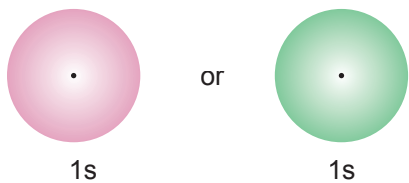


ORBITALS AND MOLECULAR REPRESENTATION

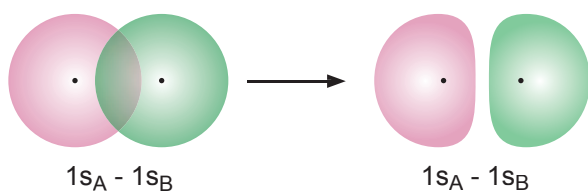
ORBITAL PICTURES FOR H AND H₂

We can also make orbital energy levels for molecules.

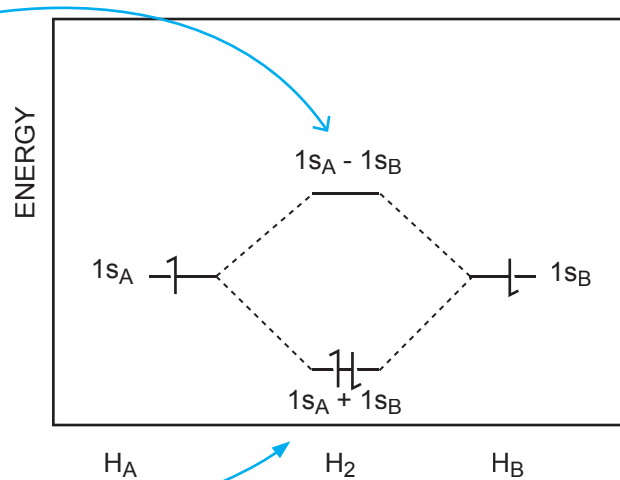
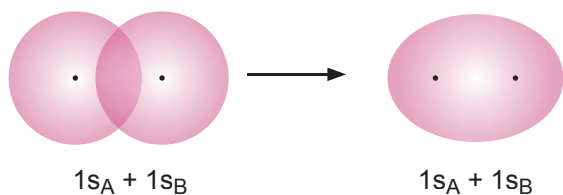
HYDROGEN ORBITAL



ANTIBONDING ORBITAL

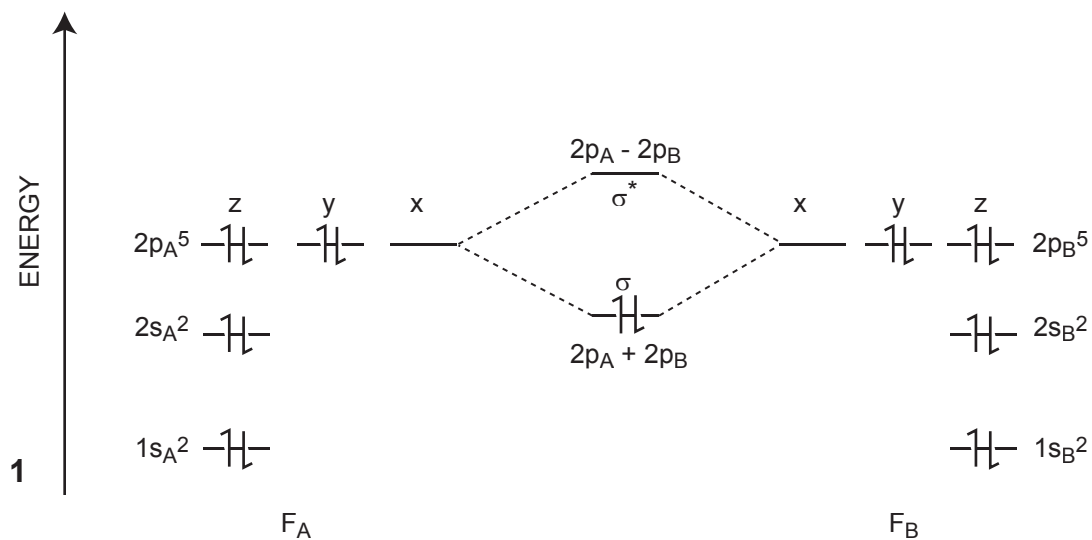


BONDING ORBITAL



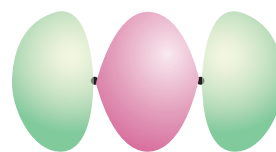
ORBITALS AND MOLECULAR REPRESENTATION

DIFLUORINE



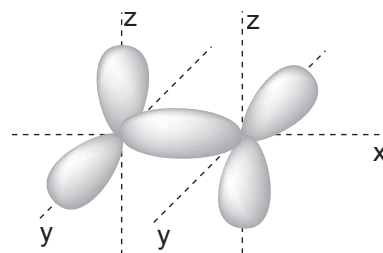
In picture 1 we show the molecular orbital structure of F_2 . In picture 2 we show the overlapping p orbitals, which form the bond between the two fluorine atoms, in red and green gradients.

The dashed lines show the remaining p orbitals which do not take part in the bonding.



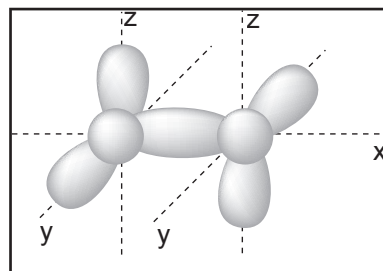
2

Construct the molecular orbital diagram for dichlorine.



3

Showing the p orbitals.



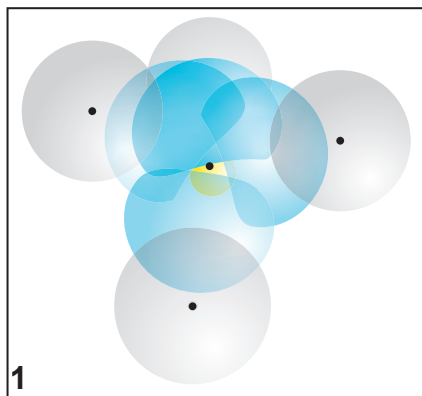
4

Showing the s and p orbitals.

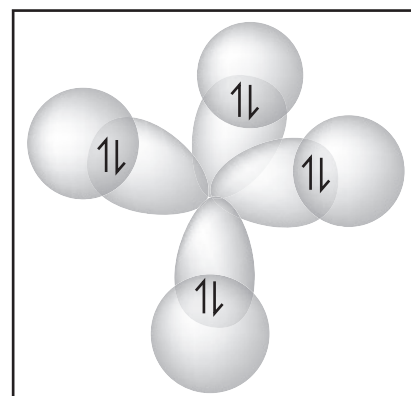
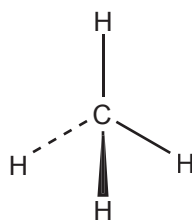
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

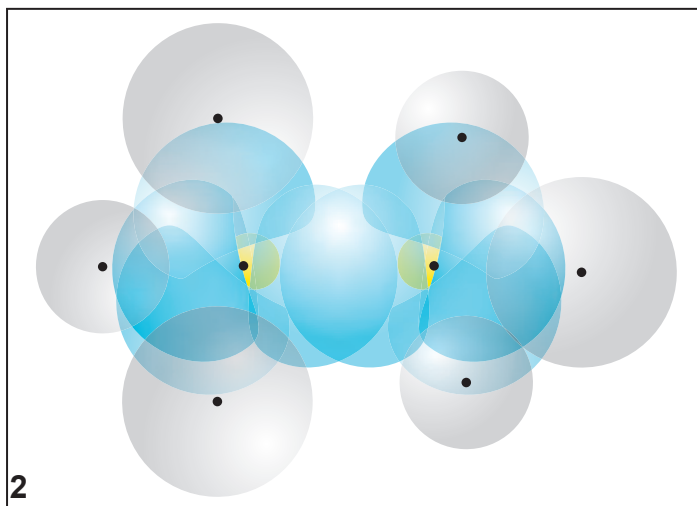
METHANE AND ETHANE



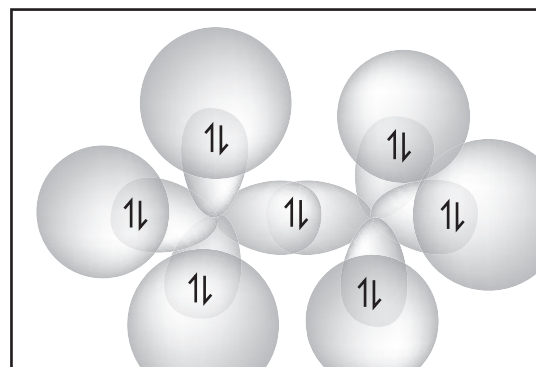
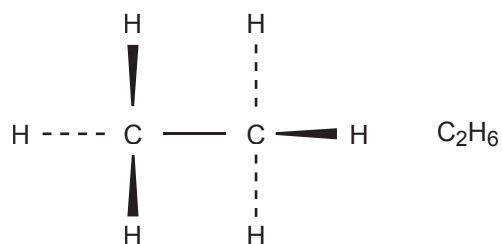
Methane CH₄



In methane and ethane, all of the bonds are σ -bonds, which means that they are formed by orbitals overlapping along a direct line between the nuclei of the two bonding atoms.



Ethane CH₆



Color conventions:

Hydrogen atoms are shown in gray.

Hybrid atomic orbitals are shown in blue and yellow.

Atomic p orbitals are shown in red and green.

Greyscale Conventions:

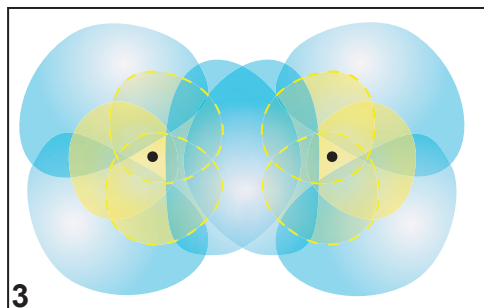
Hybrid orbitals are shown in grey.

Unhybridized atomic orbitals are shown in reddish-grey.

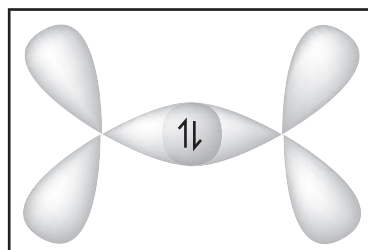
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

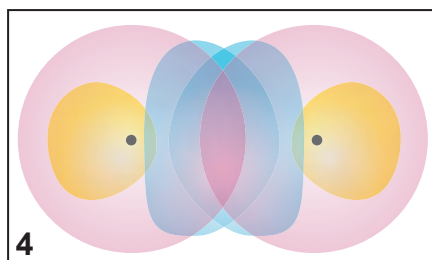
ETHENE C_2H_4



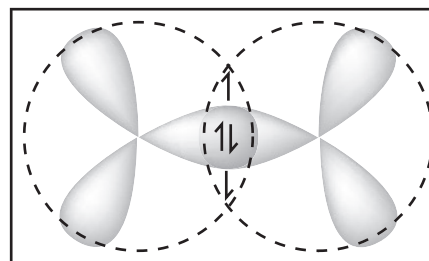
σ bond
C—C



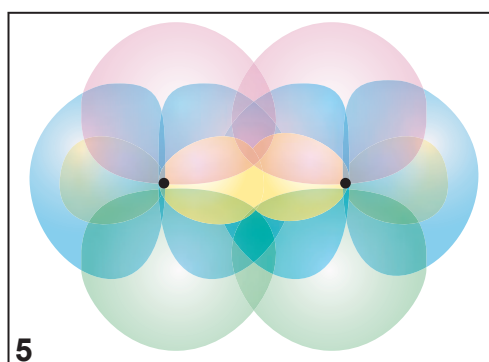
Picture 3 shows the sigma bond formed by overlapping sp^2 orbitals between the two carbon atoms of ethene. The other sp^2 orbitals are shown in dashed outline.



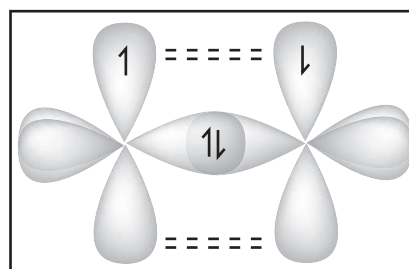
π bond
C=C



Picture 4 shows the π bond between the p orbitals of the carbon atoms. The pi bond is the overlap of the two red spheres and is actually coming out of the plane of the paper.



90° rotation

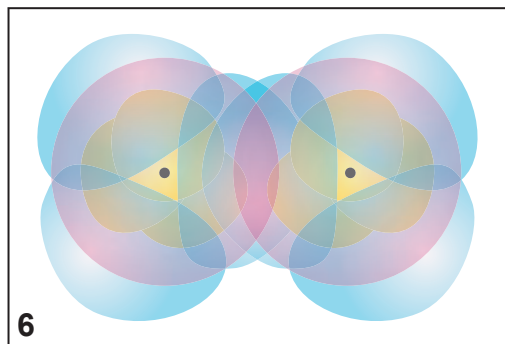


Picture 5 is similar to picture 4 but rotated 90° around the σ bond, so that the overlapping p orbitals which form the π bond are shown with the red phase above the σ bond and with the green phase below.

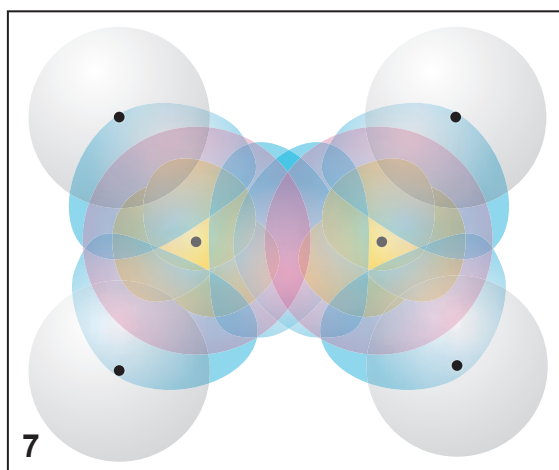
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

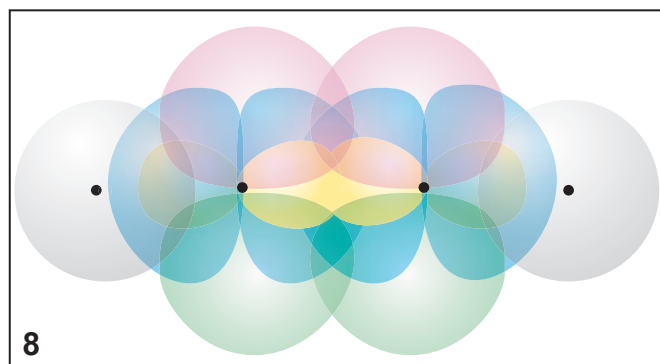
ETHENE C_2H_4



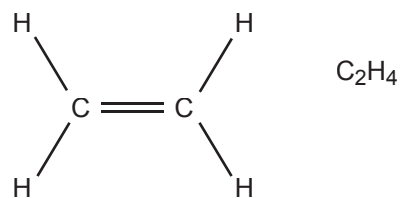
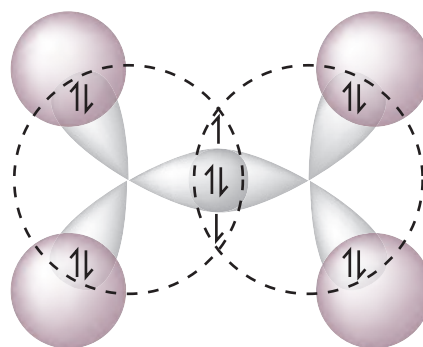
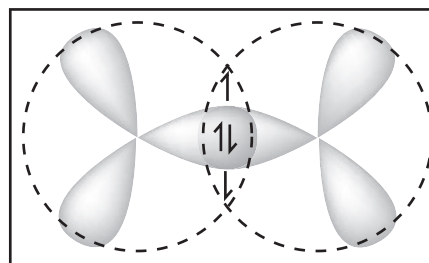
Ethene from above the trigonal plane. The carbon atoms and orbitals are shown.



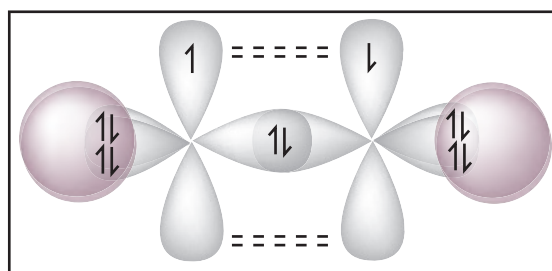
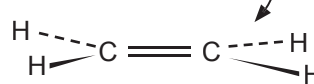
Ethene from above the trigonal plane with the hydrogen atoms shown. The bond angles and relative bond lengths are correct.



Ethene in the trigonal plane.



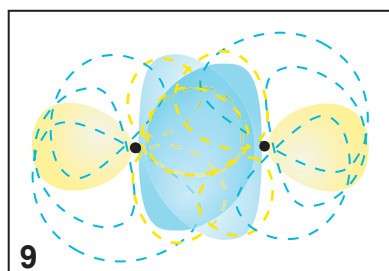
90° rotation



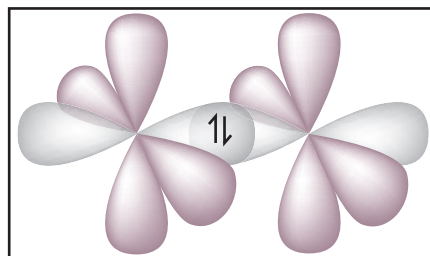
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

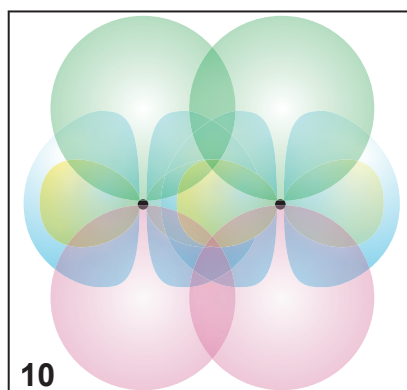
ETHYNE C_2H_2



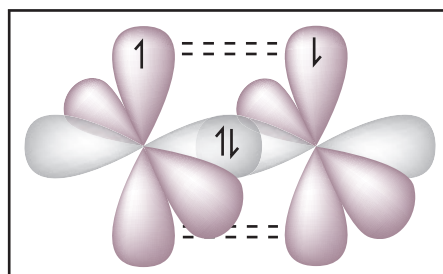
σ bond
C — C



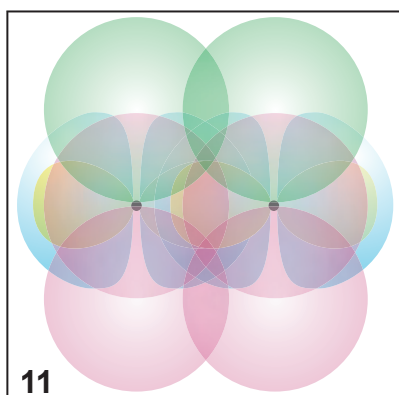
This drawing shows the sigma bond between two carbon atoms.



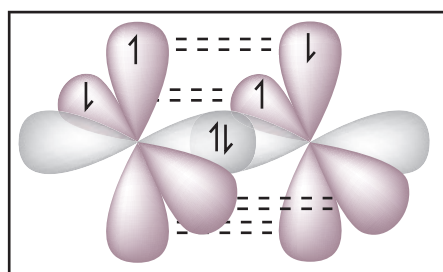
π bond
C = C



In this drawing we have added a pi bond to the ethyne.



π bond
C \equiv C

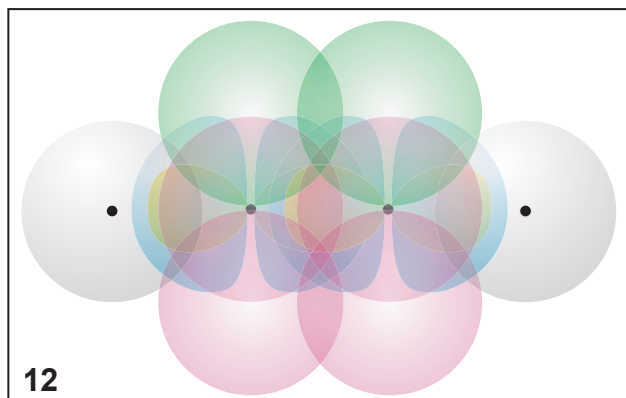


We have added the other π bond which, as it needs to be orthogonal to both the first π bond and to the σ bond, must be imagined as coming out of the paper.

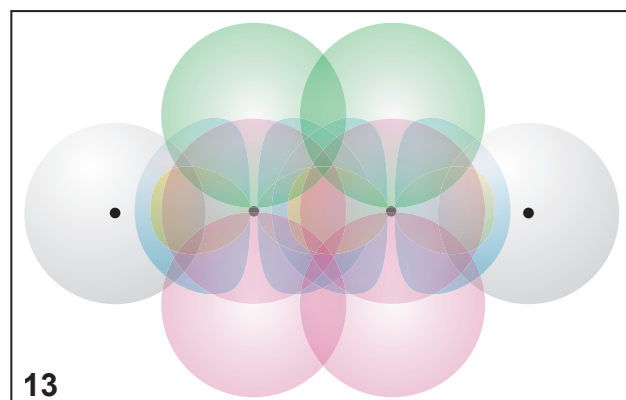
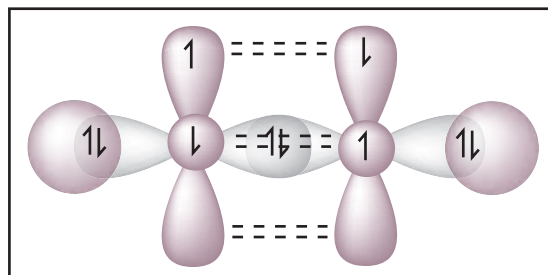
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

ETHYNE C_2H_2



Ethyne in the trigonal plane, but with the hydrogen atoms added.

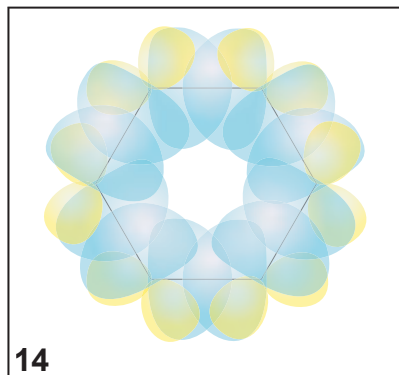


Unlike ethene, ethyne has the same form and appearance when rotated 90° around the C-C axis.

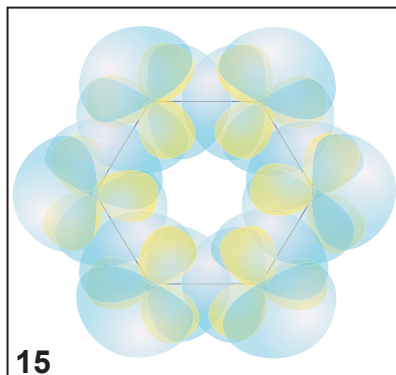
ORBITALS AND MOLECULAR REPRESENTATION

CARBON ORBITALS

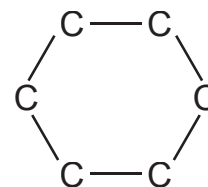
BENZENE C_6H_6



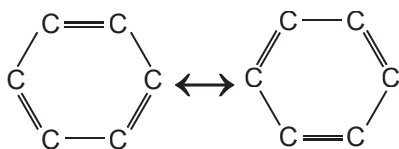
The sigma bond ring of benzene.



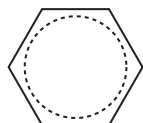
The sigma bond ring of benzene with the additional sp^2 orbitals.



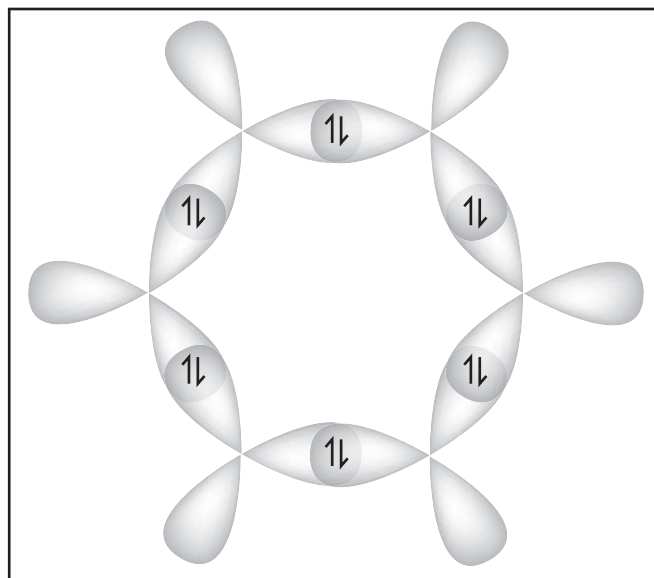
This is the ring of σ bonds whose orbitals are shown in picture 15



This is a former representation of the resonance structure of benzene.



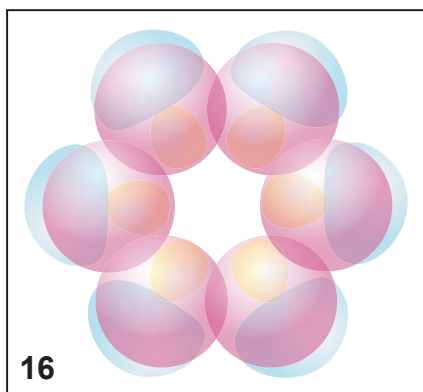
This is a contemporary representation of the resonance structure of benzene.



ORBITALS AND MOLECULAR REPRESENTATION

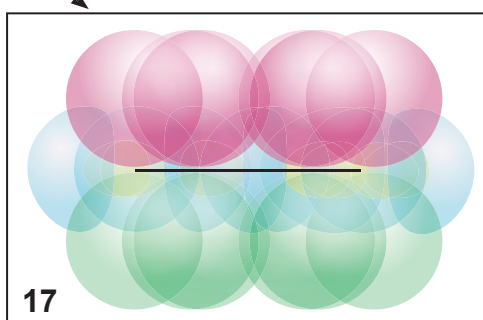
CARBON ORBITALS

BENZENE C_6H_6

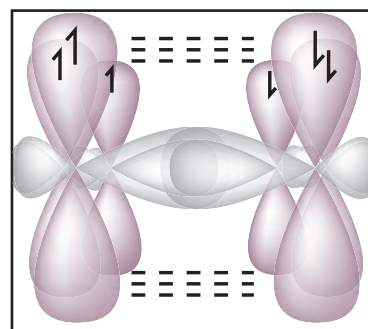
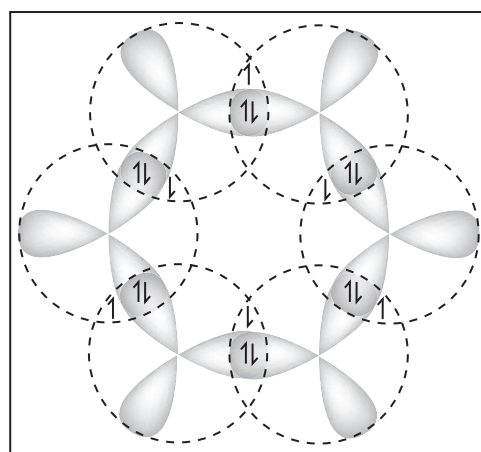


To which we have now added the pi orbitals above the ring.

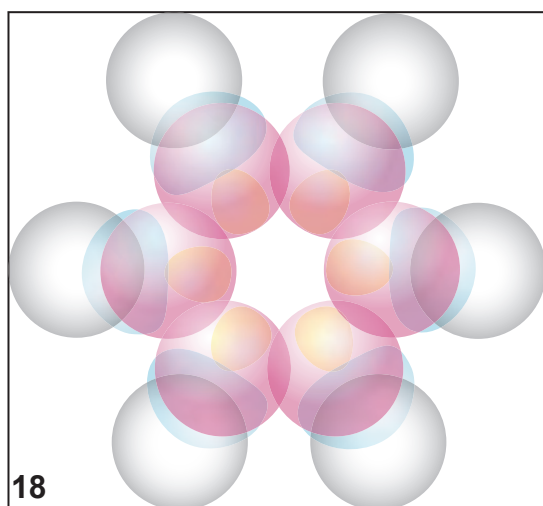
90° rotation



Benzene carbon orbitals viewed from the side.

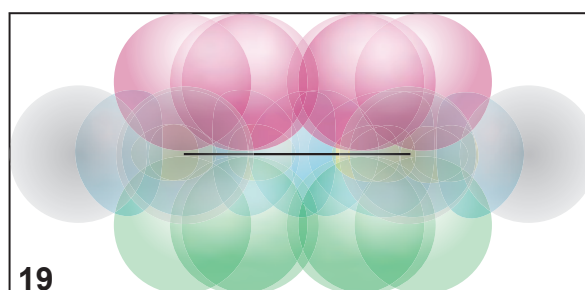


This picture illustrates the delocalization of the six 2p electrons in the benzene molecule. These six electrons are shared collectively among all six of the carbon atoms.



Adding the hydrogen atoms to picture 16 we view benzene from above, complete.

90° rotation

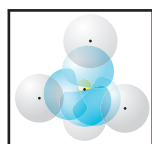


Benzene from the side, complete with hydrogen atoms.

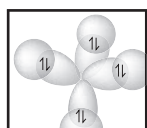
ORBITALS AND MOLECULAR REPRESENTATION

SEVERAL REPRESENTATIONS OF MOLECULES

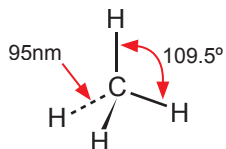
METHANE CH_4



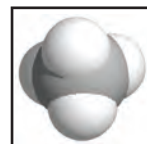
All orbitals



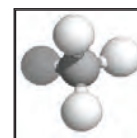
Textbook tetrahedron



Structural

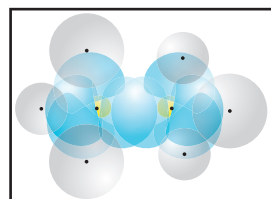


Space filling

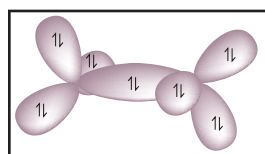


Ball and stick

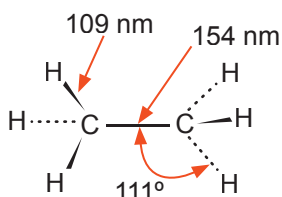
ETHANE C_2H_6



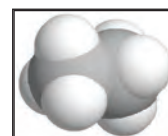
All orbitals



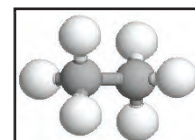
Textbook orbitals



Structural

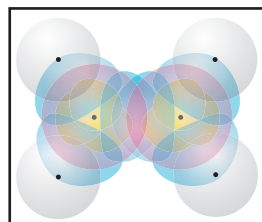


Space filling

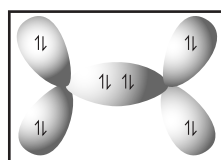


Ball and stick

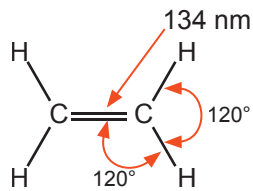
ETHENE C_2H_4



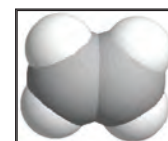
All orbitals looking down on the trigonal plane



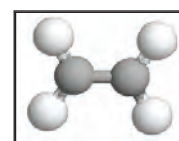
Textbook orbitals



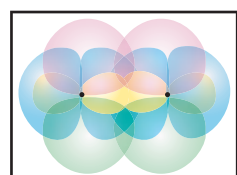
Structural



Space filling

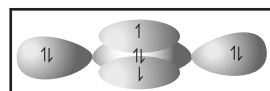


Ball and stick



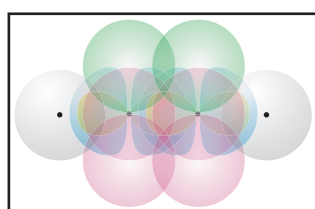
All orbitals but no hydrogen (for clarity)

Looking along the trigonal plane

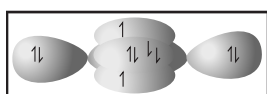


Textbook orbitals

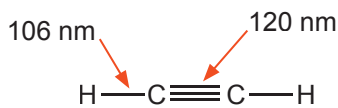
ETHYNE C_2H_2



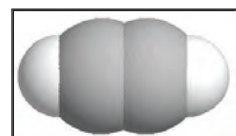
All orbitals



Textbook orbitals



Structural



Space filling

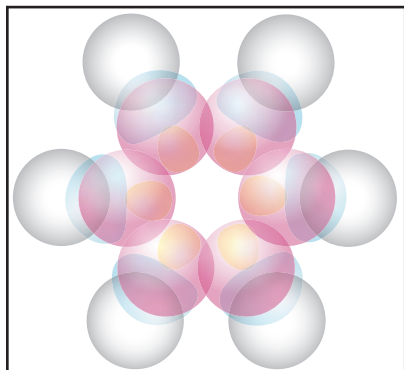


Ball and stick

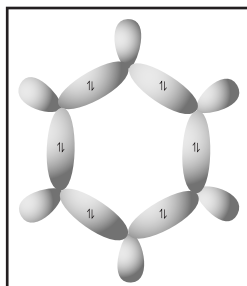
ORBITALS AND MOLECULAR REPRESENTATION

SEVERAL REPRESENTATIONS OF BENZENE

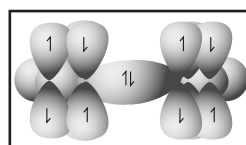
BENZENE C_6H_6



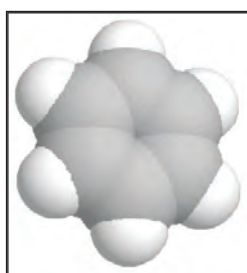
Benzene showing all orbitals



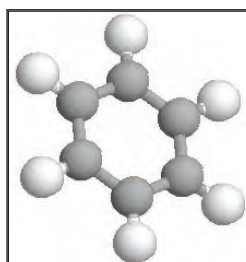
Benzene textbook σ bonds



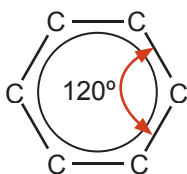
Benzene textbook σ and π bonds from the side



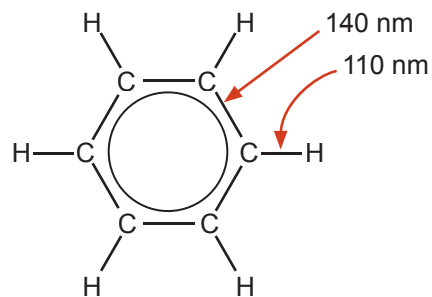
Benzene space filling



Benzene ball and stick



Benzene structural carbon ring



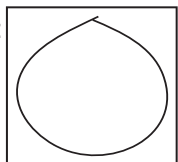
Benzene structural carbon ring and hydrogens

ORBITALS AND MOLECULAR REPRESENTATION

REPRESENTATIONS OF MOLECULES

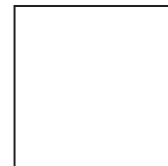
You can easily draw orbitals, bonds and molecules.

Start by drawing a circle, like this:

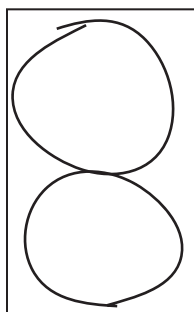


This is an s orbital.

You draw a circle (an s orbital) in the box.



Now draw one circle above another one, like this:

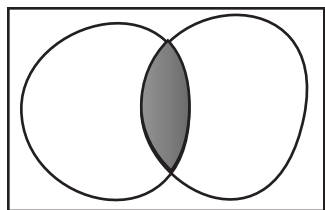


This is a p orbital.

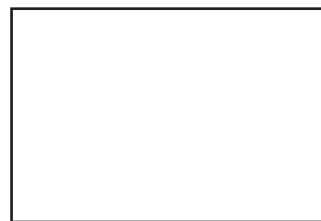
You draw a p orbital.
(two circles tangent)



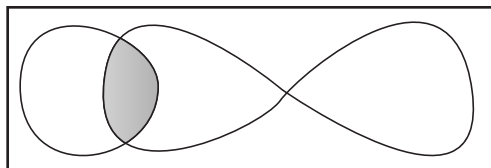
When two s orbitals from different atoms overlap, this is called a σ (sigma) bond.



You draw two overlapping circles in the box below.
This is a σ bond.



When an s and a p orbital overlap, this is a σ bond.

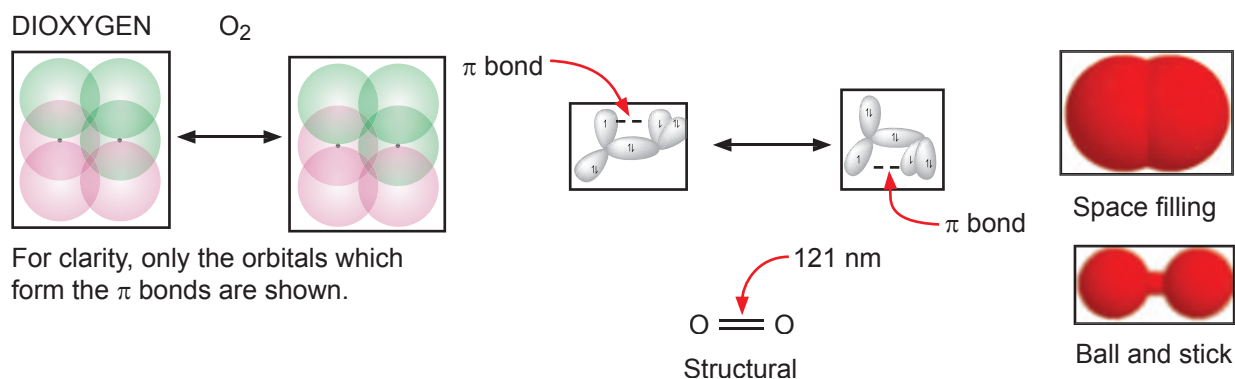
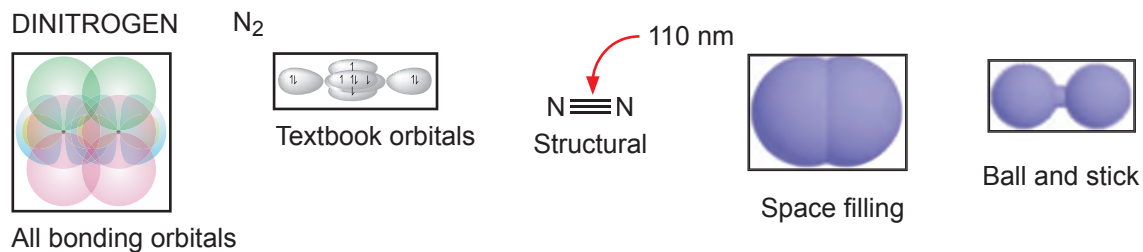


You can draw the s and p overlap.



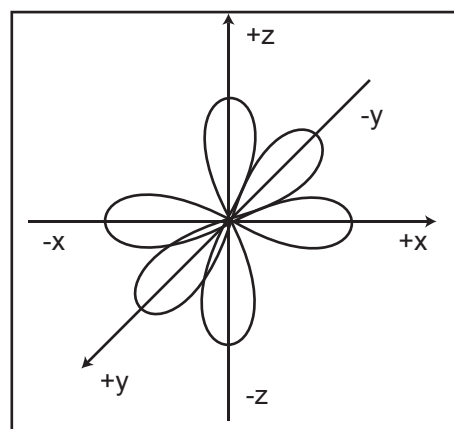
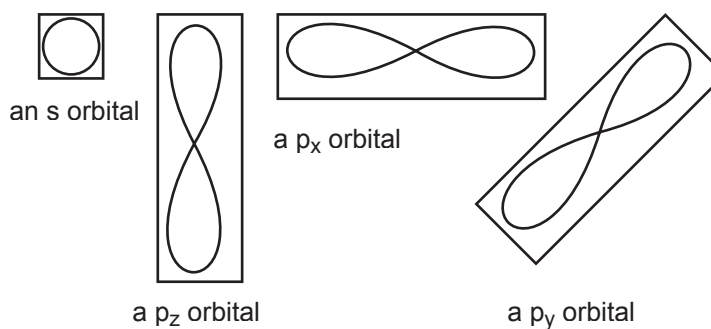
ORBITALS AND MOLECULAR REPRESENTATION

REPRESENTATIONS OF MOLECULES



SIMPLIFIED ORBITALS

We have shown molecular pictures which are as accurate as possible, however such orbitals are difficult to draw by hand. But a simplified version of them is easy to draw and shows much about molecular structure and bonding.



All three p orbitals

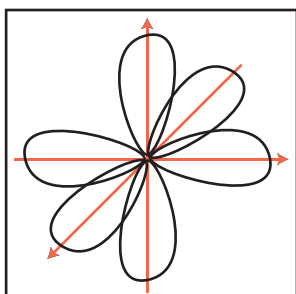
Draw the bonding orbitals for:



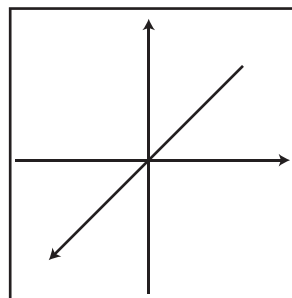
ORBITALS AND MOLECULAR REPRESENTATION

REPRESENTATIONS OF MOLECULES

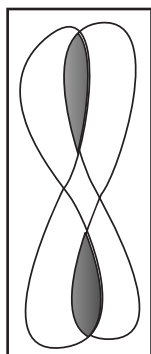
There are three orthogonal p orbitals. They can be drawn like this.



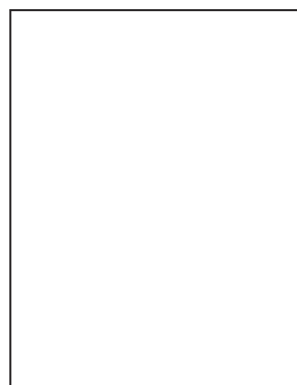
Draw your own set of p orbitals on the axes provided.



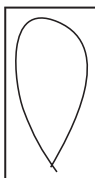
Two p orbitals (on different atoms) in the same direction can overlap forming a π (π) bond.



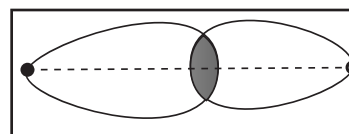
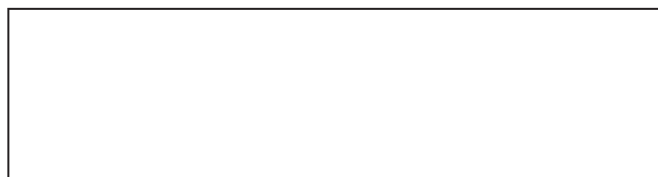
You draw two p orbitals side by side and overlapping, forming a π bond.



You can draw hybrid orbitals like this:



You draw an sp hybridized atom in the box below.

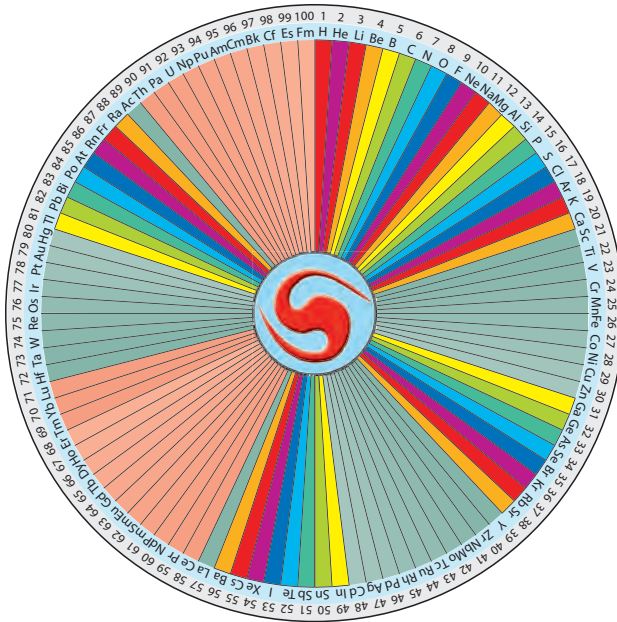


You draw an sp^2 hybridized atom.

PERIODIC TABLE

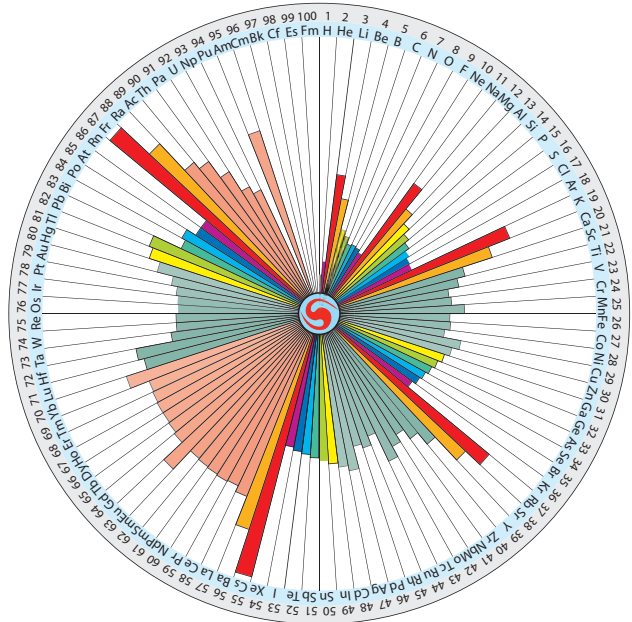
ROUND TABLES

Groups and Periods



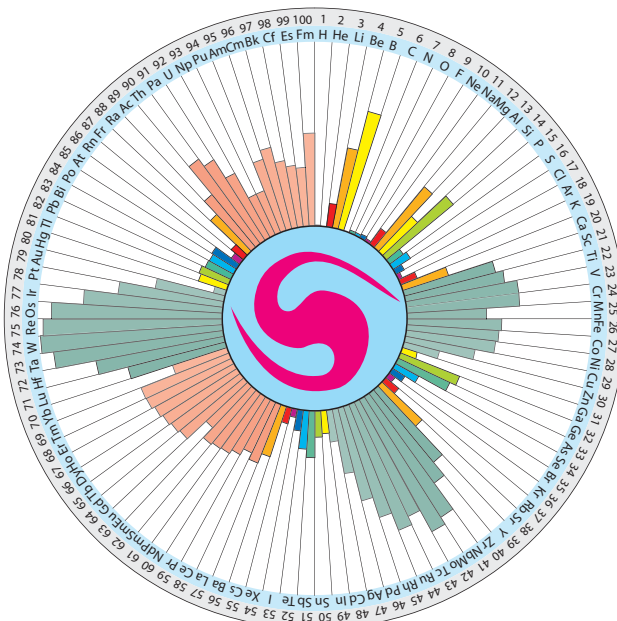
- Group 1A
- Group 2A
- Group 3A
- Group 4A
- Group 5A
- Group 6A
- Group 7A
- Group 8A
- Transition Metals
- Lanthanides and Actinides

Atomic Radii



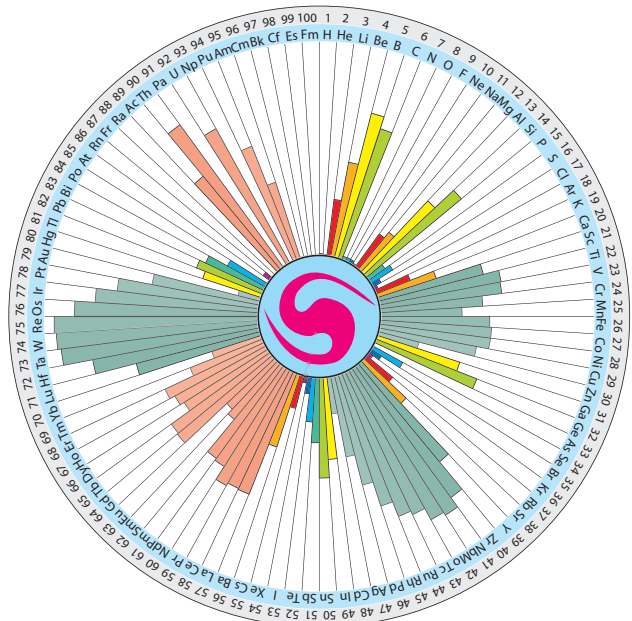
0 nm 260 nm

Melting Points



0 K 3300 K

Boiling Points

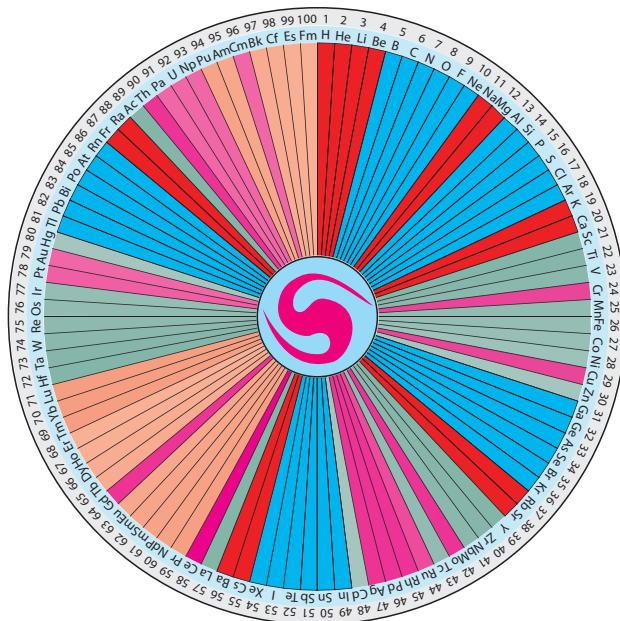


0 K 6000 K

PERIODIC TABLE

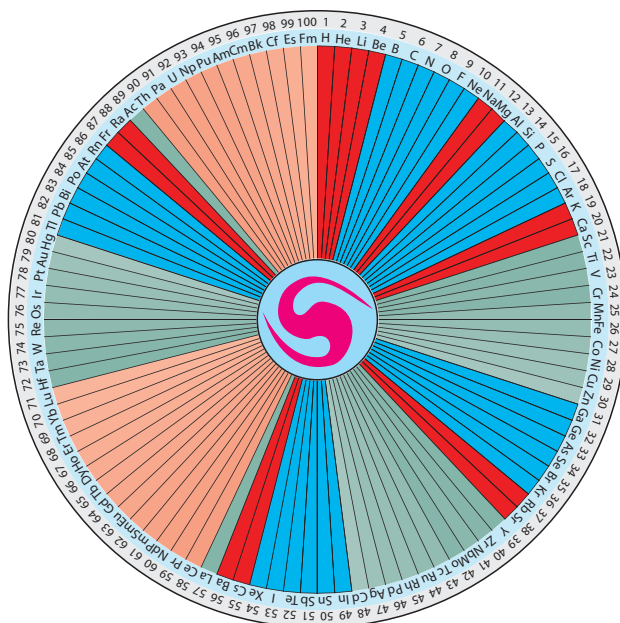
ROUND TABLES

Electron Shell Filling



- New electron in s shell.
- New electron in p shell.
- New electron in d shell.
- New electron in f shell.
- Anomalous.

This is how the new electrons would fill if there were no irregularities.



PERIODIC TABLE

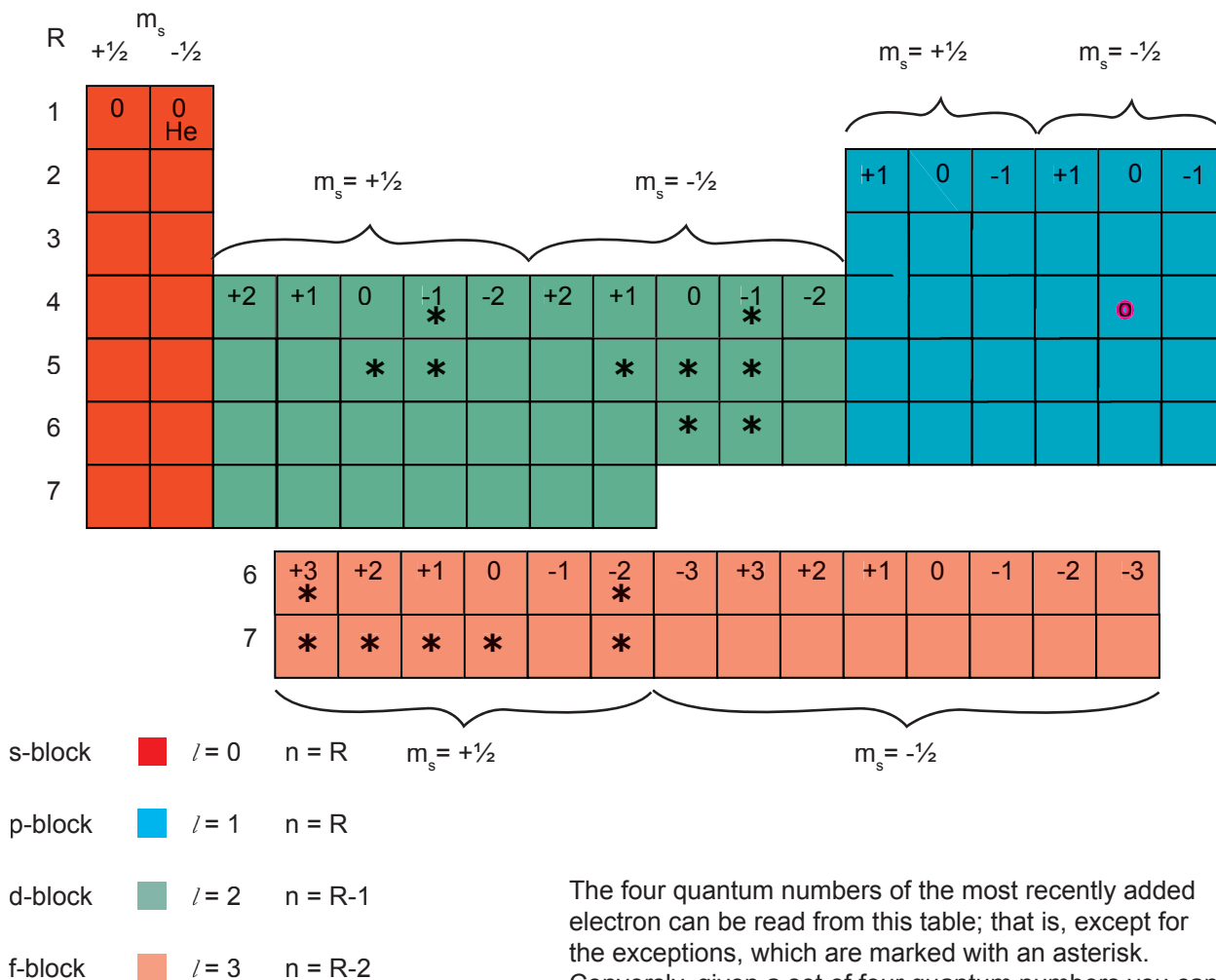
PRACTICE TABLE

Copy this page. Then, using the copy write in as many element symbols as you can. Repeat as often as you wish.

Actinium	Ac	Einsteinium	Es	Mendelevium	Md	Samarium	Sm
Aluminum	Al	Erbium	Er	Mercury	Hg	Scandium	Sc
Americium	Am	Europium	Eu	Molybdenum	Mo	Seaborgium	Sg
Antimony	Sb	Fermium	Fm	Neodymium	Nd	Selenium	Se
Argon	A	Fluorine	F	Neon	Ne	Silicon	Si
Arsenic	As	Francium	Fr	Neptunium	Np	Silver	Ag
Astatine	At	Gadolinium	Gd	Nickel	Ni	Sodium	Na
Barium	Ba	Gallium	Ga	Niobium	Nb	Strontium	Sr
Berkelium	Bk	Germanium	Ge	Nitrogen	N	Sulfur	S
Beryllium	Be	Gold	Au	Nobelium	No	Tantalum	Ta
Bismuth	Bi	Hafnium	Hs	Osmium	Os	Technetium	Tc
Bohrium	Bh	Hassium	Hs	Oxygen	O	Tellurium	Te
Boron	B	Helium	He	Palladium	Pd	Terbium	Tb
Bromine	Br	Holmium	Ho	Phosphorus	P	Thallium	Tl
Cadmium	Cd	Hydrogen	H	Platinum	Pt	Thorium	Th
Calcium	Ca	Indium	In	Plutonium	Pu	Thulium	Tm
		Iodine	I	Polonium	Po	Tin	Sn
Californium	Cf	Iridium	Ir	Potassium	K	Titanium	Ti
Carbon	C	Iron	Fe	Praseodymium	Pr	Tungsten	W
Cerium	Ce	Krypton	Kr	Promethium	Pm	Uranium	U
Cesium	Cs	Lanthanum	La	Protactinium	Pa	Vanadium	V
Chlorine	Cl	Lawrencium	Lr	Radium	Ra	Xenon	Xe
Chromium	Cr	Lead	Pb	Radon	Rn	Ytterbium	Yb
Cobalt	Co	Lithium	Li	Rhenium	Re	Yttrium	Y
Copper	Cu	Lutetium	Lu	Rhodium	Rh	Zinc	Zn
Curium	Cm	Magnesium	Mg	Rubidium	Rb	Zirconium	Zr
Dubnium	Db	Manganese	Mn	Ruthenium	Ru		
Dysprosium	Dy	Meitnerium	Mt	Rutherfordium	Rf		

PERIODIC TABLE

QUANTUM NUMBERS OF MOST RECENTLY ADDED ELECTRON



The magnetic quantum number, m , is the number from +3 to -3 marked on the top of each column.

The four quantum numbers of the most recently added electron can be read from this table; that is, except for the exceptions, which are marked with an asterisk. Conversely, given a set of four quantum numbers you can locate the position of the element on the table.

For example, if

$$n = 3$$

$$L = 1$$

$$m = 0$$

$$m_s = -\frac{1}{2}$$

then we can find the element where we have placed the small red 'o', which is bromine.

Find the elements which have the following sets of quantum numbers.

$$n = 2, L = 0, m = 0, m_s = +\frac{1}{2}$$

$$n = 4, L = 2, m = +2, m_s = -\frac{1}{2}$$

What are the quantum numbers of:

neon

sodium

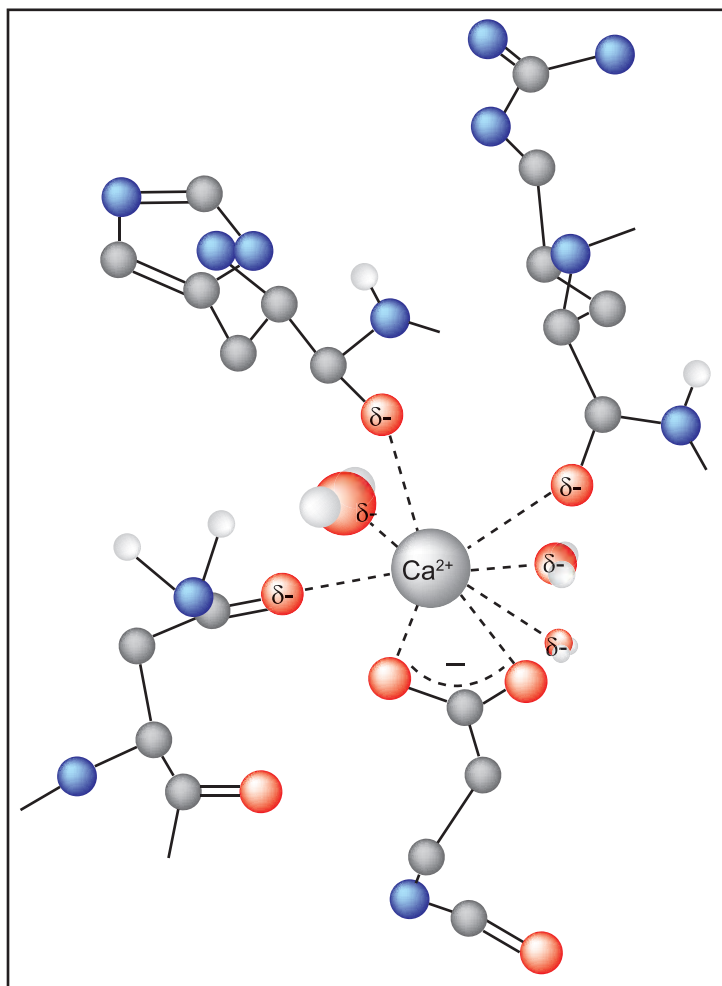
vanadium

gallium

hydrogen

oxygen?

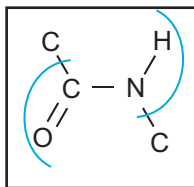
PROTEINS



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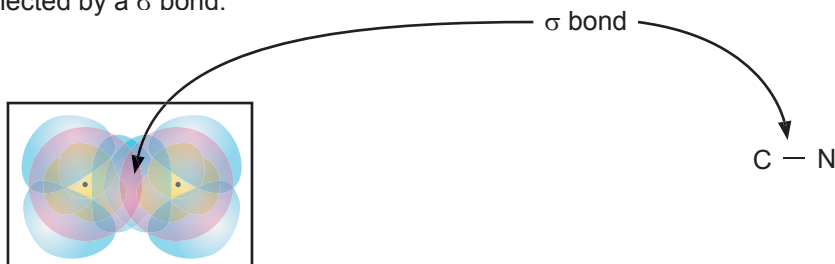
PROTEINS

THE PEPTIDE BOND

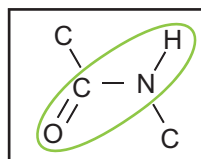


The peptide bond, shown above enclosed in the blue curves, generates the basic structural unit for proteins.

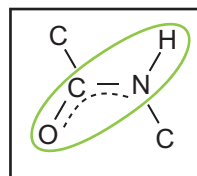
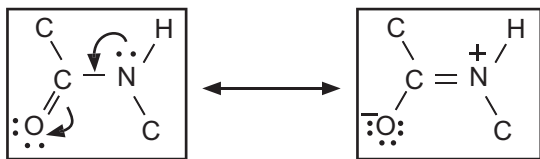
The carbon and nitrogen atoms are both hybridized sp^2 and they are connected by a σ bond.



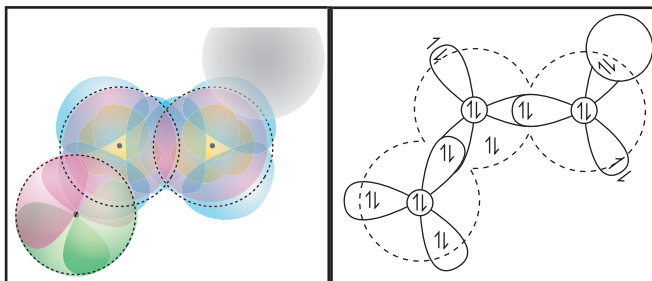
In addition to the σ bond, there is a resonance which allows the unshared electrons of the nitrogen to overlap the p orbitals of the CO (carbonyl) group, giving rise to an effective π bond which, combined with the sp^2 planarity of the carbon and nitrogen atoms, holds the whole peptide bond in a plane.



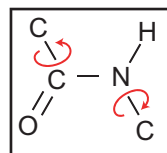
Rigid amide plane outlined in green



The dashed curve indicates the resonance between the carbon-oxygen and the carbon-nitrogen π bonds. This is what gives the amide structure its planar rigidity.



In these pictures we have added the oxygen atom and shown the two p orbitals which lie in the plane of the paper in color. Note how one of the oxygen p orbitals overlaps one of the carbon sp^2 orbitals to form a σ bond. We have also added dashed circles to represent the p orbitals on each of the three atoms which are directed out of the plane of the paper. See how the p orbital of the central carbon atom overlaps the p orbitals of both of the other atoms, forming π bonds with each of them. We have also added the hydrogen atom shown in gray. If the top of the hydrogen is clipped off, that is due to printing limitations; the real atom is spherical.

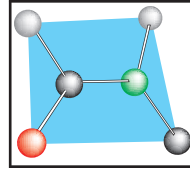


Rotatable bonds by which the amide structure connects to other amide structures to form the backbone of the protein.

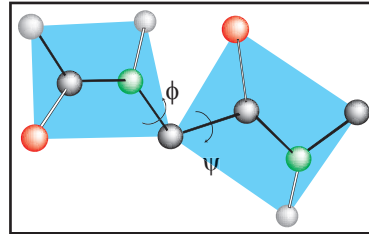
PROTEINS

AMIDE PLANES

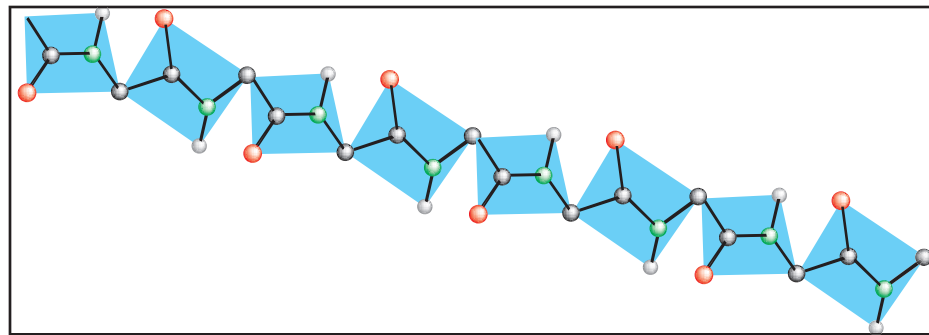
Now, for clarity, we show the amide plane in blue.



In proteins, two amide planes are joined by a mutual bond to a carbon atom, called the C_{α} atom. Each amide plane can rotate about its bond to the C_{α} atom. The angle of rotation between the N and the C_{α} is named ϕ (phi) and the angle of rotation between the C_{α} and the C atom is called ψ (psi).



Multiple amide planes can be joined to form polypeptide chains.



In proteins, polypeptide chains also form larger units, of which two of the most important varieties are α helices and β sheets.

Two additional effects, however, beyond the peptide bond are important in determining the structure of these forms. These effects are steric hindrance and hydrogen bonding.

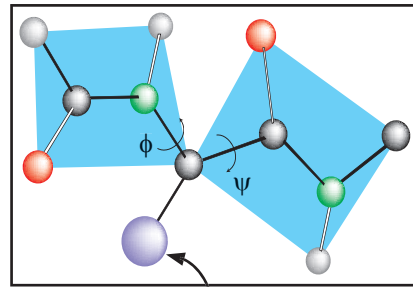
PROTEINS

AMIDE PLANES

In real proteins the hydrogen atoms in the amide plane are often replaced by amino acids. This is what gives proteins their great variety and effect.

In proteins, the C_{α} atom has an amino acid residue connected to it.

The amino acid residues are fairly large molecular fragments, which push away from each other by steric hindrance, causing the polypeptide chain to rotate around the single bonds connecting the C



Amino acid residue

Where have amino acids been observed in nature, besides in proteins?

We have shown that the amide planes are connected via a C_{α} atom with two rotational degrees of freedom. Explain why this fact shows that the C_{α} atom only has single bonds.



A left handed spiral.



A right handed spiral.

Look for examples of spirals in the natural world, as well as spiral objects constructed or drawn by humans. Describe the spirals, especially noting whether they are right handed or left handed.

PROTEINS

ALPHA HELIX

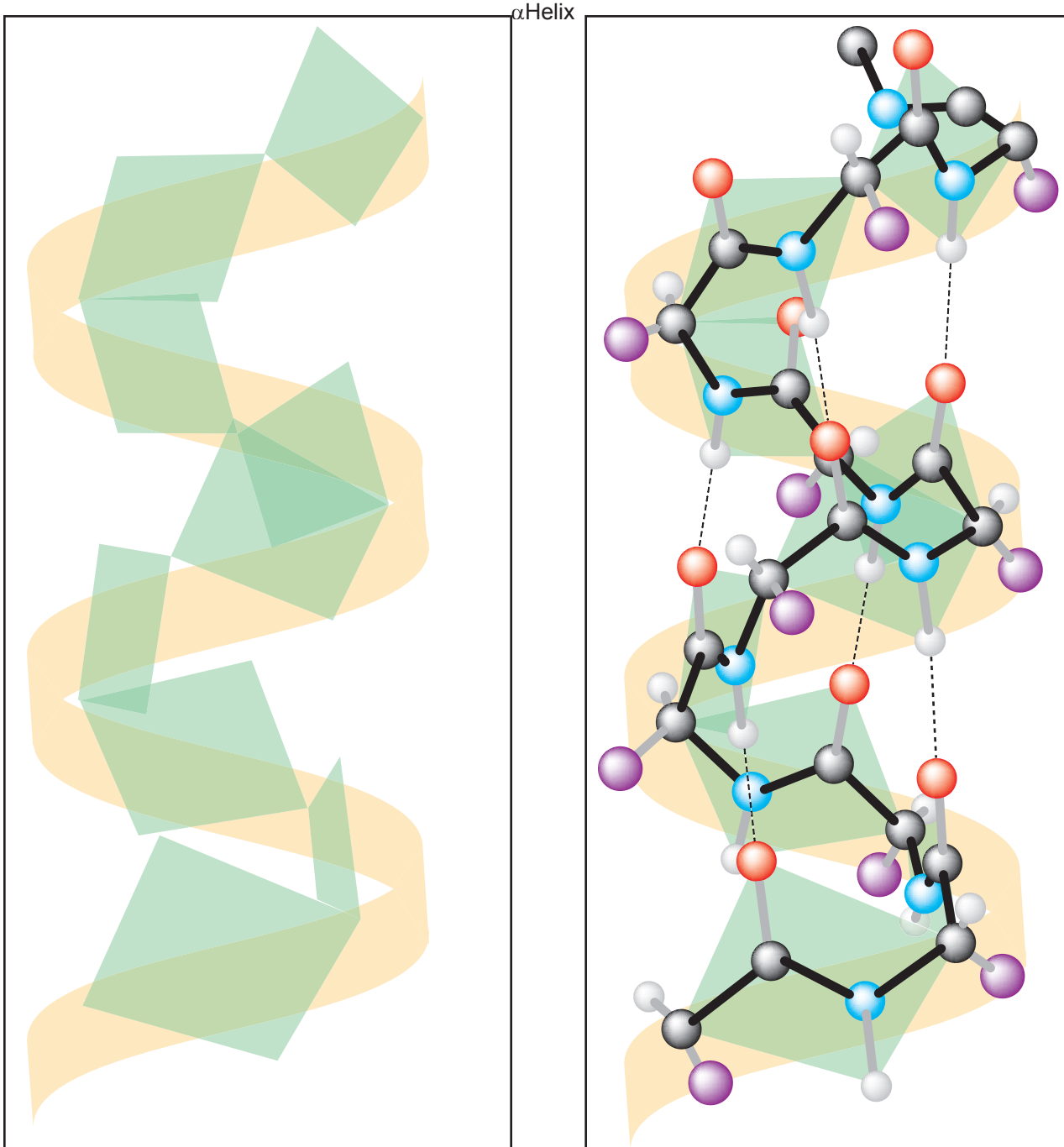
Two important structural features of proteins are α -helices and β -sheets.

The amino acid residues force the peptide planes to twist so as to minimize the steric hindrance.

In the picture below the amide planes are shown in green.

In the picture below a certain type of bonding is represented by the dotted lines. You should be able to deduce what kind of bonding that is and describe what effect it has on the structure of the alpha helix.

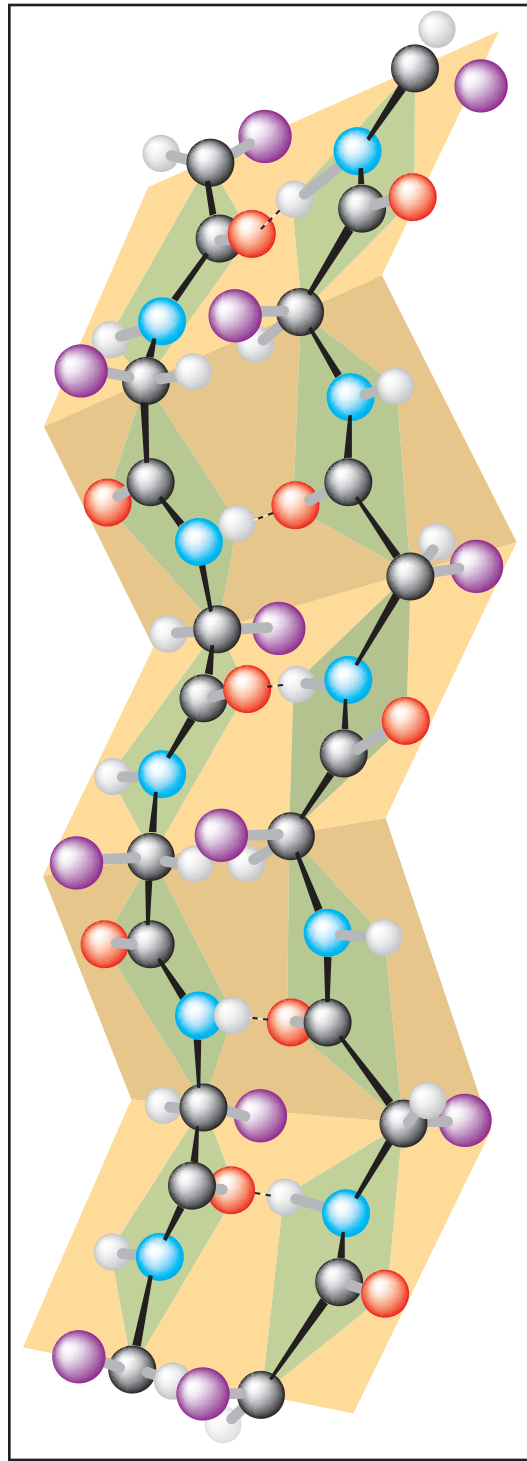
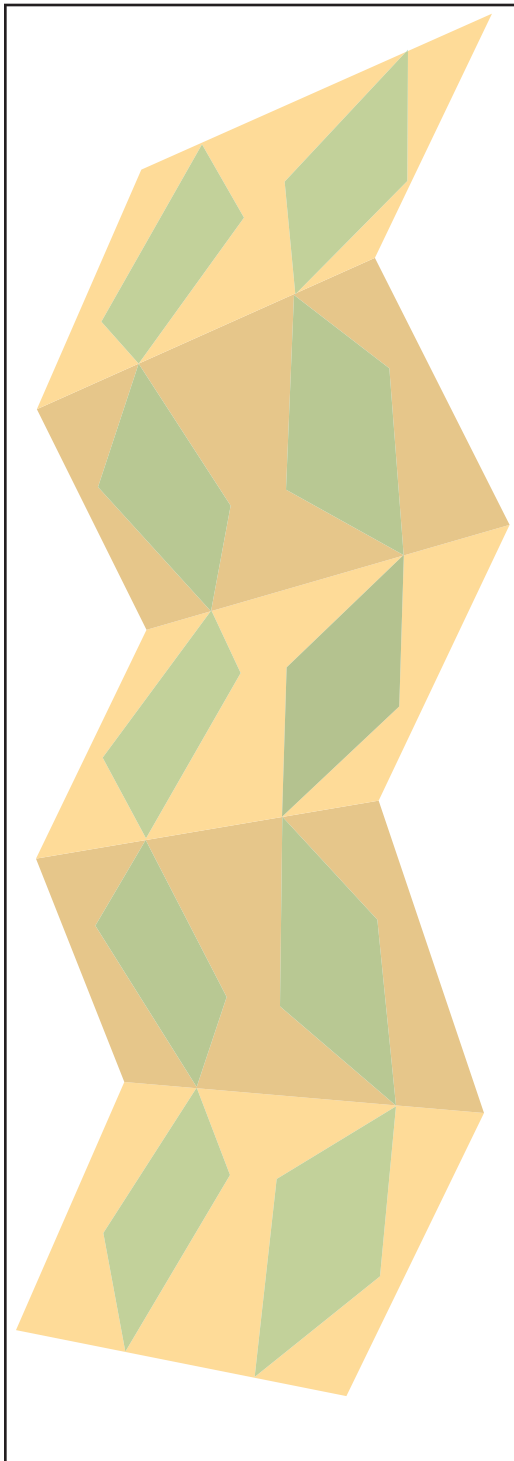
Is the α -helix right handed or left handed?



PROTEINS

BETA SHEET

β -Sheet



PROTEINS

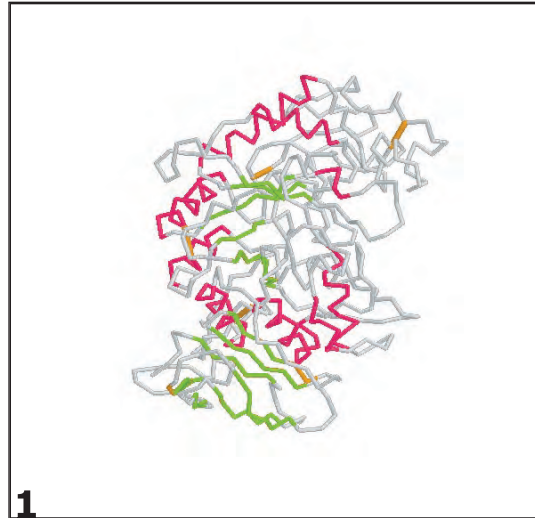
AMALAYSE

The next six pictures show human pancreatic alpha amalyse, which is an essential enzyme for digesting starch.

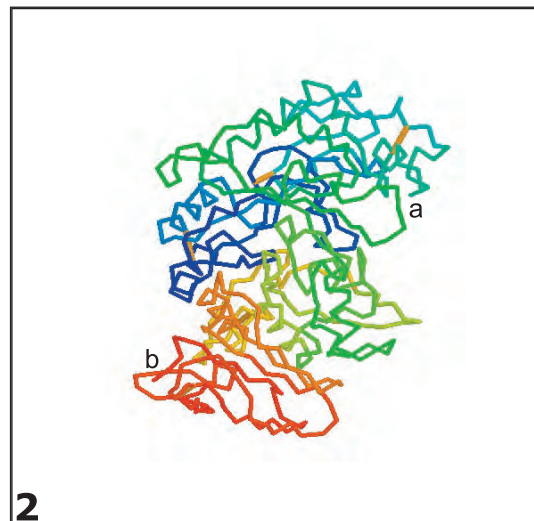
We are using this protein molecule to demonstrate the interplay of several different forms of bonding in one molecule.

First examine the backbone structure of the molecule in picture 1. Locate the helices.

What kind of bonding holds the backbone together? Why would ionic bonding not work?

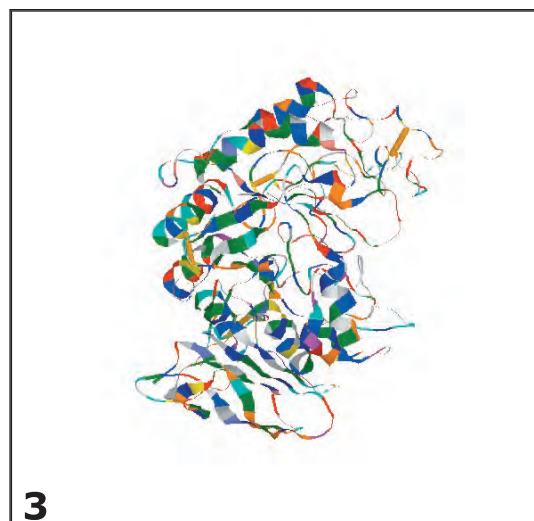


In picture 2 you can trace the backbone by following the spectral sequence of colors. Starting at a, you can follow the backbone to b (or vice-versa).



Picture 3, in ribbon form, makes the helices stand out clearly. You can also find several beta sheets near the bottom of the molecule.

Each colored patch represents an amino acid. In figure 3, count the number of amino acids that make up the different helices.

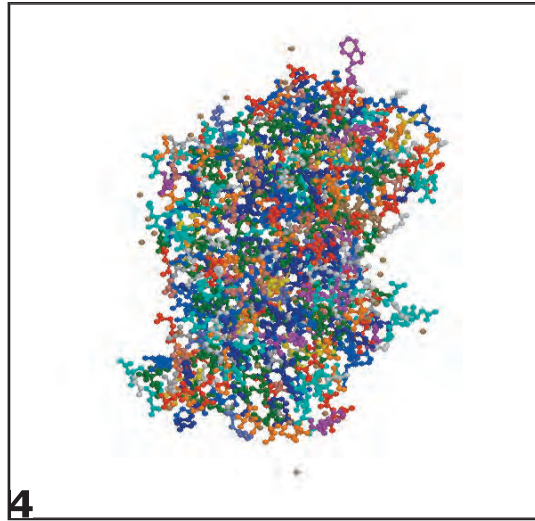


PROTEINS

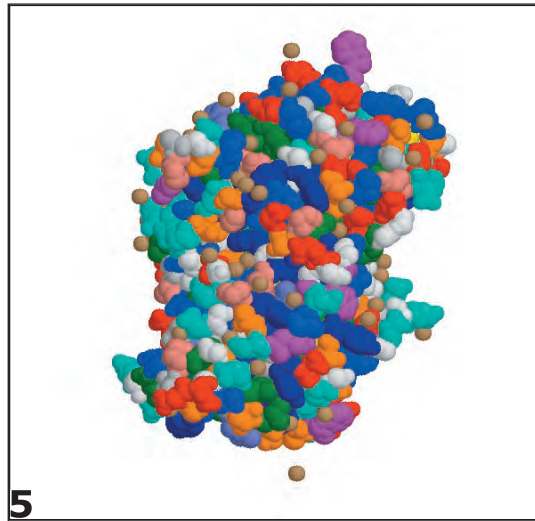
PROTEIN STRUCTURE

Picture 4 is a ball and stick representation which makes the individual atoms stand out. The colors are differentiated according to the individual amino acids.

Why is it valuable for chemists, teachers and students to be able to view several different forms of the molecule?

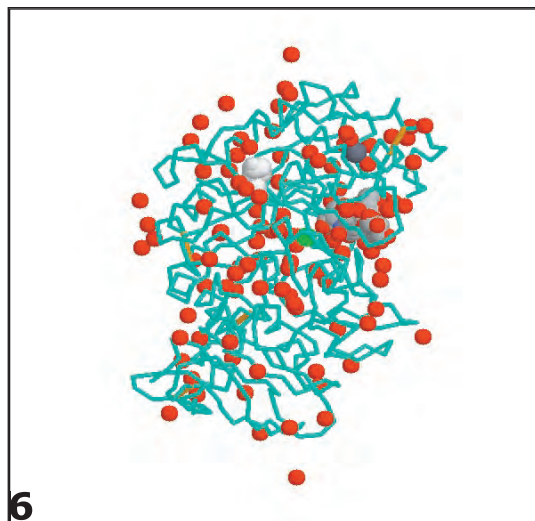


The space filling representation in picture 5 helps to see the overall shape of the molecule. It is also colored according to the amino acids.



In picture 6 the backbone is printed in blue, the oxygen atoms (which show the associated water molecules) in red, the disulfide bonds in orange and the ligands in gray and white. You can also locate the chloride and calcium ions.

Each amylase molecule contains several hundred waters. What kind of bonding connects the waters to the rest of the amylase?



PROTEINS

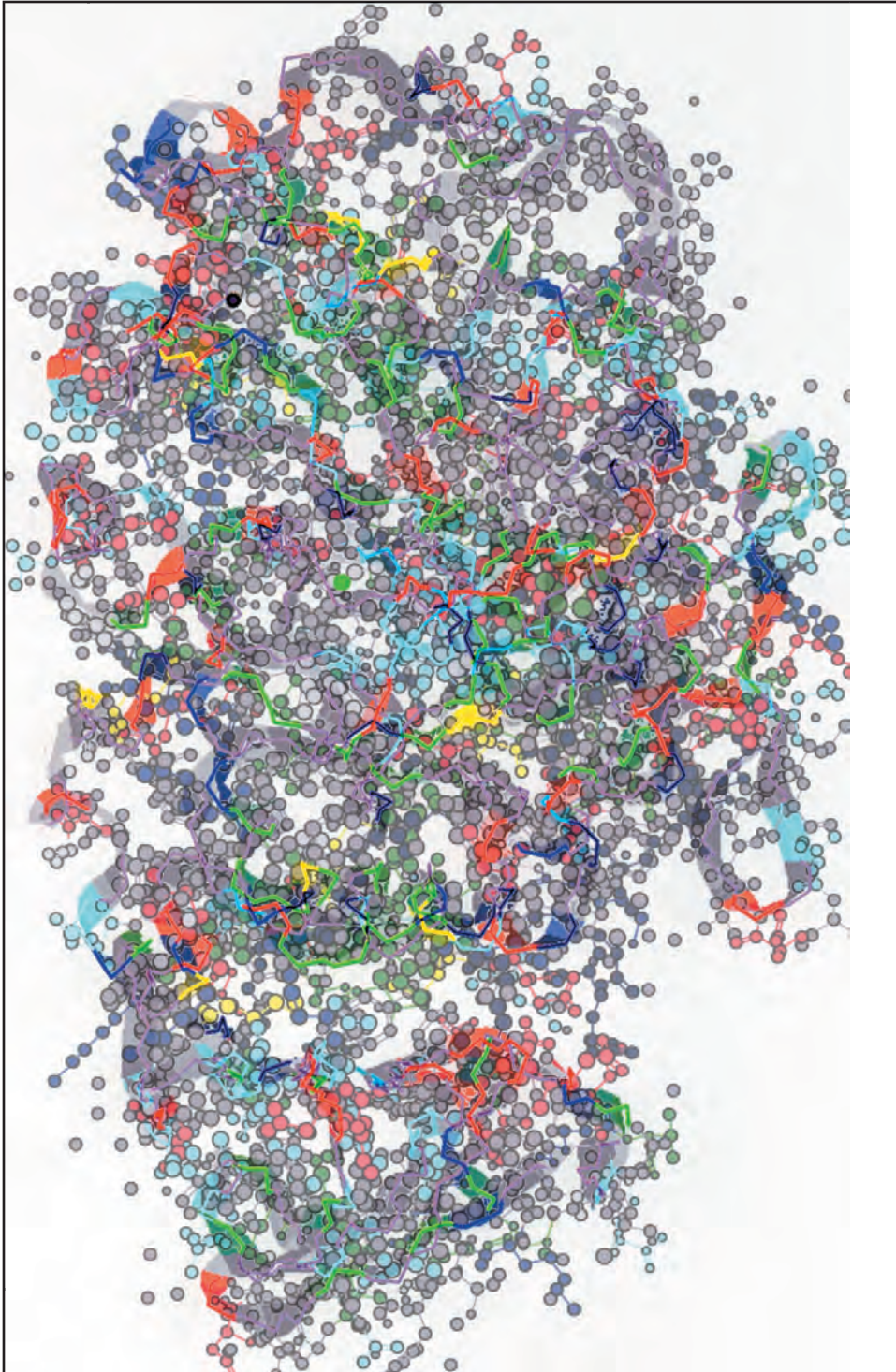
ANALYSE



This is called the ribbon view, of human pancreatic alpha amylase, and is useful to show the linear arrangement, or backbone, of the amino acids.

PROTEINS

ANALYSE

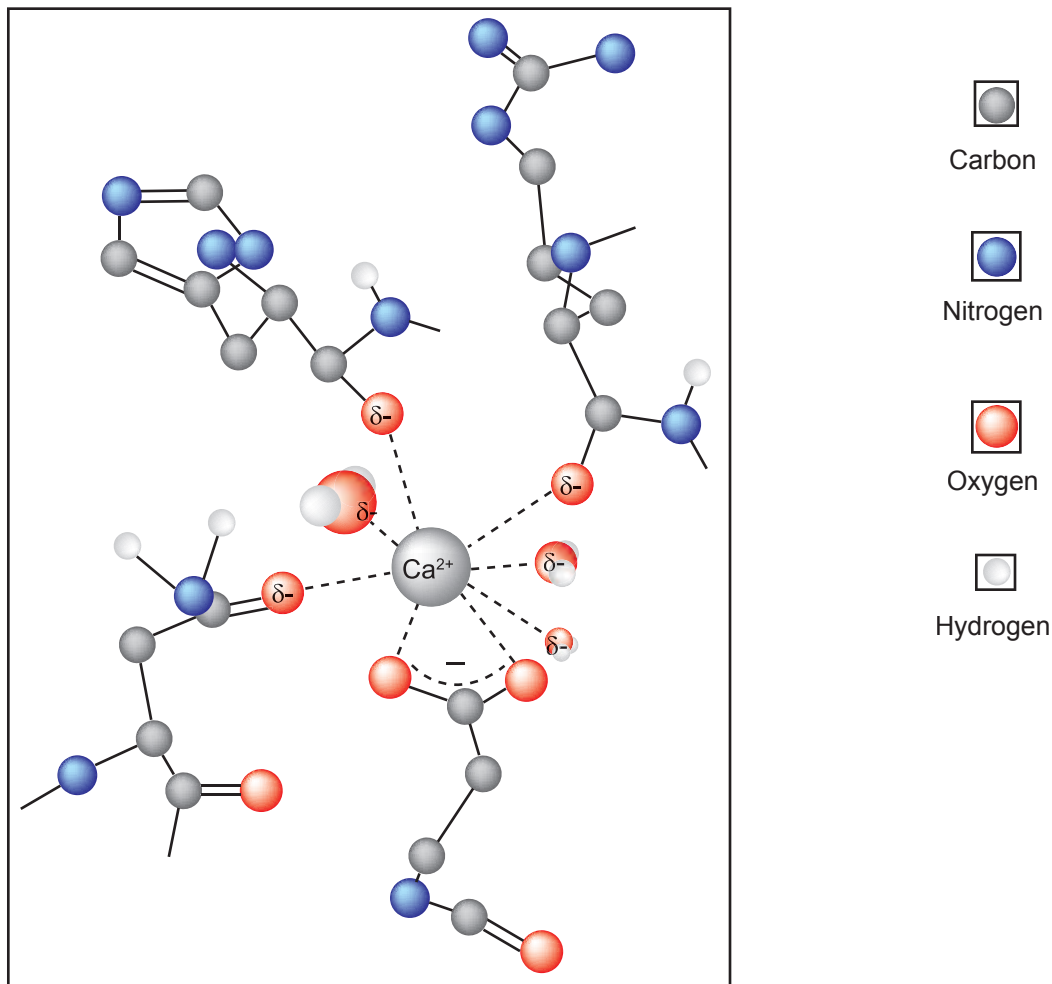


This view superimposes the atomic ball and stick view on top of the ribbon view and is perhaps most useful to get an impression of the actual complexity of the molecule.

Locate the calcium ion in the above picture. It is shown in black.

PROTEINS

CALCIUM ION SITE IN AMALAYSE



This is a picture of the calcium ion and its surroundings and connections in an amylase molecule.

Each amylase molecule contains one doubly charged calcium ion, Ca^{2+} . Find the calcium ion in picture 99.

What, in terms of the atomic structure of calcium, makes it natural for the ion to be doubly charged?

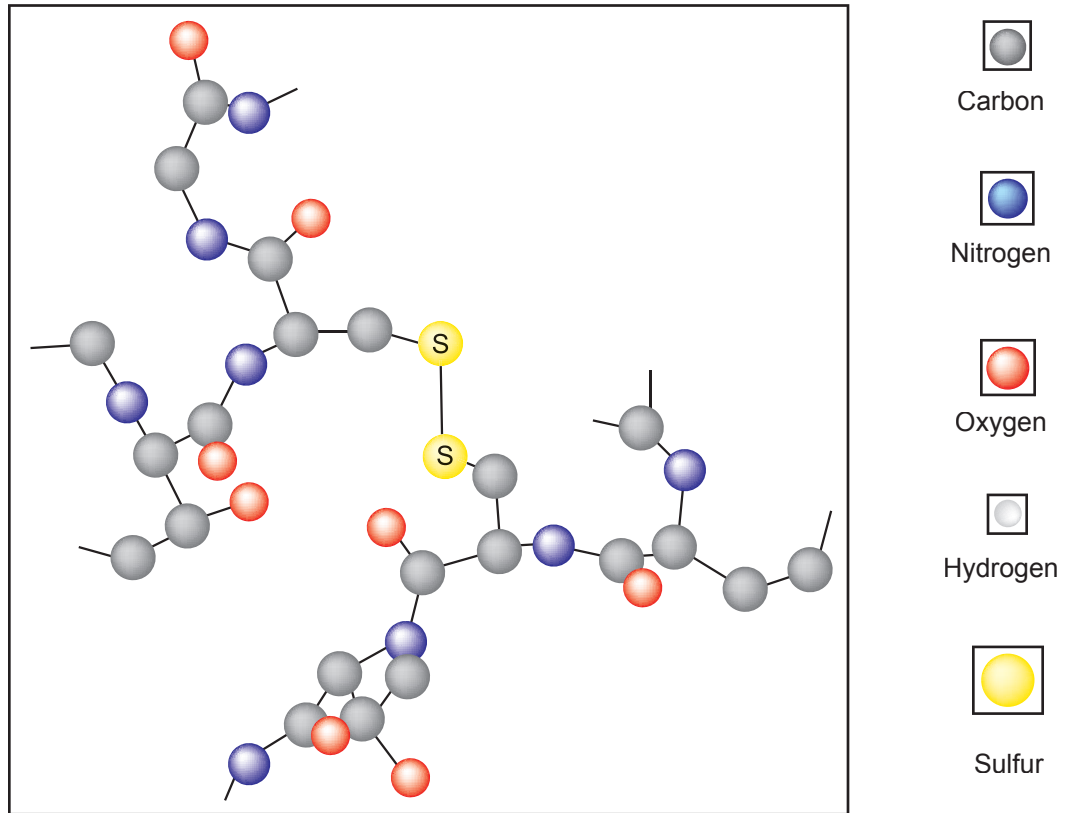
We know from experiment that the calcium ion in amylase is doubly charged. Otherwise, which would be more unlikely, Ca^+ or Ca^{2+} ?

Suppose the calcium ion in amylase were given two electrons, what effect would you expect this to have on the structure of the molecule?

In picture 99, count the number of bonds shown between Ca^{2+} and other atoms in the molecule. From the number of bonds alone, explain why these cannot be covalent bonds.

PROTEINS

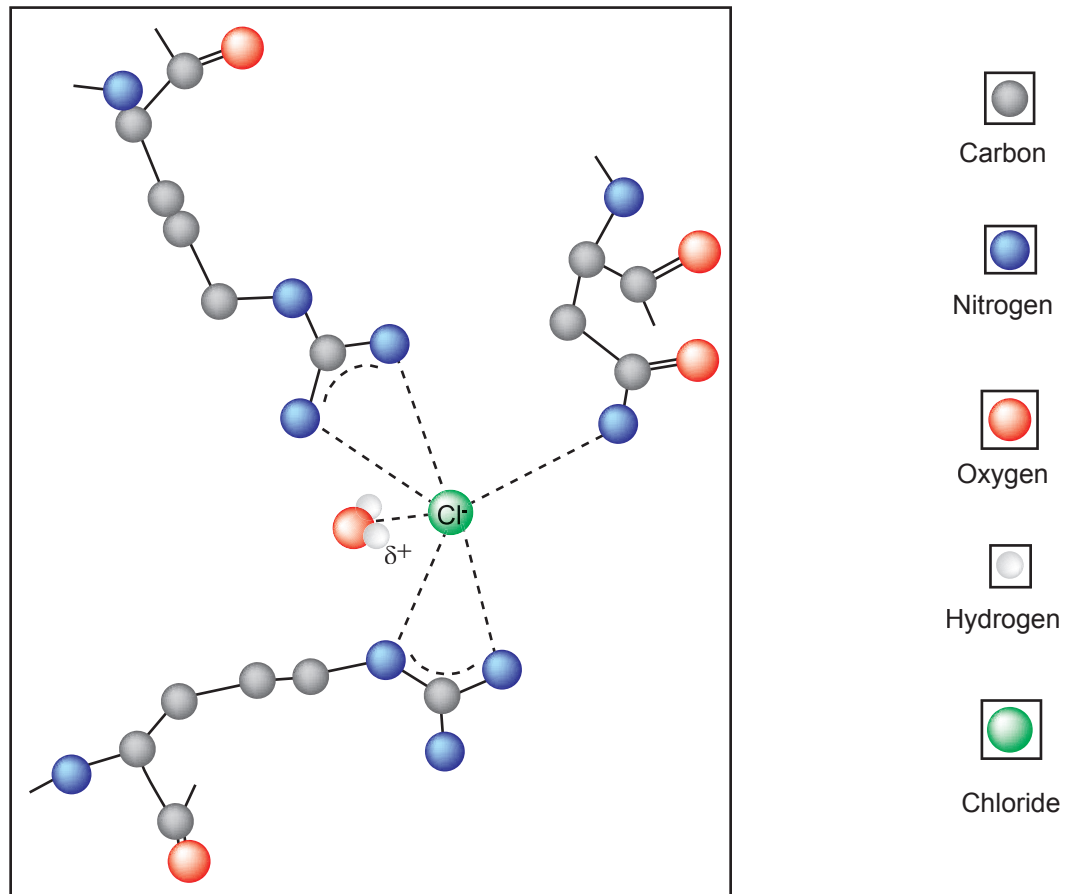
DISULFIDE BRIDGE IN AMALAYSE



This is a picture showing the local linkage of the disulfide bridge in the human pancreatic alpha amylase molecule.

PROTEINS

CHLORIDE ION SITE IN AMALAYSE



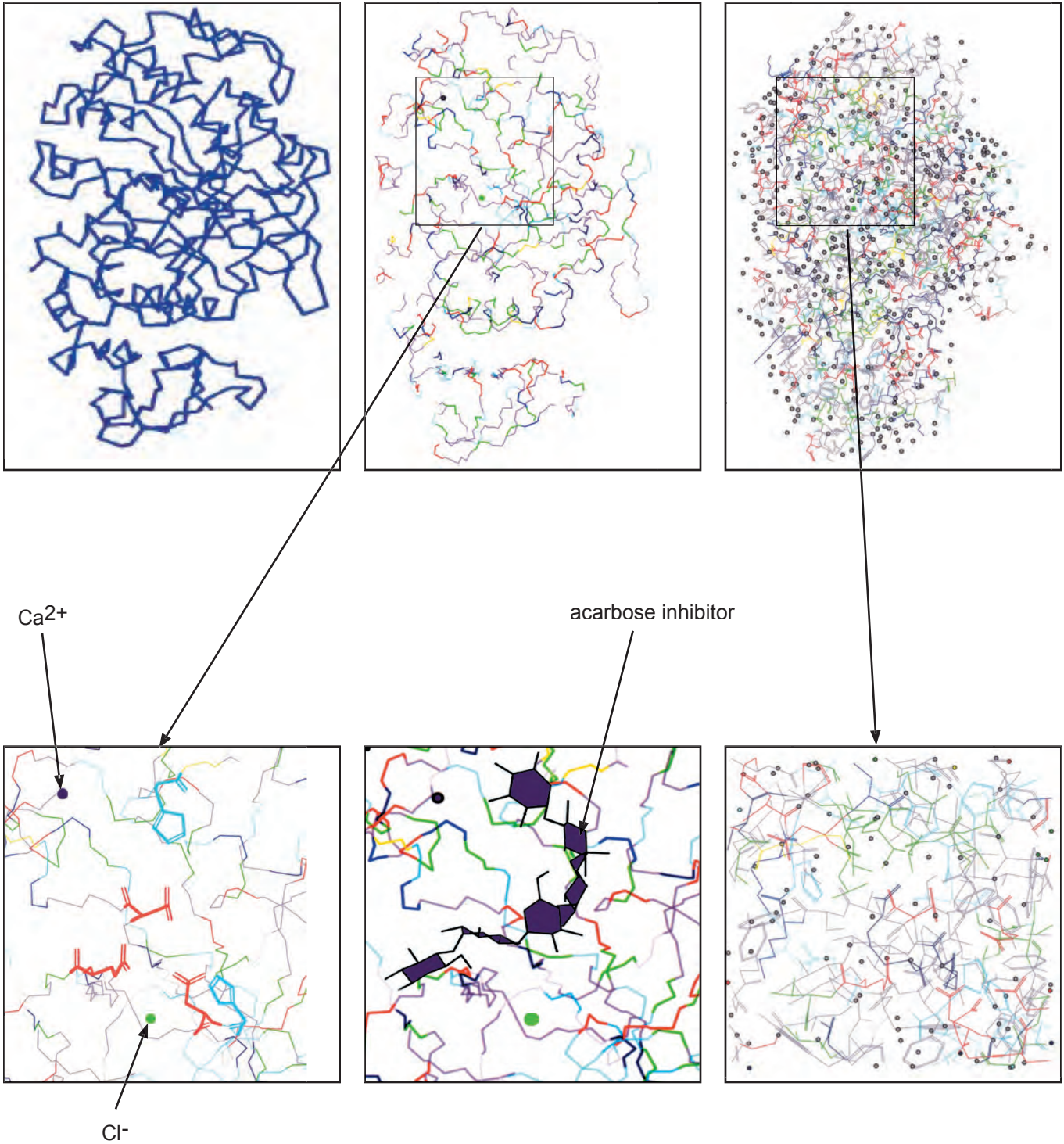
This is a picture of the locality of the chloride ion in human pancreatic alpha amylase.

Why is the chloride ion only singly charged, when we know that the calcium ion is doubly charged?

PROTEINS

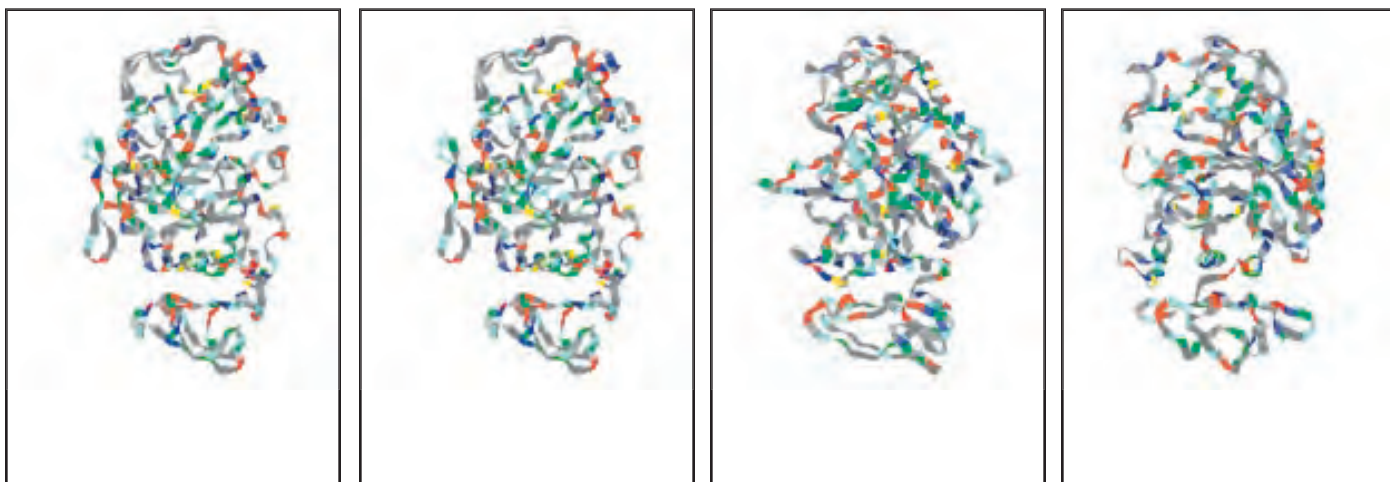
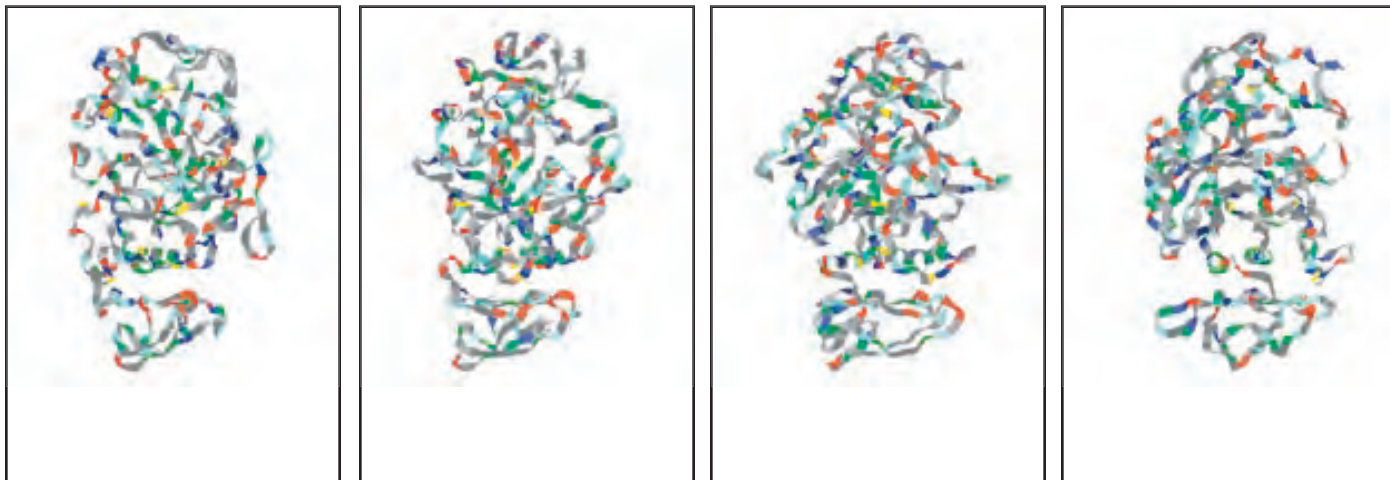
SUBSTRUCTURES IN ANALYSE

These pictures exhibit the location of various substructures in the human pancreatic alpha amylase molecule.



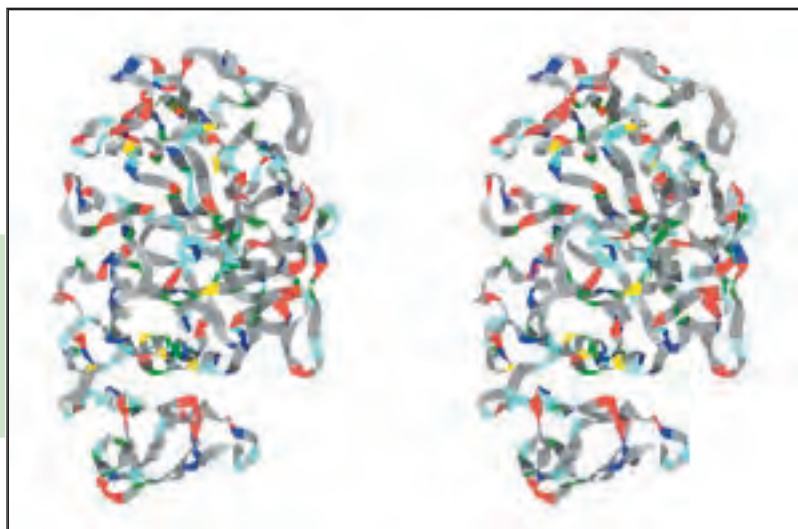
PROTEINS

ROTATING ANALYSE



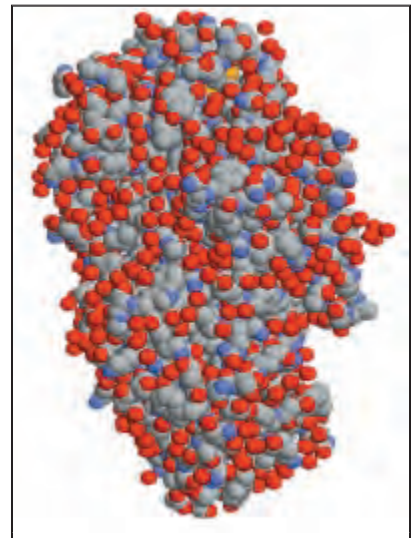
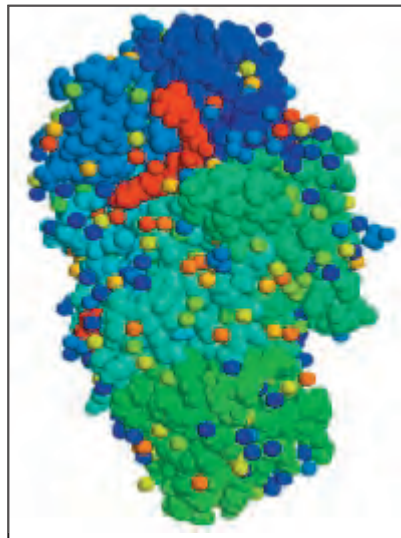
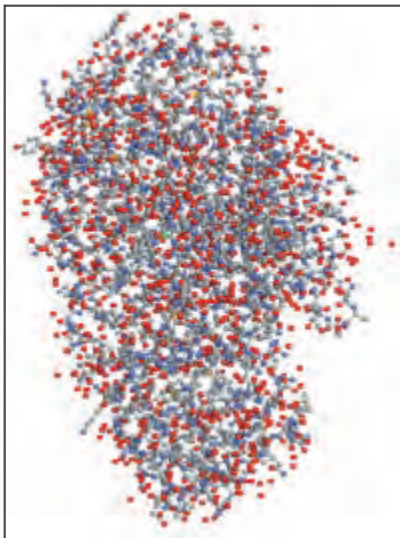
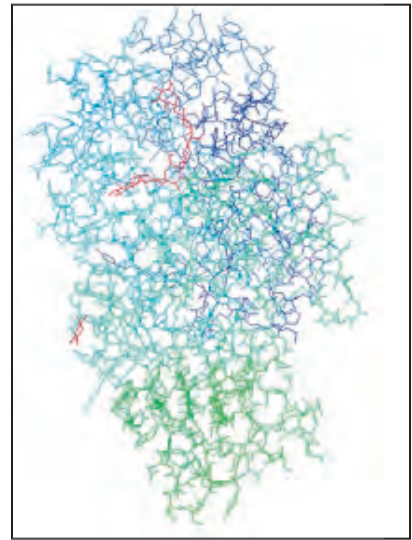
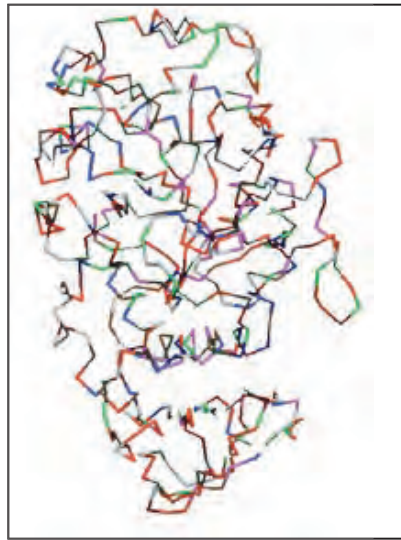
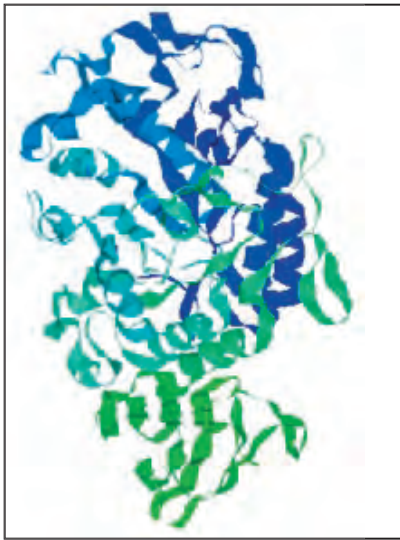
This page shows eight views of the human pancreatic alpha amylase ribbon structure, successively rotated through 45 degrees.

Print out the picture on the right. From a fairly close distance you may be able to superimpose the images by crossing your eyes. Then you will see a 3-D image of the molecule. This is usually easier for older people than for young people.

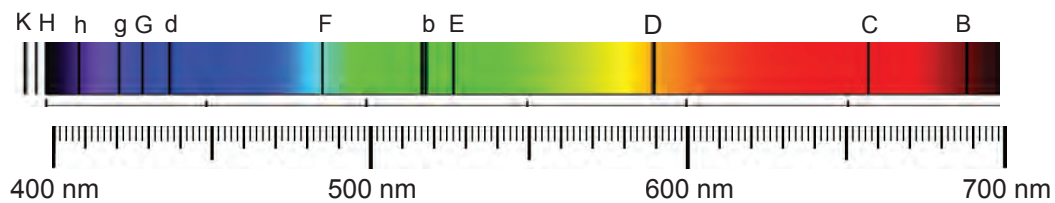


PROTEINS

VIEWS OF ANALYSE



SPECTROSCOPY AND THE STARS



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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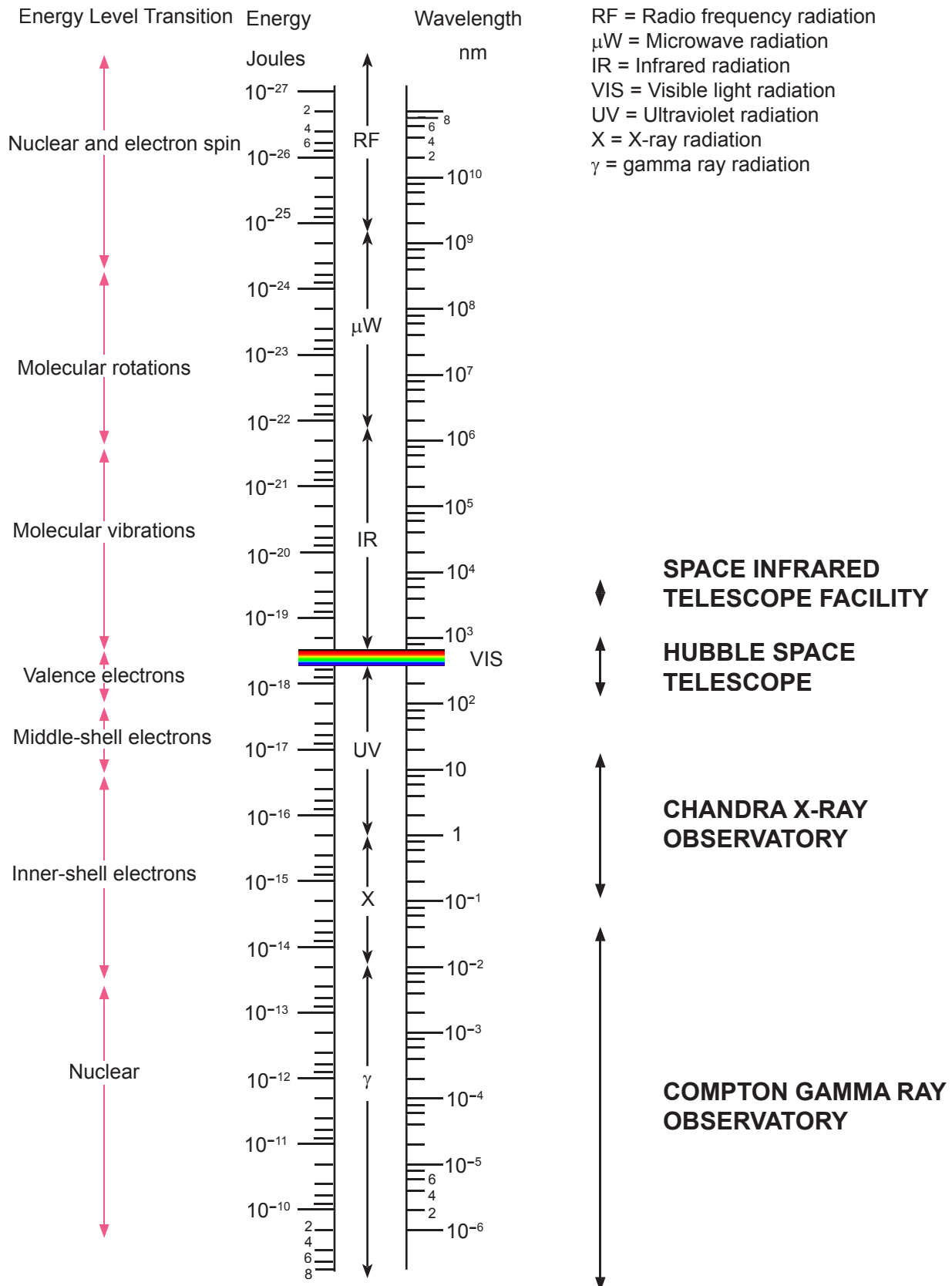
SPECTROSCOPY AND THE STARS

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- 2 Electromagnetic Ruler: The ER Ruler
- 3 The Rydberg Equation
- 4 Absorption Spectrum
- 5 Fraunhofer Lines In The Solar Spectrum
- 6 Dwarf Star Spectra
- 7 Stellar Spectra
- 8 Wien's Displacement Law
- 8 Cosmic Background Radiation
- 9 Doppler Effect
- 10 Spectral Line profiles
- 11 Red Shifts
- 12 Red Shift
- 13 Hertzsprung-Russell Diagram
- 14 Parallax
- 15 Ladder of Distances

SPECTROSCOPY AND THE STARS

ELECTROMAGNETIC RADIATION RULER: THE ER RULER



SPECTROSCOPY AND THE STARS

THE RYDBERG EQUATION

The wavelengths of one electron atomic emission spectra can be calculated from the Rydberg equation:

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where λ = wavelength (in m.) and Z is the atomic number. $Z = 1$ for hydrogen.

R is called the Rydberg constant and

$$R = 1.096776 \times 10^7 \text{ m}^{-1}$$

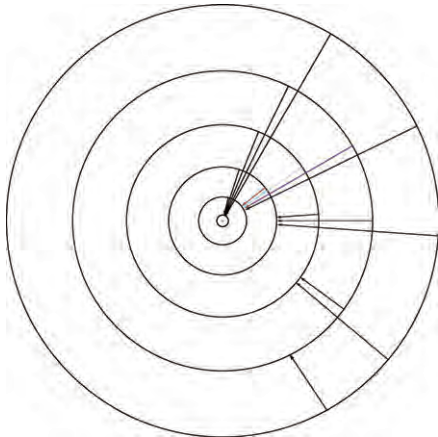
and we also require that $n_2 > n_1$

Why is it Z^2 , instead of, say, Z ?

What if $n_2 < n_1$?

What is wrong with $n_2 = n_1$? Give both a mathematical answer and an energy level answer.

We will calculate the red Balmer line.



For the red Balmer line $n_1 = 2$ and $n_2 = 3$. Note very carefully the difference between the subscripts and the energy level. Also note that n_1 refers to the energy state after emission.

Is $n_1 = 2$ for all the lines in the Balmer series?

For hydrogen, is $n_1 = 2$ for any line not a Balmer line?

For hydrogen, what do we call the lines where $n_1 = 1$?

So for the red Balmer line:

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{2^2} - \frac{1}{3^2} = 0.1389$$

$$\frac{1}{\lambda} = RZ^2 \times 0.1389 = 1.523 \times 10^6 \text{ m}^{-1}$$

$$\lambda = 6.564 \times 10^{-7} \text{ m} = 656.4 \text{ nm}$$

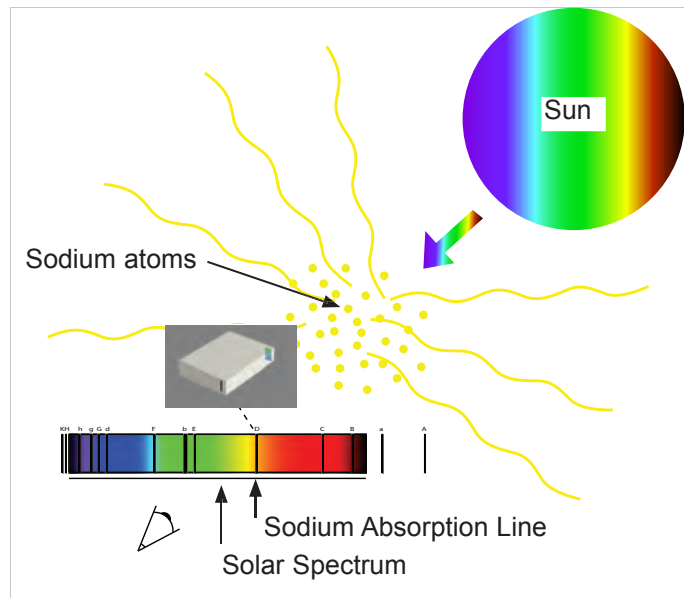
Use the Rydberg equation to find the wavelength of the transition from $n = 4$ to $n = 3$ for singly ionized helium.

In what region of the spectrum is this wavelength?

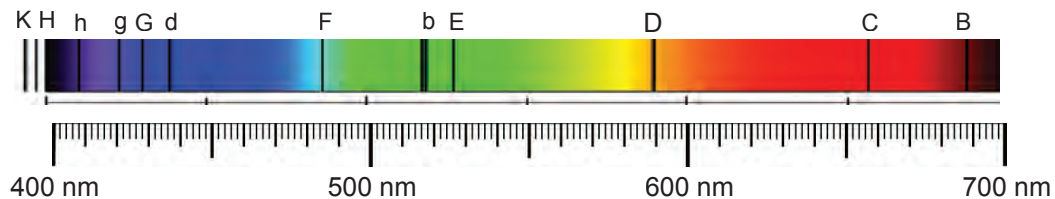
SPECTROSCOPY AND THE STARS

ABSORPTION SPECTRUM

Several factors are required to produce an absorption line. First, there must be a continuous emission background. Then, between the continuous emission and the observer there must be some cooler atoms which absorb and re-emit a particular wavelength of light. Then the absorption line results from the geometry. The cooler atom absorbs light in the line of sight but re-emits it in all directions. Thus most of the light (of that particular wavelength) which would have reached the observer is instead spread out in all directions. The observer sees this as a black line (missing light) against a continuous spectrum. The observer sees this as a black line (missing light) against a continuous spectrum.



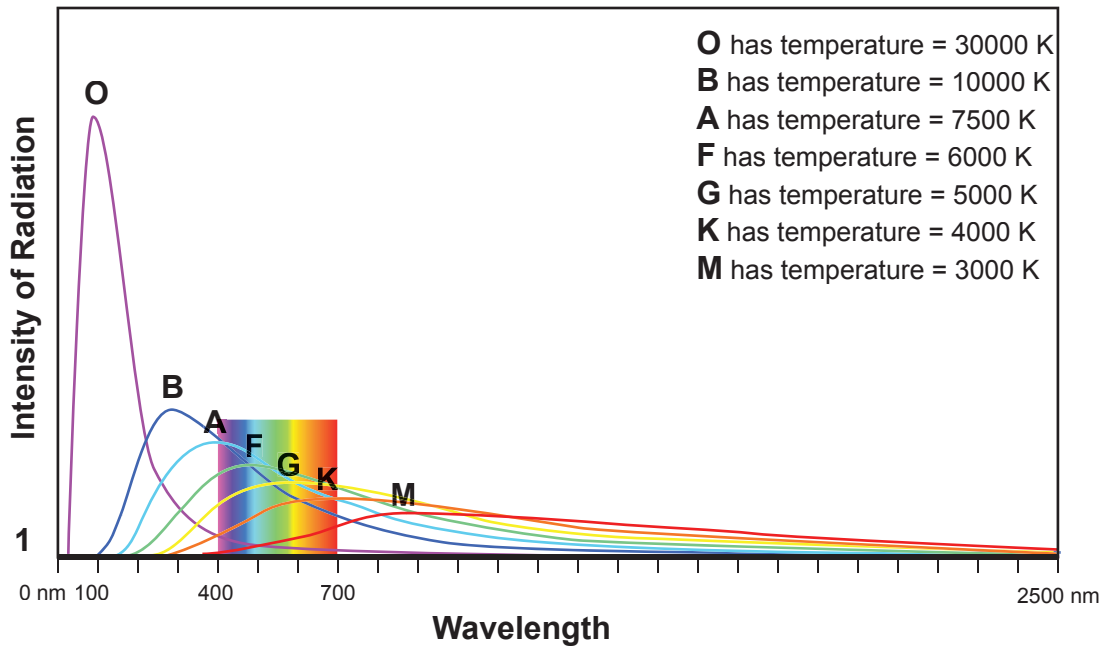
FRAUNHOFER ABSORPTION LINES IN THE SOLAR SPECTRUM



Use the scale to measure and list the wavelength of each of the Fraunhofer absorption lines shown in picture 2. Check to see if any of them are familiar to you from the hydrogen spectrum.

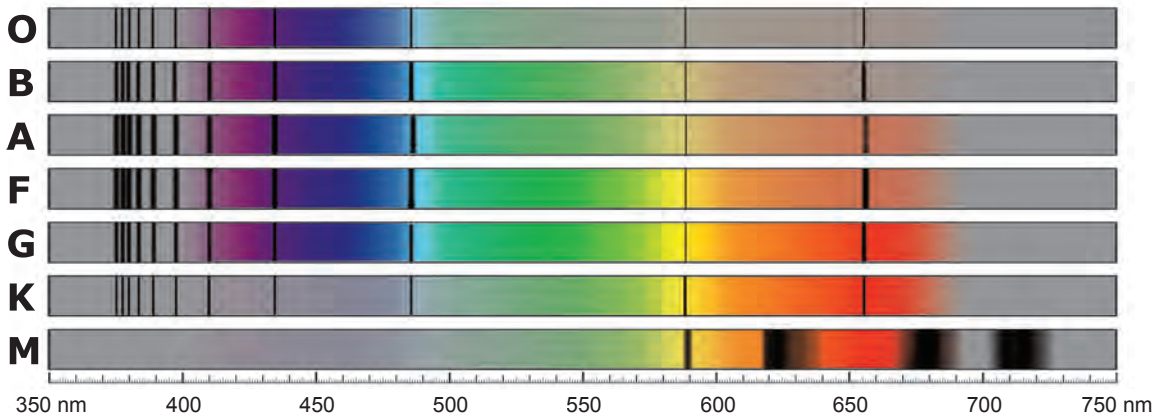
SPECTROSCOPY AND THE STARS

BLACK BODY RADIATION AND STELLAR SPECTRA



In picture 1, find the wavelength at which each spectral class has maximum radiation. Our sun is a G type star. In what color range does our sun radiate most intensely.

Suppose we had evolved in a solar system with an M type 'sun'; predict in what wavelength range we might have evolved vision and give your reasons.



2 Wavelength

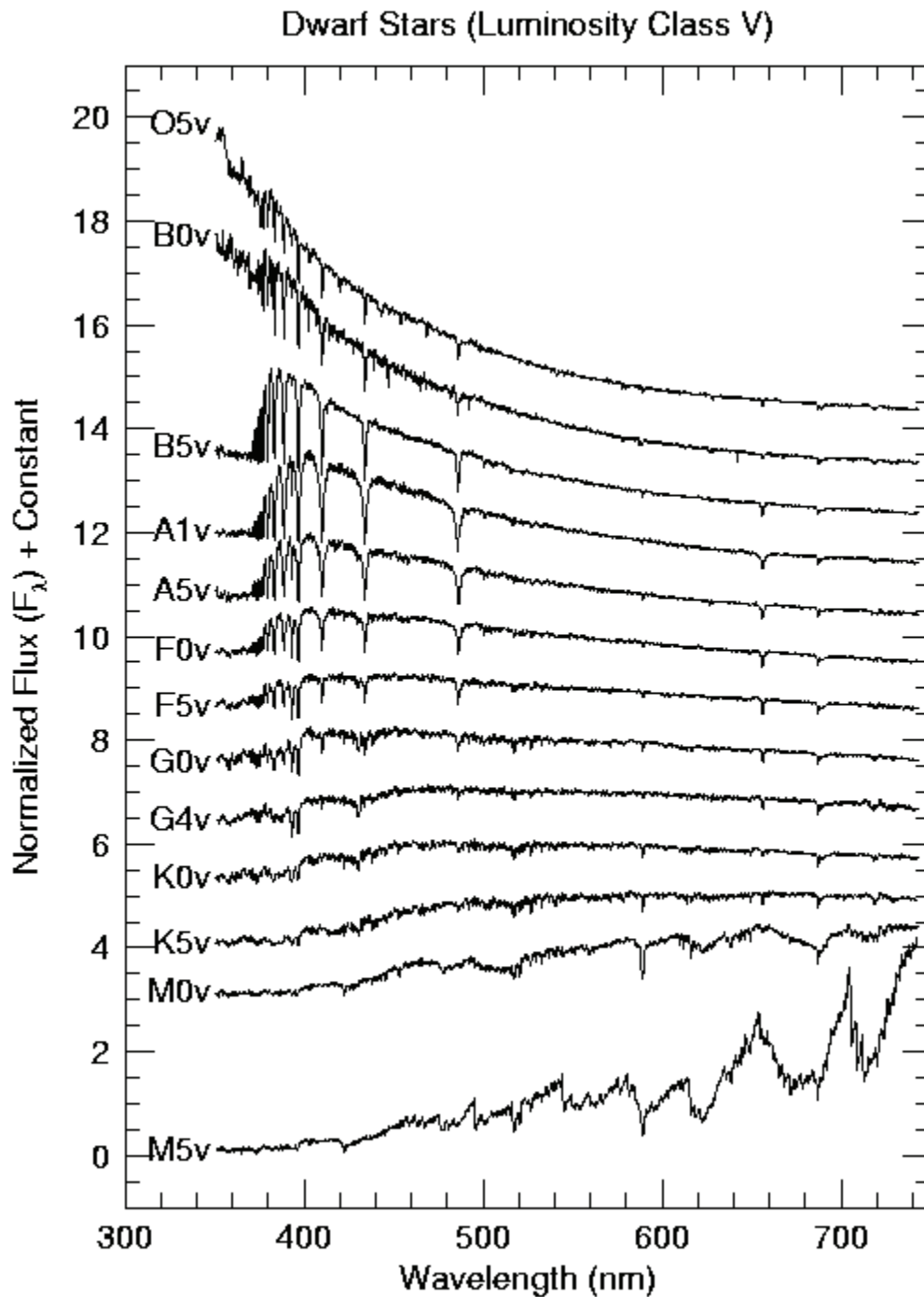
For each spectrum shown in picture 2, find a star on the main sequence of the Hertzsprung-Russell diagram which might have produced that kind of spectrum and mark the star with the spectral class: O, B, A, F, G, K or M.

In picture 2, for the stellar classes OBAFGK, which line is not part of the Balmer series?

SPECTROSCOPY AND THE STARS

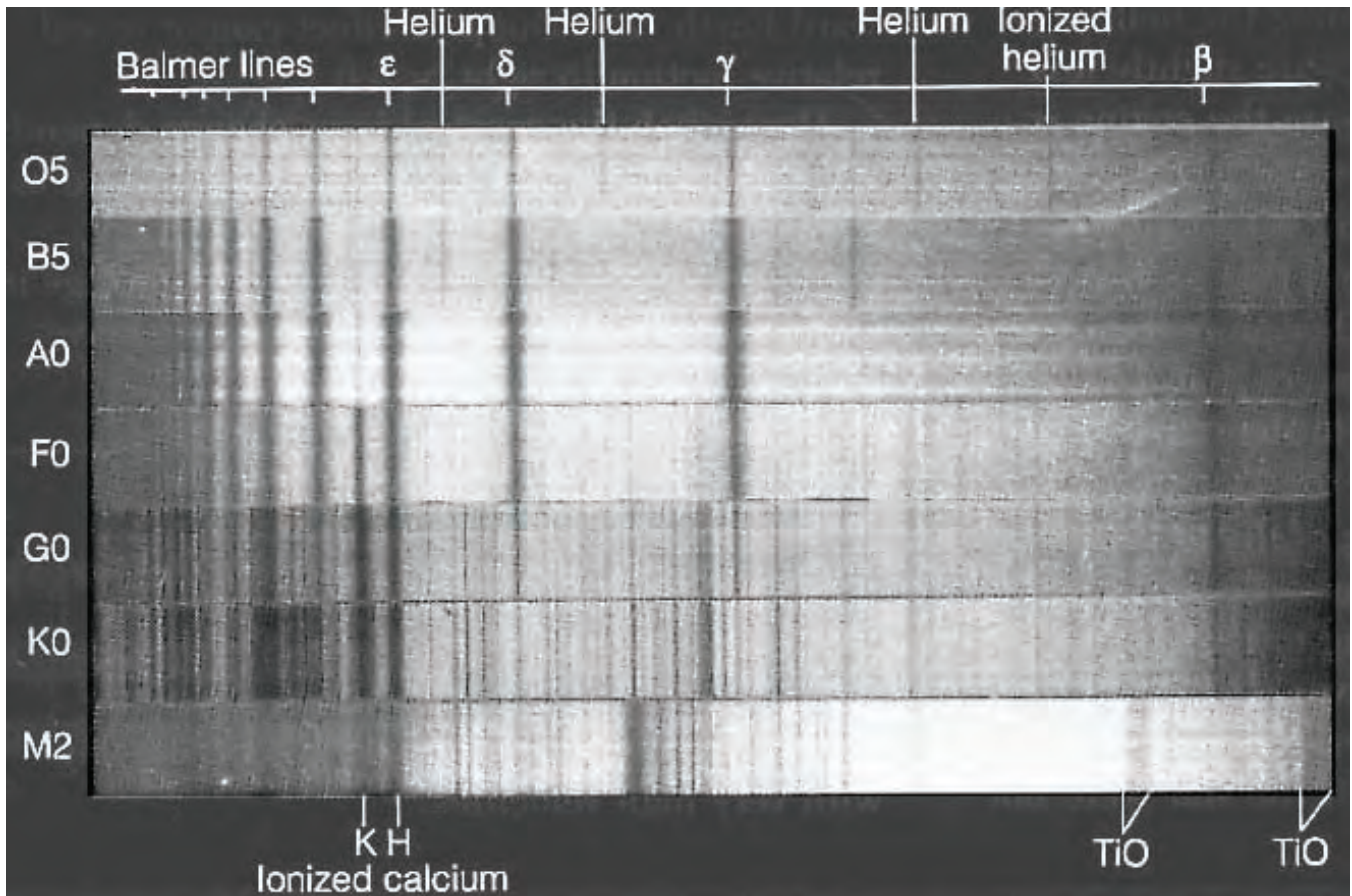
DWARF STAR SPECTRA

Measure the wavelengths of the prominent dips in the fluxes shown on this page and compare them with the spectral lines on the previous page.



SPECTROSCOPY AND THE STARS

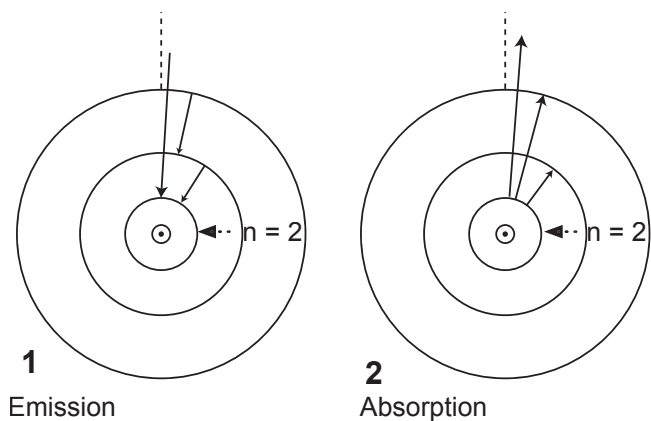
STELLAR SPECTRA



Here is a set of real stellar spectra, from very hot O type stars down to relatively cool M type stars. Many of the stronger lines are labeled. The lines with Greek letters label the Balmer lines of hydrogen.

The Balmer line labeled β is the 486 nm line. What are the wavelengths of the Balmer γ and δ lines? Approximately where is the edge of the visible spectrum; draw a vertical line marking the edge. What kind of electromagnetic radiation is involved in the lines to the left of the visible spectrum? Would the ionized calcium lines be visible? Approximately what color, in an emission spectrum, would the TiO (titanium oxide) bands be?

THE ORIGIN OF BALMER LINES



Picture 1 shows electrons moving into the $n = 2$ orbital of hydrogen, either from higher energy ($n > 2$) orbitals or from the ionized state.

Picture 2 shows electrons being energized out of the $n = 2$ orbital.

SPECTROSCOPY AND THE STARS

WIEN'S DISPLACEMENT LAW

Wien's Displacement Law

$$\lambda_{\max} = \frac{2.898 \times 10^{-3} \text{ mK}}{T}$$

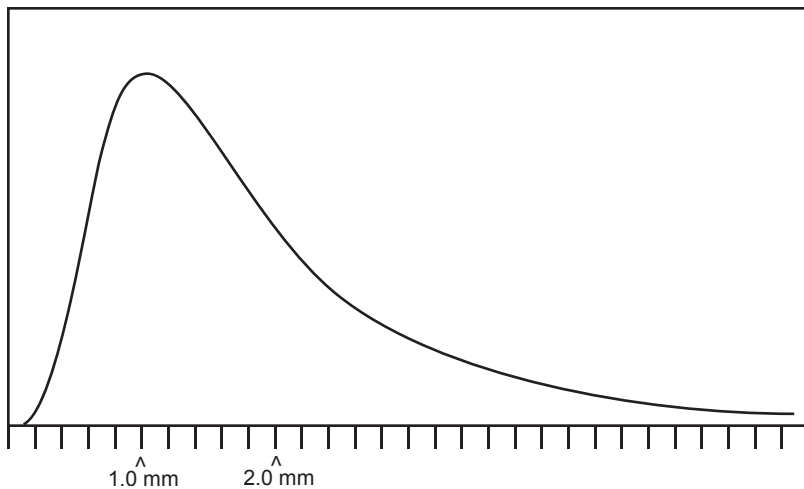
Suppose $T = 5000 \text{ K}$. Then we can substitute that value into Wien's Displacement Law:

$$\lambda_{\max} = \frac{2.898 \times 10^{-3} \text{ mK}}{5 \times 10^3 \text{ K}}$$

$$\lambda_{\max} = 5.796 \times 10^{-7} \text{ m} = 579.6 \text{ nm}$$

Is λ_{\max} in the visible wavelength region and, if so, what color is it?

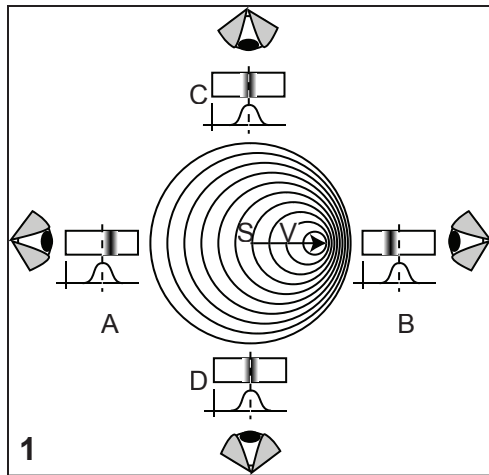
THE COSMIC BACKGROUND RADIATION



Find λ_{\max} for the Planck curve above (by measurement) and use the result in Wien's Displacement Law to calculate the temperature of the universe.

SPECTROSCOPY AND THE STARS

DOPPLER EFFECT



In picture 1 a light emitting source S is moving to the right at velocity V. The same spectral line is observed at the four positions A, B, C, and D. Use the picture to tell whether the line is red shifted or blue shifted or unchanged at each of the four observing positions.

Using the Doppler equation:

$$\frac{\lambda_{\text{obs}} - \lambda_{\text{lab}}}{\lambda_{\text{lab}}} = \frac{V}{c}$$

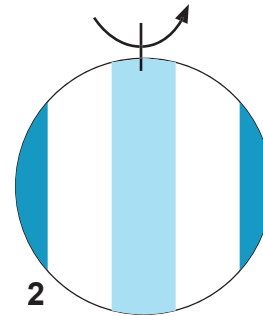
we can find the velocity V of the source of electromagnetic radiation by measuring a spectral line λ_{obs} coming from the moving source and comparing it to the same spectral line λ_{lab} from a non moving source. (c is the speed of light.)

Suppose we measure the light blue Balmer line from an astronomical spectrum at $\lambda_{\text{obs}} = 500 \text{ nm}$. We know that for this line $\lambda_{\text{lab}} = 486.4 \text{ nm}$. Then:

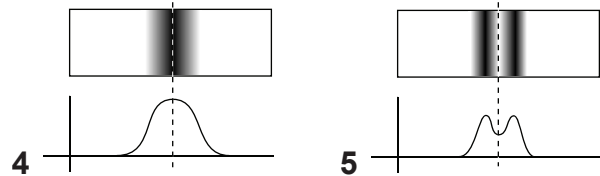
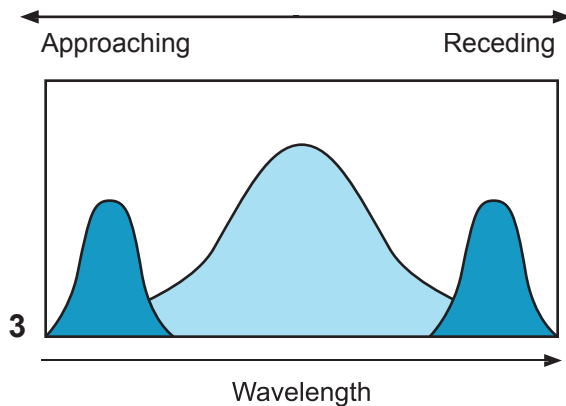
$$\frac{\lambda_{\text{obs}} - \lambda_{\text{lab}}}{\lambda_{\text{lab}}} = \frac{500 \text{ nm} - 486.4 \text{ nm}}{486.4 \text{ nm}} = 2.79 \times 10^{-2}$$

$$V = c \times 2.79 \times 10^{-2} = 8,388 \text{ kms}^{-1}$$

In the example above, is the source moving toward us or away from us? How do we know?



Suppose picture 2 shows a rotating star (like our sun). The left edge of the star is rotating toward us, while the right edge is moving away. Therefore the light from the left edge will be bluer than the light from the center and the light from the right edge will be redder than the light from the center.

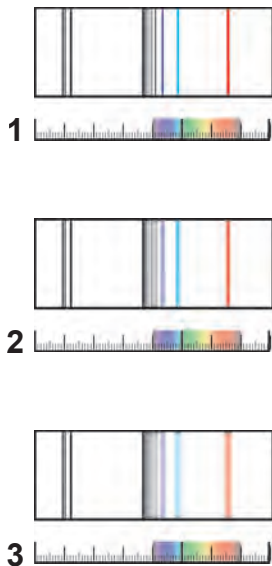


If the spectral line shown in picture 4 is broadened due to the Doppler effect, what do you suppose might cause a spectral line to be split like the one in picture 5?

SPECTROSCOPY AND THE STARS

SPECTRAL LINE PROFILES

Actual spectra are rarely the simple set of lines you can see in a discharge tube spectrum. There are processes which split lines and processes which broaden lines. These processes result in complex spectra and, in the case of molecules, in band spectra. Studying spectra give most of our information about these processes and often led to their discovery.



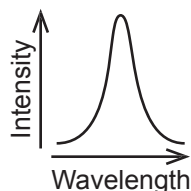
Describe the difference in appearance of the visible Balmer lines in spectra 1, 2, and 3.

Natural Line Broadening

Even though we often consider atoms and molecules to have exact energy states, all of these states actually have an energy spread due to Heisenberg uncertainty principle.

This is generally introduced via $\Delta t \Delta E \geq h/2\pi$

However, it does not seem to be clearly pointed out that slower (vibrational, rotational, forbidden or metastable) reactions having a larger Δt would have a correspondingly smaller ΔE .

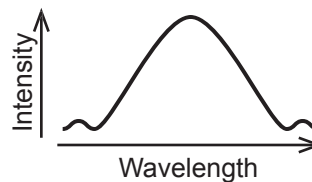


Thermal or Doppler Broadening

Atoms and molecules are in motion. The component of this motion toward or away from the observer changes the wavelength of the emitted or absorbed radiation due to the Doppler effect.

Pressure Broadening

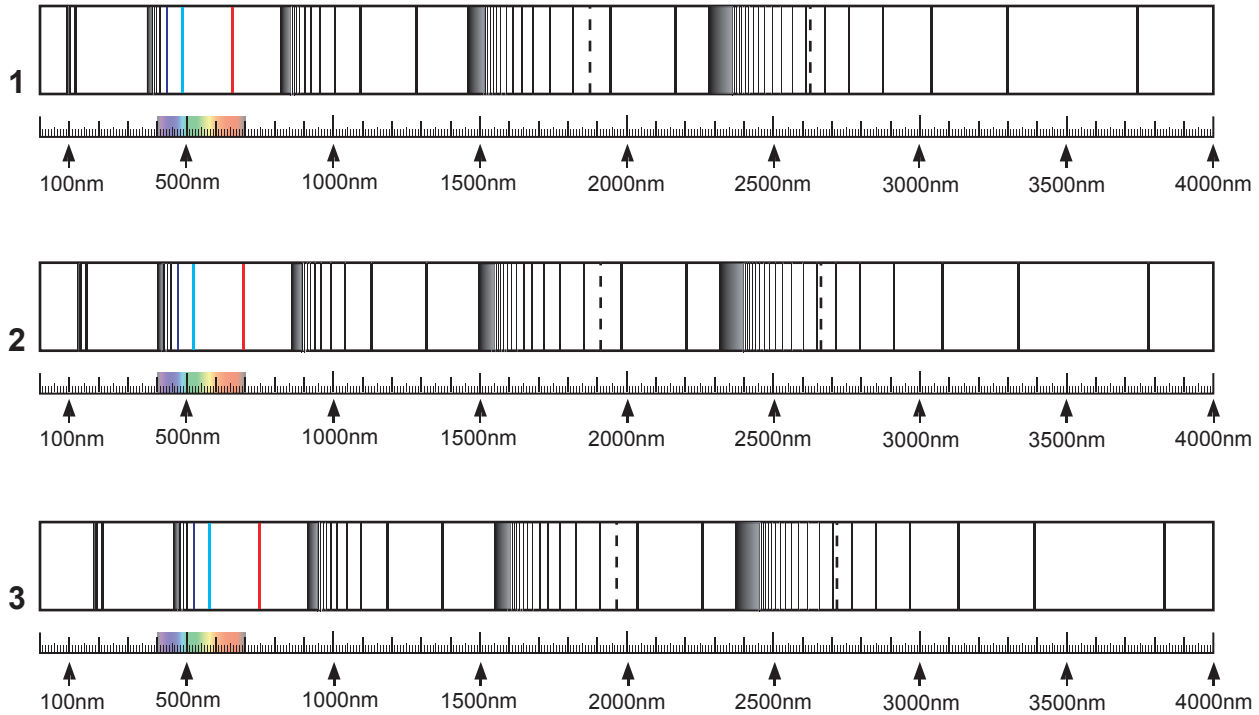
In the atmosphere of a high pressure star the atoms and molecules (in a cool star) collide frequently. This means they have only a short time to emit or absorb radiation before collisions change their energy state. Thus the energy states are effectively spread out by the collisional energy and the spectral line is broadened. In a high pressure stellar atmosphere this effect will be more important than the natural line width or Doppler broadening.



SPECTROSCOPY AND THE STARS

RED SHIFTS

The Hydrogen Spectrum

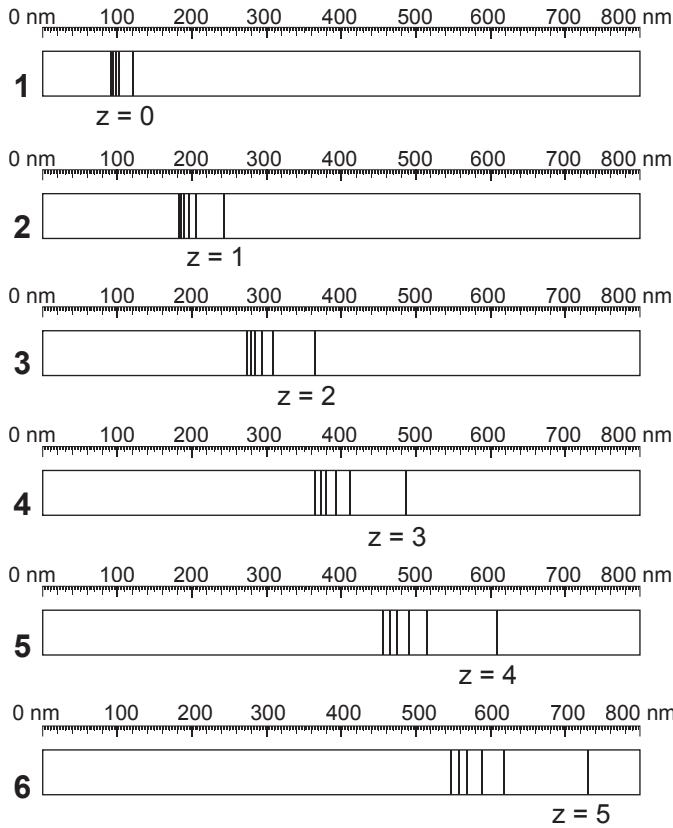


Measure the position of the red Balmer line in the three spectra above. Do the same for the blue and purple lines and make a table of your results.

Use the Doppler equation and the known fact that for the red Balmer line $\lambda_{\text{lab}} = 656.6 \text{ nm}$ to find the velocity of the source in pictures 1, 2, and 3. Determine whether the source is approaching or receding from the lab.

SPECTROSCOPY AND THE STARS

RED SHIFT



Pictures 1 through 6 show the Lyman series of hydrogen spectral lines with no redshift (picture 1) and at redshifts up through five. In each picture the line on the right is called the Lyman alpha line and is very important for determining redshifts. The line on the left is the Lyman ionization limit. Measure the Lyman alpha line for each z and make a chart of the results. Determine whether the Lyman alpha line is in the infrared, visible or ultraviolet for each z and, if it is in the visible, estimate its color. Include this information on your chart also.

If λ' is the observed wavelength and λ is the emitted wavelength, we have the two relations

$$z = \frac{\lambda' - \lambda}{\lambda}$$

which is the definition of z , and

$$\frac{c}{\lambda'} = \left[\frac{1 - \frac{v}{c}}{1 + \frac{v}{c}} \right]^{1/2} \times \frac{c}{\lambda}$$

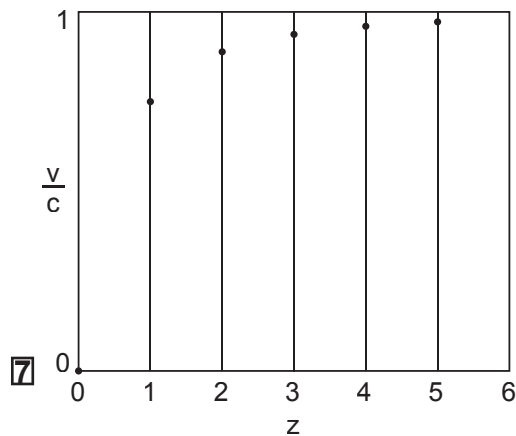
which is the Doppler equation, where c is the speed of light and v is the velocity at which the source of the radiation is moving away from the observer.

We can solve for v/c , which is the fraction of the speed of light the source is moving.

$$\frac{v}{c} = \frac{2z + z^2}{(1 + z)^2}$$

from which we can make the table

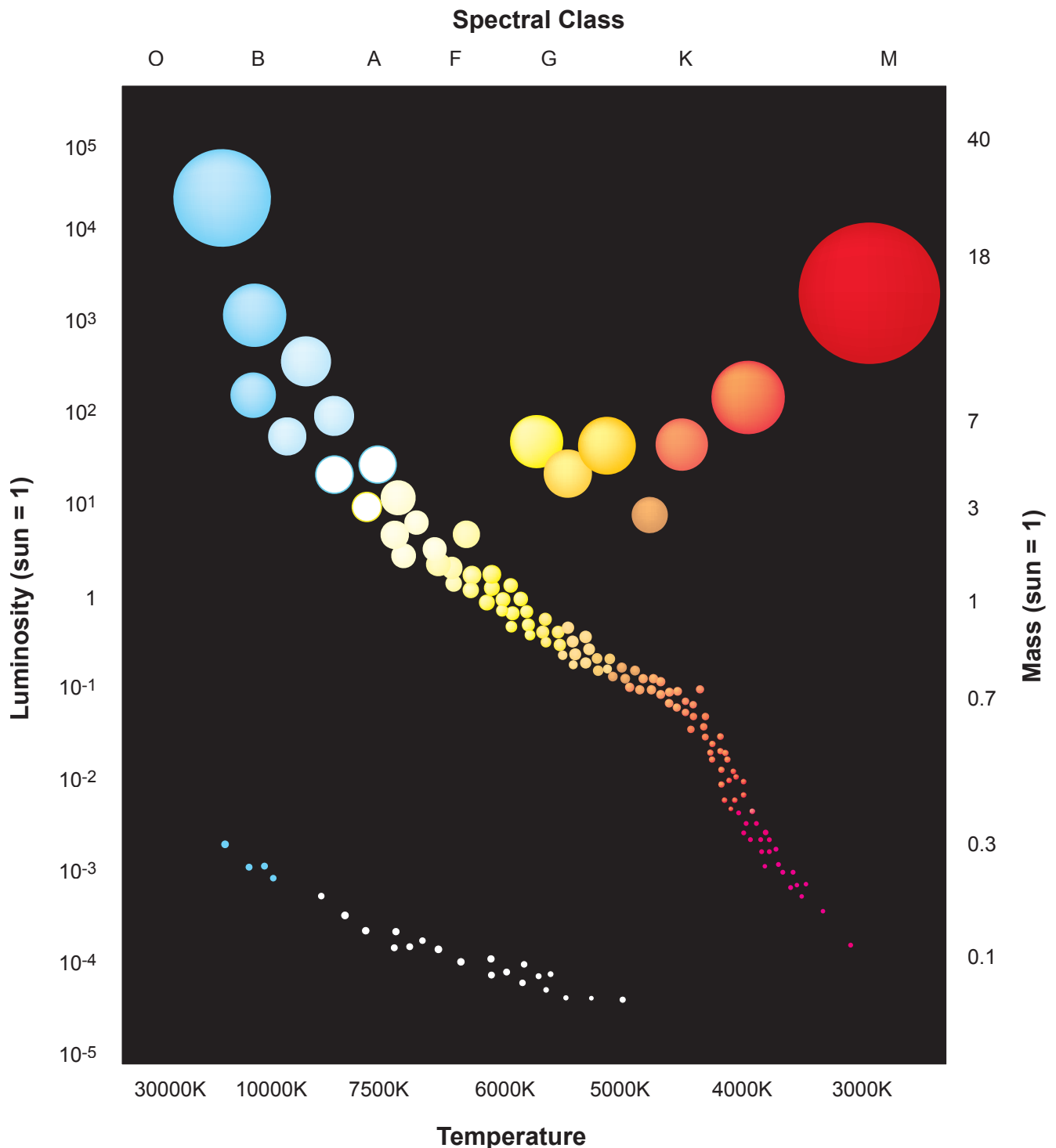
z	$\frac{v}{c}$
0	0
1	3/4
2	8/9
3	15/16
4	24/25
5	35/36



Draw the curve connecting the data points in picture 7 and extend the curve to $z = 6$.

SPECTROSCOPY AND THE STARS

THE HERTZSPRUNG-RUSSELL DIGRAM



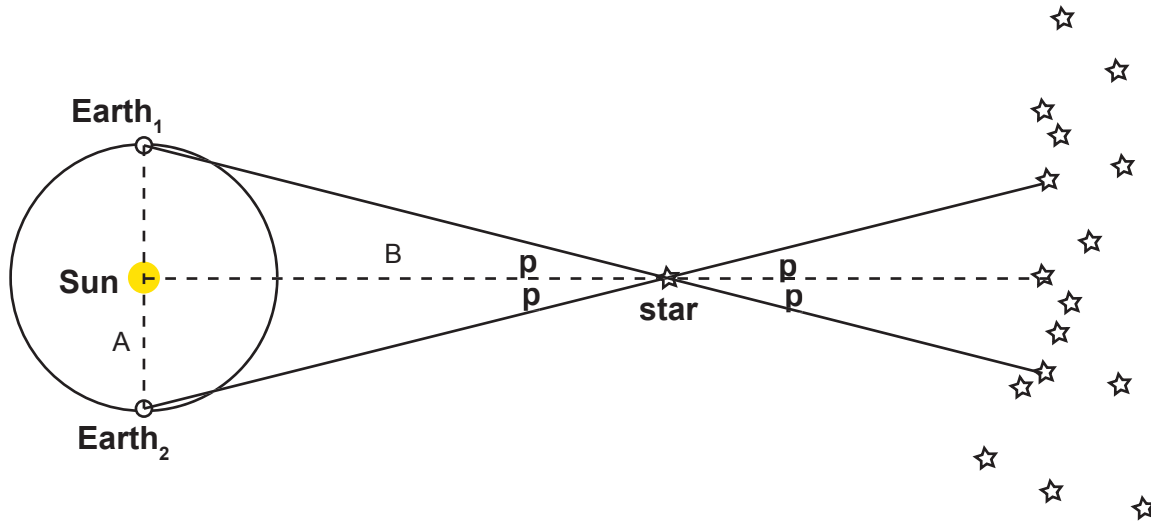
The band of stars running from the upper left to the lower right of the Hertzsprung-Russell diagram is called the main sequence. Find the stars on the main sequence which have similar properties to the sun.

Each spectral class is also divided into ten subclasses, such as O0, O1, ..., O9, B0, ... Knowing that the sun is a G2 star, find and mark the star on the Hertzsprung-Russell diagram which is most like the sun.

SPECTROSCOPY AND THE STARS

PARALLAX

Trigonometric Parallax



1

Measure angle p in picture 1. In astronomy, this is called the trigonometric parallax angle.

In actual practice, the angles p are much smaller than the example shown here, but the same method applies. A is the distance from the Earth to the Sun, B is the distance from the Sun to the star - which, for a real star is essentially the same as the distance from the Earth to the star. From trigonometry we have:

$$\tan(p) = \frac{A}{B}$$

This is the definition of the tangent function. To calculate the value, you punch in the number for p on your calculator and then press the **tan** button.

Since we are trying to find B , we rearrange the equation:

$$B = \frac{A}{\tan(p)}$$

Now measure A in picture 1 and calculate B . Then measure B to check your answer.

The actual distance from the Earth to the Sun is 1.50×10^{11} m. Suppose the trigonometric parallax angle to a nearby star is 1.00 arcsecond. Find the distance of the star in meters. (The astronomical name for this distance is 'parsec'.)

Circle = 360° (360 degrees)
 $1^\circ = 60'$ (60 arc minutes)
 $1' = 60''$ (60 arc seconds)

Assuming that the stars on the right of picture 1 are so far away that their appearance does not change due to the motion of the Earth in its orbit, describe how the position of the nearby star will appear to change as the Earth moves from one side of its orbit to the other side (six months later).

Explain how we might use that change of appearance to find the distance from the Earth of the nearby star.

Spectroscopic Parallax

Refer back to the Hertzsprung-Russell diagram on page 12. Notice that near the center of the main sequence the spread of intrinsic luminosities is rather small. If we can spectroscopically locate a star on that part of the main sequence, then we know how bright it really is. By comparing that intrinsic luminosity with the star's apparent brightness on Earth, we can estimate the distance to the star. This is called the star's spectroscopic parallax.

SPECTROSCOPY AND THE STARS

THE LADDER OF DISTANCES

Parallax measurements

Parallax measurements can directly determine distances of stars up to a few hundred parsecs. Beyond that, their motions are too small to be accurately observed. We need other methods to determine distances.

Method of Similar Objects

The basic idea behind the method of similar objects is that if we know the true, or intrinsic, brightness of a star or other celestial object, we can compare that with its apparent brightness (how bright it looks to us) and calculate the distance. We have various methods of estimating intrinsic brightness.

Herzsprung-Russell Diagram

The Herzsprung-Russell diagram, shown on the next page, has been a primary tool for organizing stellar properties.

The Herzsprung-Russell diagram plots the intrinsic brightness, or luminosity, of a star on the vertical axis versus its color, or spectral type, on the horizontal axis. You can see that most stars lie on a fairly narrow band called the main sequence. So if we observe the spectral type of a star we can make a good estimate of its intrinsic luminosity and by comparing this with its apparent brightness, we can find its distance. In this manner we can find the distances to many stars much farther away than by trigonometric parallax.

Star Clusters

You can see that there is a fair amount of guesswork involved in using the Herzsprung-Russell diagram to determine distances (e.g., does a star really lie on the main sequence or not?). Fortunately many stars occur in groups or clusters; these may range from a few dozen up to a million stars or more. So by examining many of the stars in the cluster, we can determine their average distance with much more confidence.

Cepheid Variables

There are a great many types of stars and some types have very special properties. There are stars which vary in intrinsic luminosity and some of these do so in a regular pattern. A useful type are the Cepheid variables which have brightness up to 10,000 times the sun and vary more slowly the brighter they are. These stars can be observed in other galaxies and used to find the distances to some of the galaxies.

Galactic Brightness

The Cepheid variables got us to other galaxies, but to only some of the closer ones. But we have been able to observe that some of the types of galaxies have a maximum brightness. Galaxies often come in large groups and by observing the brightest galaxies in the groups we can estimate the distance to the group.

Quasars

Quasars are immensely bright objects, generally believed to be giant black holes ripping apart all of the matter in their vicinity. They are so bright that they can be observed at vast distances and we can measure their (approximate) distance by the Hubble Law

The Hubble Law

The Hubble law comes from the discovery that distant objects in the universe are moving apart, because space time itself is expanding. There is a direct connection between the distance between two objects and the speed with which they are moving apart. Since we can observe that speed through the red shift of spectra created by the Doppler effect, we can use the spectrum to determine the distance.

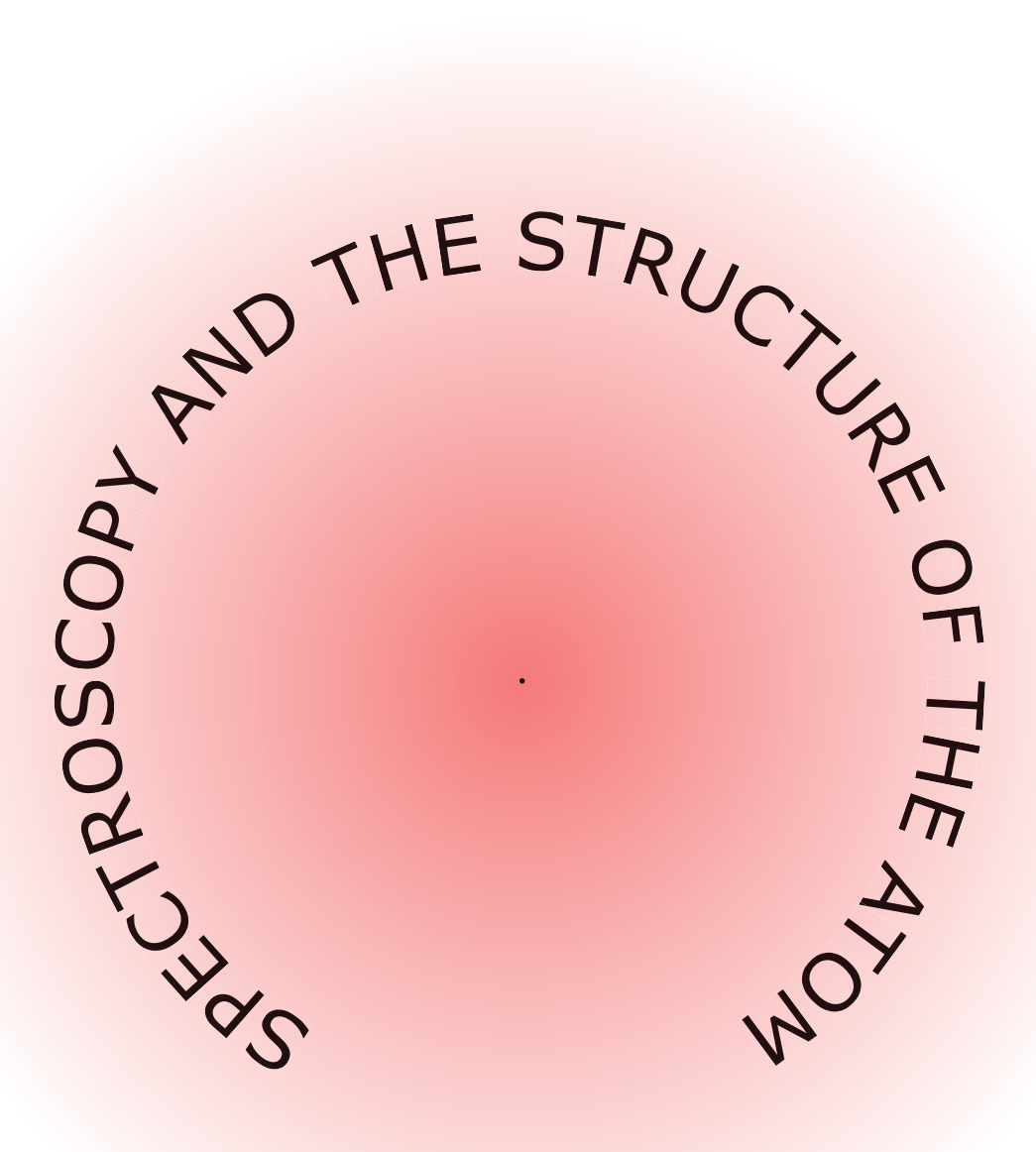
Using the velocities of recession calculated for $z = 0, 1, 2, 3, 4, 5$ and a Hubble constant of 75 (km/s)/Mpc (where Mpc means megaparsec) we get the following table of distances

z	Distance
0	0 Mpc
1	3.00×10^3 Mpc
2	3.56×10^3 Mpc
3	3.75×10^3 Mpc
4	3.84×10^3 Mpc
5	3.89×10^3 Mpc

For reference, 3.0×10^3 Mpc is about ten billion light years.

Cosmic Background Radiation

Current studies of the microwave radiation left over from the birth of the universe seem to indicate that it is about 156 billion light years in diameter.



SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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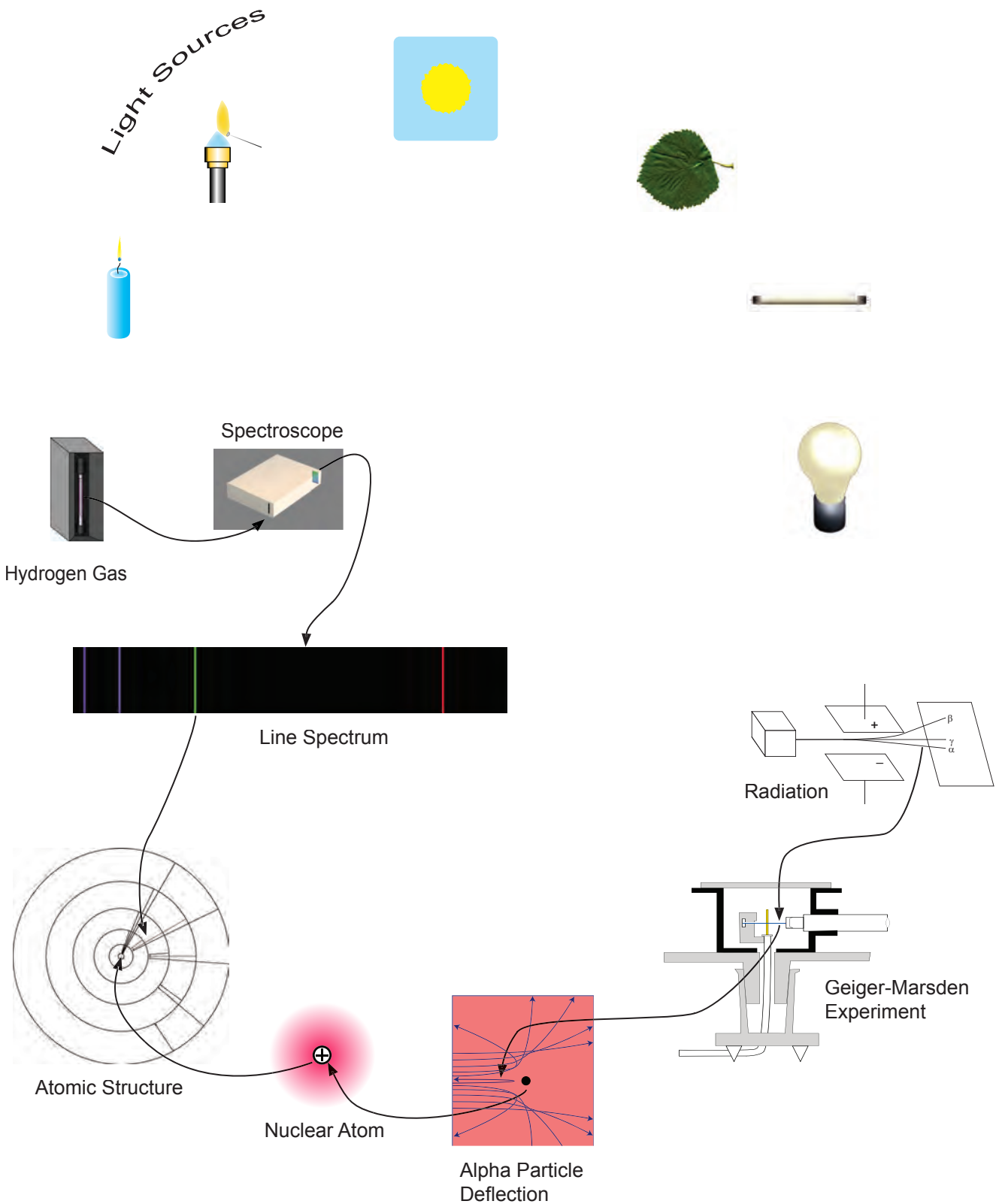
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

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SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ROAD MAP



SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

THE DISCOVERY OF ATOMIC STRUCTURE

A simple example of the energy changes involved in particular transitions and the resulting spectrum is the hydrogen emission spectrum. This spectrum is especially interesting for historical, theoretical and practical reasons. Over a period of 40 years, from 1885 to 1925, all of the lines in the emission spectrum in the ultraviolet, visible and infrared regions were found experimentally and were identified with various electron transitions. Spectroscopic experiments like the above gave the major experimental evidence for the Bohr theory of the atom and eventually for the modern quantum theory.

By 1885 the concept of the atom was generally accepted by chemists although not by all physicists. However, little was known about the structure of the atom. What was known was a reasonably good idea of the size and mass of atoms and the belief that electric charge was somehow involved.

Around 1897 two major advances occurred. One was the discovery of radioactivity by H. Becquerel through the accidental exposure of a photographic plate left in a closed drawer with a piece of uranium. The other discovery was no accident at all, but was the discovery that negative electric charge was carried by a discrete particle, which came to be called the electron, by J. J. Thomson in his laboratory in Cambridge, England.

Ernest Rutherford, a New Zealand scientist working in Thomson's laboratory, discovered one type of radiation called alpha particles and studied their properties, such as their scattering by various substances. In 1909 he asked two of his younger colleagues, Hans Geiger and Ernest Marsden, to experiment with scattering alpha particle by a thin gold foil. They discovered, to their surprise, that a very few of the alpha particles were scattered almost straight back. Rutherford drew the conclusion that the atom must consist of a very small, hard and heavy positively charged center and a larger and looser negatively charged part, and thus was born the idea of the nuclear atom.

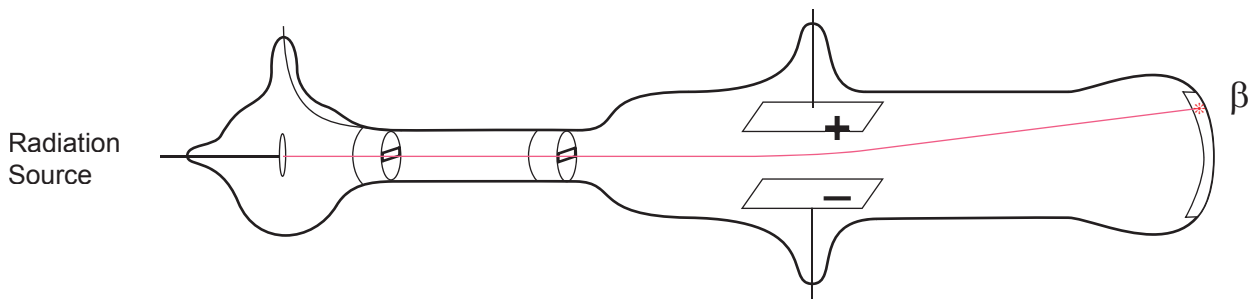
To return to spectroscopy. Now that the general structure of an atom was known, the questions of how hydrogen atoms, which were known to have a positive nucleus and only one electron, could emit several series of discrete spectra, needed answering. In 1913 the Danish scientist, Niels Bohr, published a new idea that the electron could only 'orbit' the nucleus in a finite number of energy states and never in between. He was able to mathematically calculate the spectral series so his idea was taken seriously and eventually became one of the fundamental steps towards modern quantum mechanics.

Imagine yourself in the situation of H. Becquerel. While pursuing entirely different lines of research you noticed that a photographic plate which was protected from the light and should have shown no image when it was (presumably accidentally) developed, did show a vague image. One thing you notice was that the plate had been kept in a drawer with a piece of uranium ore. Where do you go from there? What do you do?

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

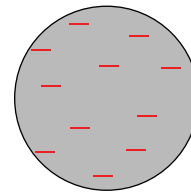
DISCOVERY OF THE ELECTRON

The discovery of the electron by J. J. Thomson (1897) and the research on radioactivity by H. Becquerel and M. Curie showed that the atom contained negative and positive particles. But where were they? Thomson suggested a 'raisin toast' model in which negative electrons were spread through a positive cloud. E. Rutherford and his co-workers in a brilliant sequence of experiments in which α -particles were used as atomic probes developed the NUCLEAR ATOM.

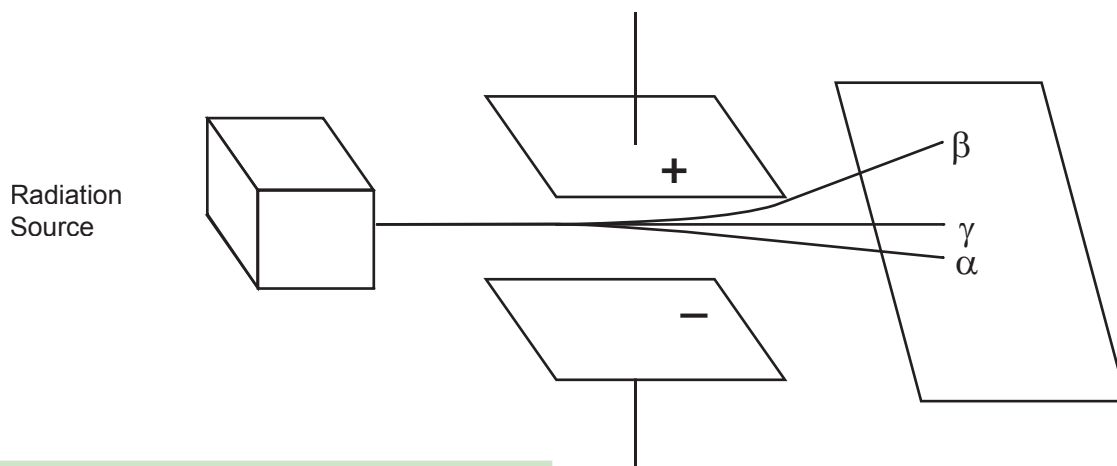


This is a picture of a Crooke's tube, the apparatus with which J. J. Thomson discovered the electron.

Other scientists attempted this experiment before Thomson but the beam did not deflect. Thomson got the beam to deflect by making sure that the tube contained a high vacuum. Can you explain why this made a difference?



Thomson model of the atom.

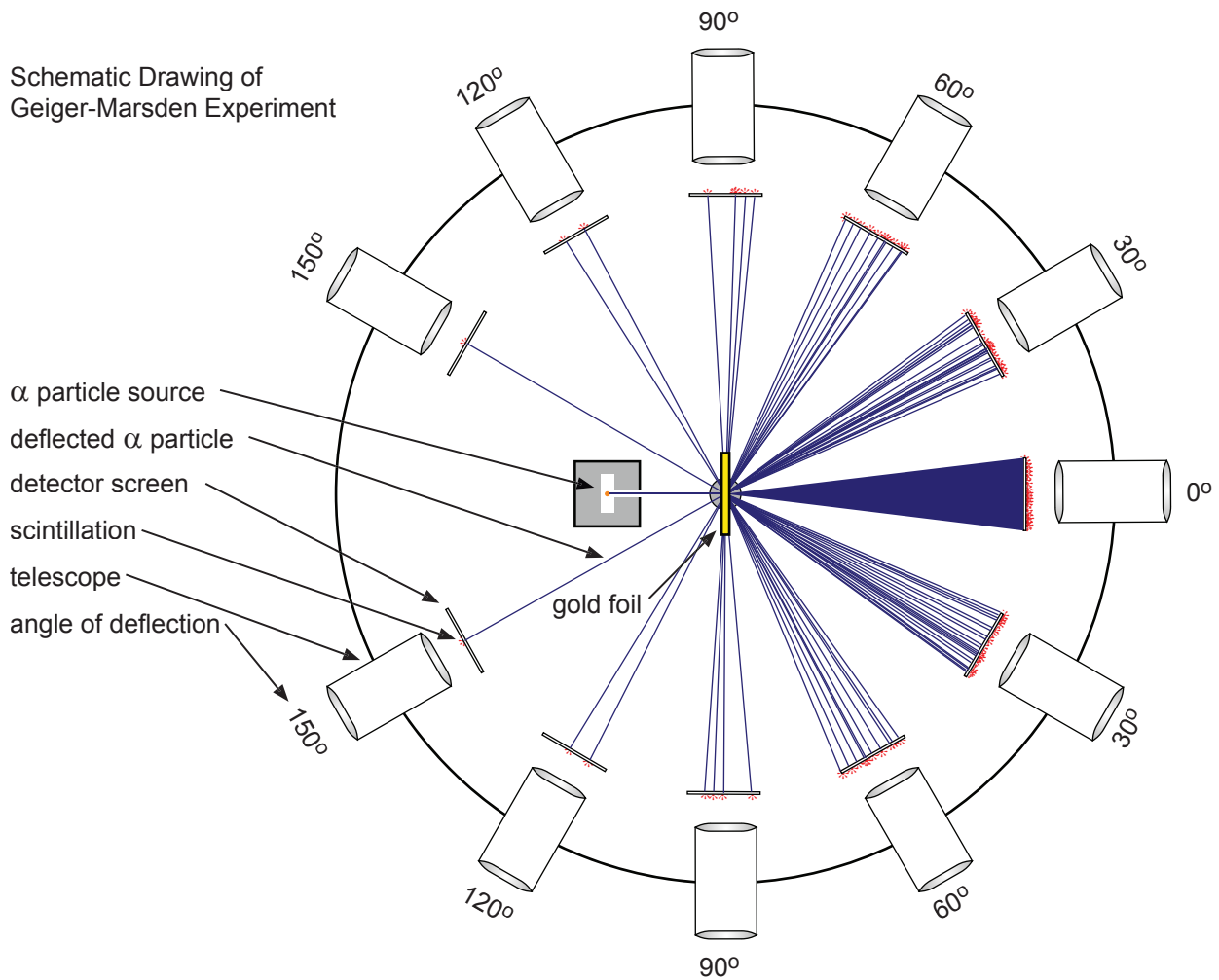


This is a picture of an experiment separating α , β , and γ radiation. Explain how you can determine the sign of the charges on the different forms of radiation.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

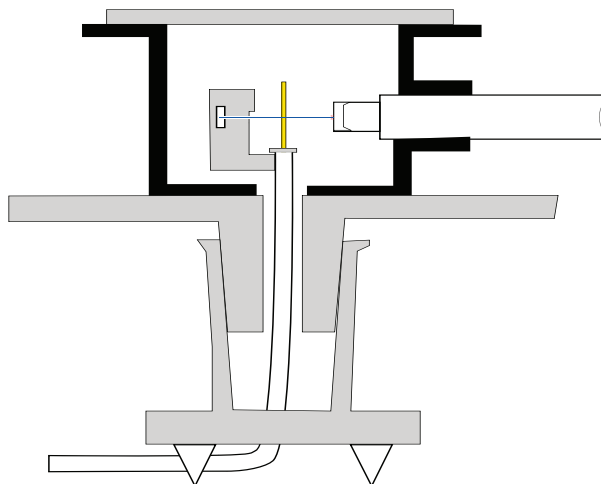
GEIGER-MARSDEN EXPERIMENT

Schematic Drawing of Geiger-Marsden Experiment

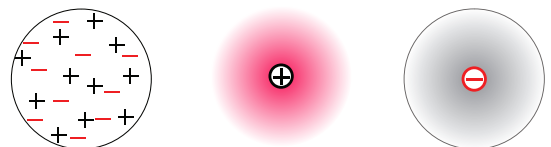


Side View of Geiger-Marsden Experiment

This is the experimental arrangement by which Geiger and Marsden produced the data from which Rutherford developed the idea of the nuclear atom. The next page will show the essential chemistry of the experiment and then we show a picture of an atom where the nucleus is drawn to correct scale relative to the electron cloud.

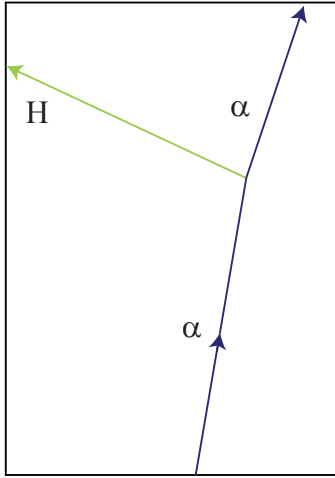


Using the fact that the alpha particle is positive and the experimental results on the next page, decide which of the three atomic models shown on the right is correct.

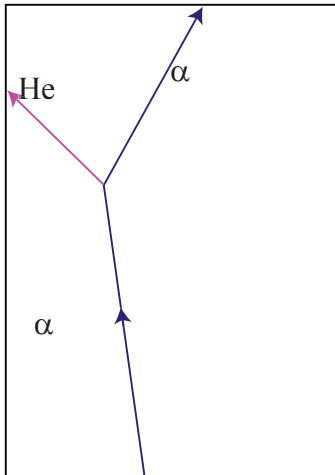


SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

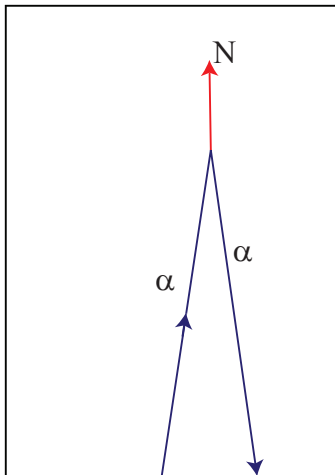
ALPHA PARTICLE DEFLECTION



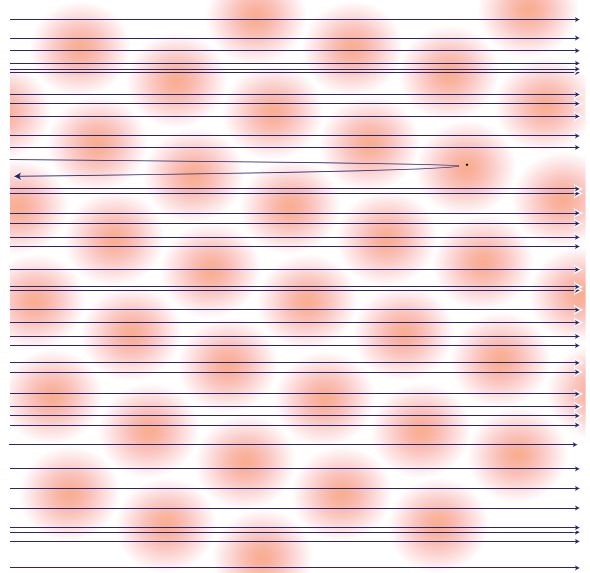
From a stream of alpha particles, one of them hits a hydrogen nucleus and knocks it away, while being itself only slightly deflected.



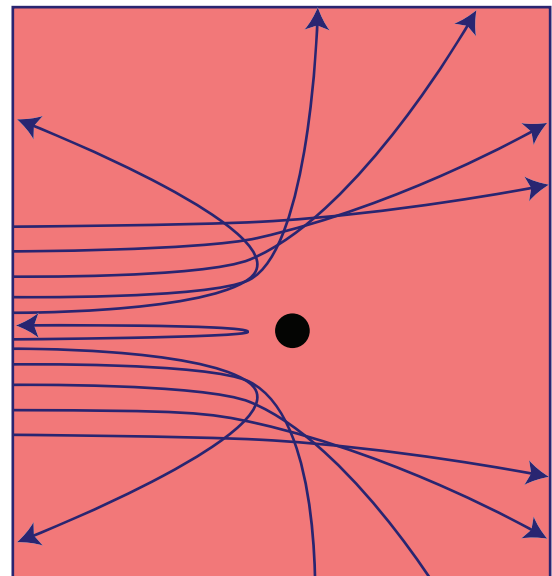
When an alpha particle hits a helium nucleus, both of them are deflected equally, showing that they are equal in mass. Why does this deflection show that the alpha particle and the helium nucleus have the same mass?



When an alpha particle hits a nitrogen nucleus, the alpha can be returned to sender while moving the nitrogen much less.



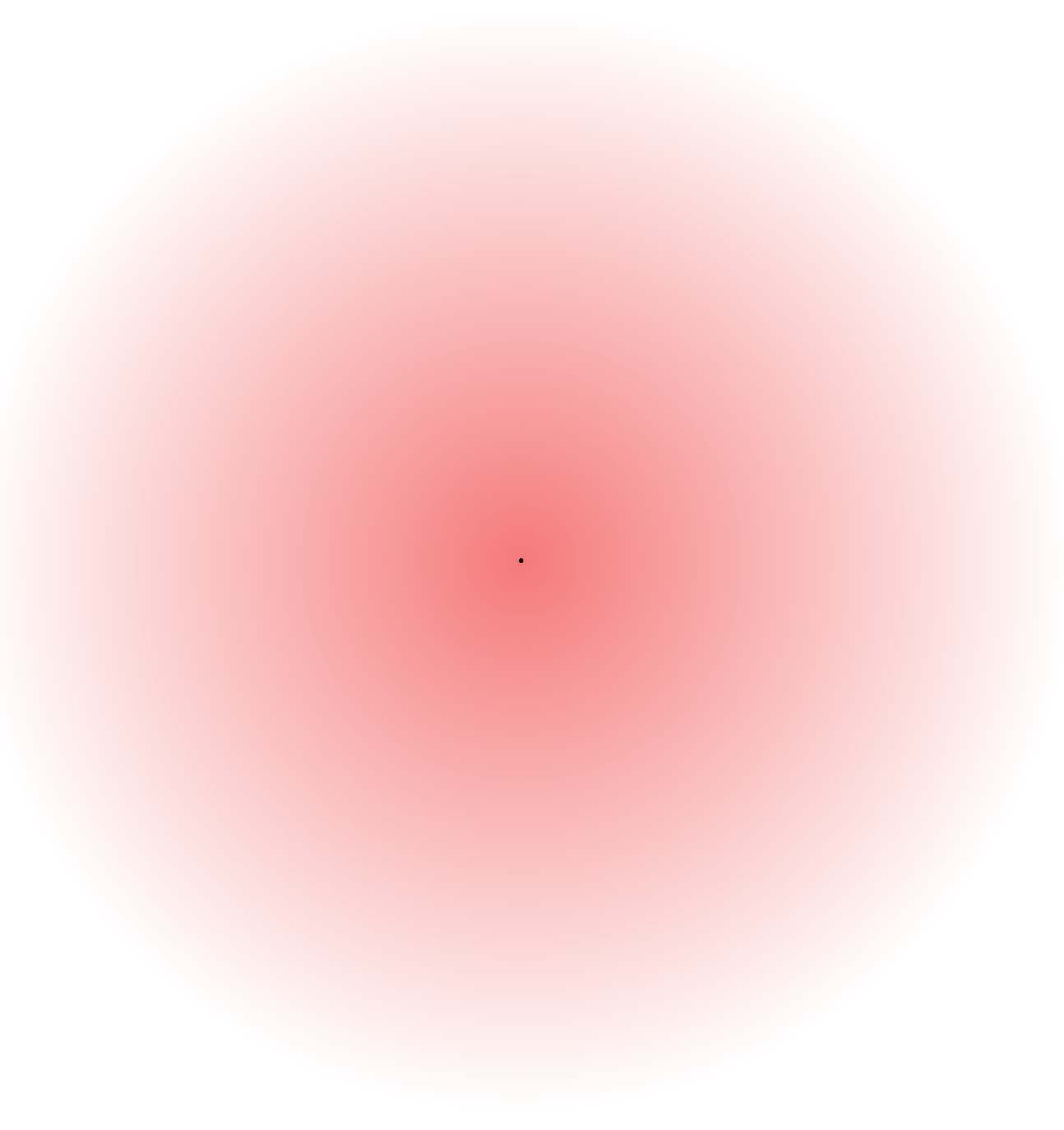
Most alpha particles will pass straight through many layers of atoms, showing that the atom is mostly empty space. An occasional alpha particle, however, will be deflected at a large angle.



For a given nuclear mass and charge, how much an alpha particle is deflected by a nucleus depends upon how close it approaches the nucleus.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ELECTRON CLOUD AND NUCLEUS



A picture of the hydrogen atom,
showing the actual size comparison between the
electron cloud (in red) and the nucleus (in black).

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ATOMIC SIZE

Let us imagine making an atom of hydrogen. Start with a proton and an electron far apart and not moving with respect to each other. Call the energy of this situation zero. Then allow the electron and proton to attract each other as opposite charges do. As they approach each other the electrostatic potential energy will become negative but they will also speed up (mostly the electron) and the kinetic energy will become positive. At a certain distance (about 32 picometers) the sum of the potential and kinetic energy will be at a minimum and that will set the size of the atom.

The kinetic energy of an electron in an atom is mostly determined by the Heisenberg uncertainty principle, which has the equation

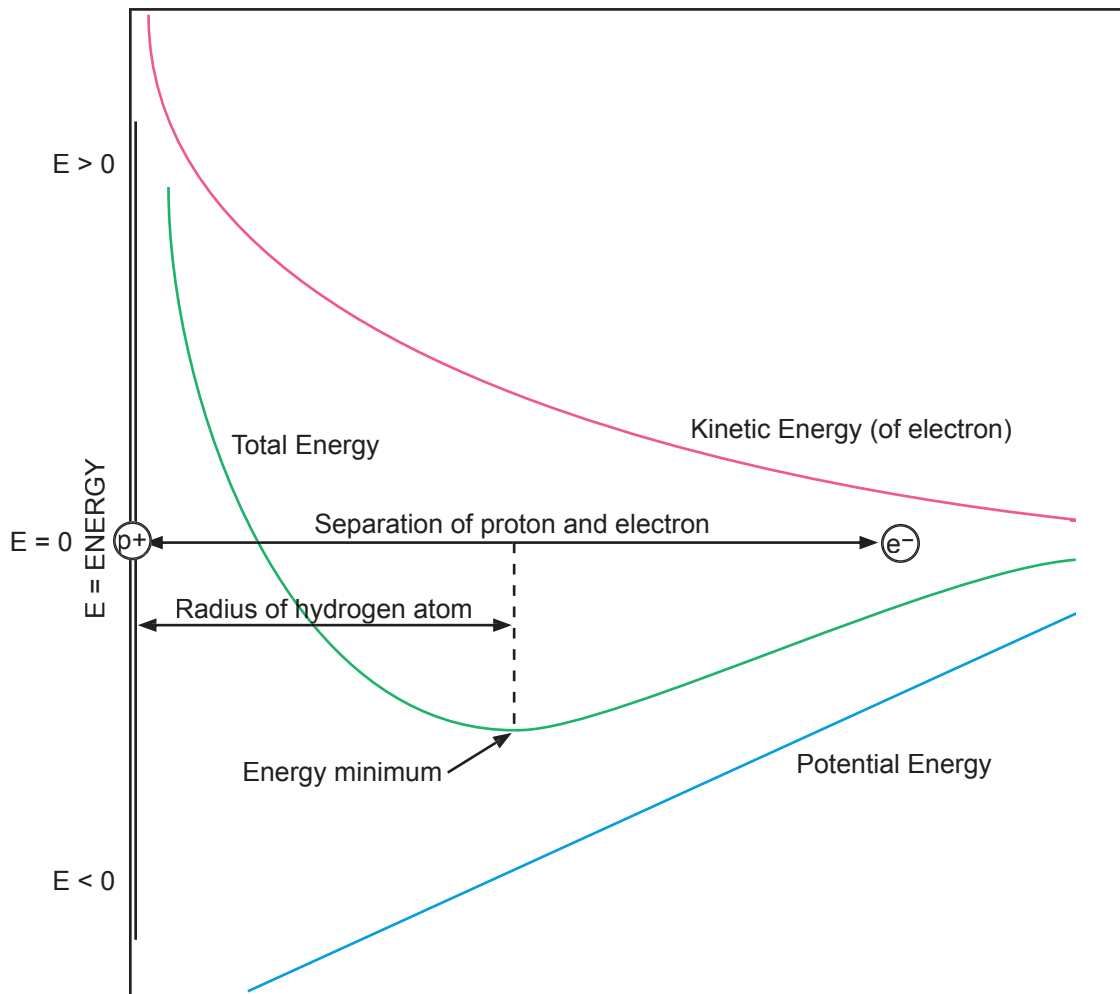
$$(\Delta x)(\Delta p) > \frac{h}{4}$$

where Δx is the uncertainty in the location and Δp is the uncertainty in the momentum. If we tried to constrain the electron too close to the proton, then the uncertainty in the momentum would increase and with that the kinetic energy would increase, according to the equation.

$$K = \frac{p^2}{2m} = \frac{mv^2}{2}$$

where K is the kinetic energy of a particle, p is the momentum and m is the mass of the particle.

Total Energy = Kinetic Energy + Potential Energy



Why can we disregard the kinetic energy of the proton?

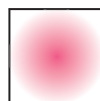
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

WHAT AND WHERE ARE ELECTRONS?

We know that each electron has a definite electrical charge, which we can write as e^- and that $e^- = 1.602 \times 10^{-19} \text{ C}$ and we know that each electron has a definite (small) mass m and that $m = 9.11 \times 10^{-31} \text{ kg}$.

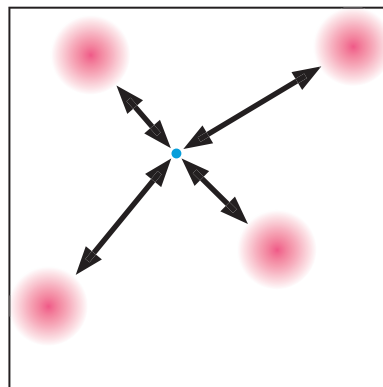
What is harder to know is where an electron is located. We know from quantum mechanics that an electron can only be probably located in any given volume of space, although for a given electron, the probability of it being somewhere, in all space, is one.

Suppose the blue dot in picture 2 represents an atomic nucleus with four protons, what kind of force would the black arrows represent?
 How would you interpret the red arrows in picture 3?
 Why are the black arrows drawn thicker than the red arrows?
 What kind of atom will be neutral when it has four electrons? Where is it located on the periodic table?
 In picture number 4, is the size of the nucleus (blue dot) drawn correctly to scale with the size of the electron cloud? If not, would it be larger or smaller and by about how much?

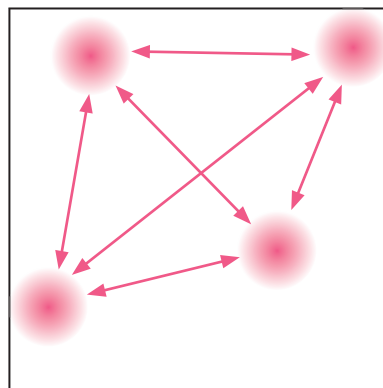


1

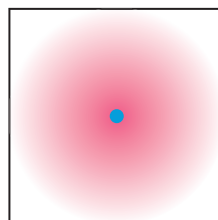
There is a finite probability of an electron being anywhere in space. We often represent this by drawing **electron cloud pictures**, where the deeper color represents a greater probability of the presence of an electron.



2



3

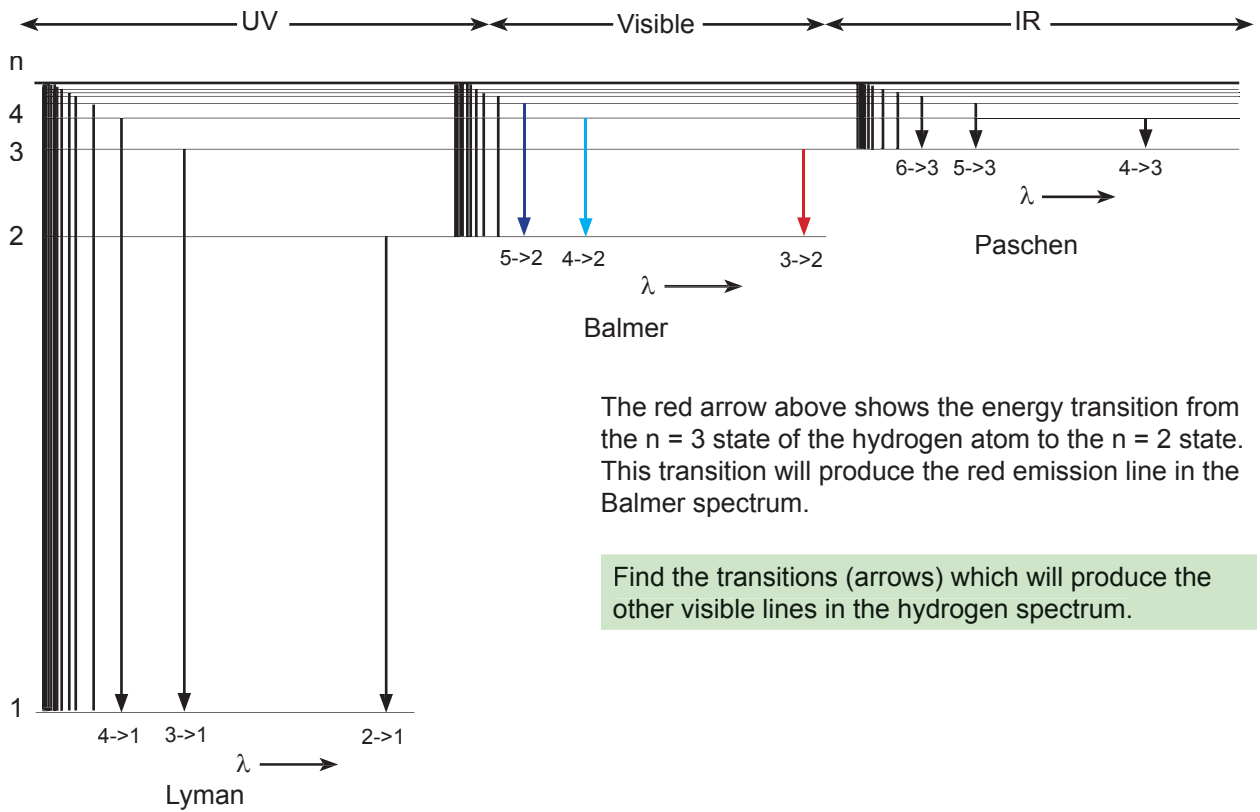
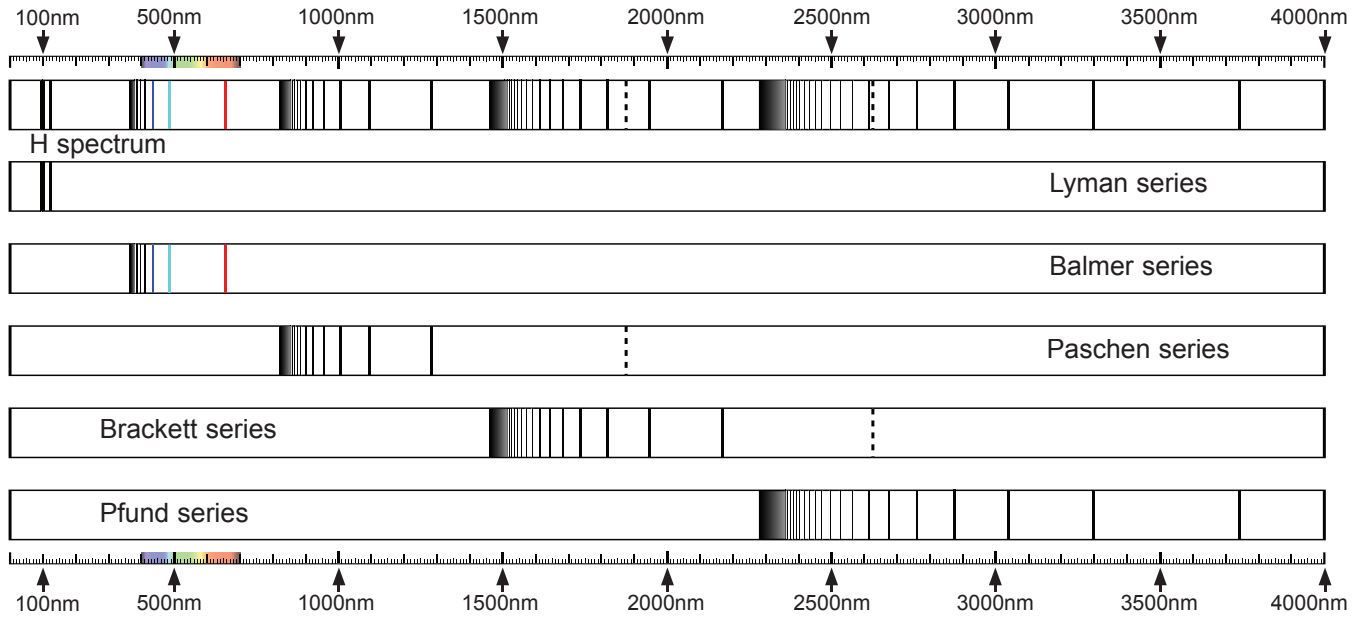


4

In an isolated atom the electron probability forms a spherical cloud around the nucleus. It is thickest at the nucleus and falls off away from the nucleus. The electron cloud and the nucleus together form the atom.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

HYDROGEN SPECTRUM AND ENERGY SERIES

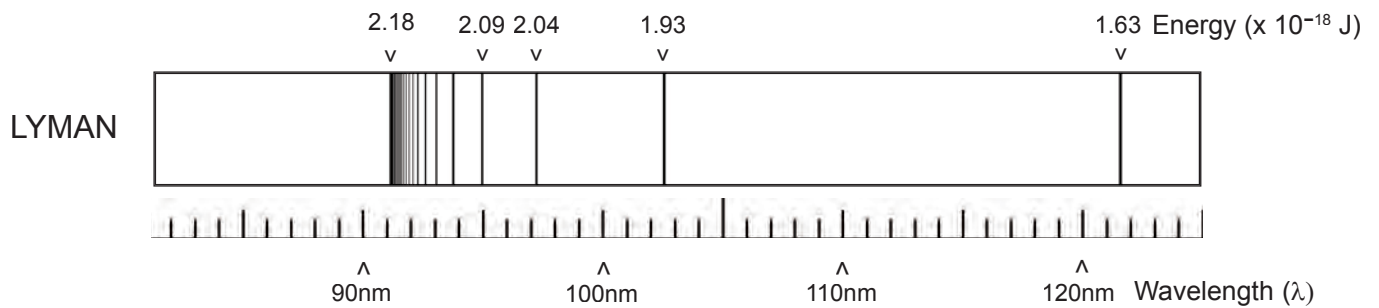


The red arrow above shows the energy transition from the $n = 3$ state of the hydrogen atom to the $n = 2$ state. This transition will produce the red emission line in the Balmer spectrum.

Find the transitions (arrows) which will produce the other visible lines in the hydrogen spectrum.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

LYMAN, BALMER AND PASCHEN SERIES OF H



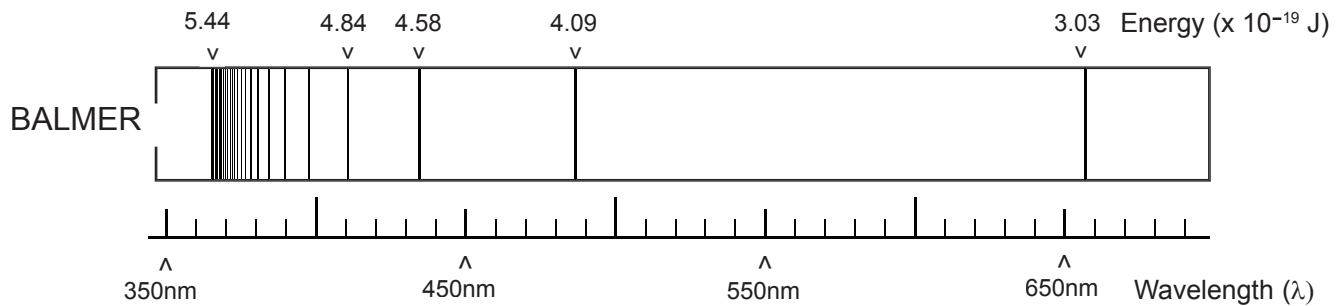
The wavelengths of one electron atomic emission spectra can be calculated from the Rydberg equation:

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

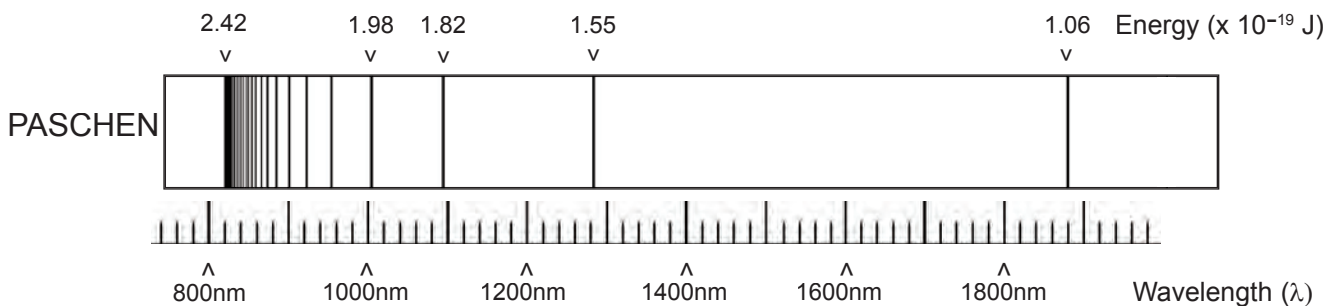
where λ = wavelength (in m.) and Z is the atomic number. $Z = 1$ for hydrogen.

R is called the Rydberg constant and $R = 1.096776 \times 10^7 \text{ m}^{-1}$

$n_1 = 1, n_2 = 2, 3, 4 \dots$



$n_1 = 2, n_2 = 3, 4, 5 \dots$



$n_1 = 3, n_2 = 4, 5, 6 \dots$

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

FROM THE SPECTRUM TO ATOMIC STRUCTURE

STEP ONE: Measure the energy difference between $n = 3$ and $n = 2$ on the Energy Diagram for H.
 STEP TWO: Using the Spectral Chart for H, measure the wavelength and calculate the energy of the longest wavelength Balmer line, using $E = hc/\lambda$.
 STEP THREE: Compare your results for Step 1 and Step 2. They should be about the same, up to the limits of accuracy.

STEP FOUR: Repeat the procedures for Steps 1 through 3, finding the energy difference between $n = 2$ and $n = 1$, and comparing it with the energy of the longest wavelength Lyman line.

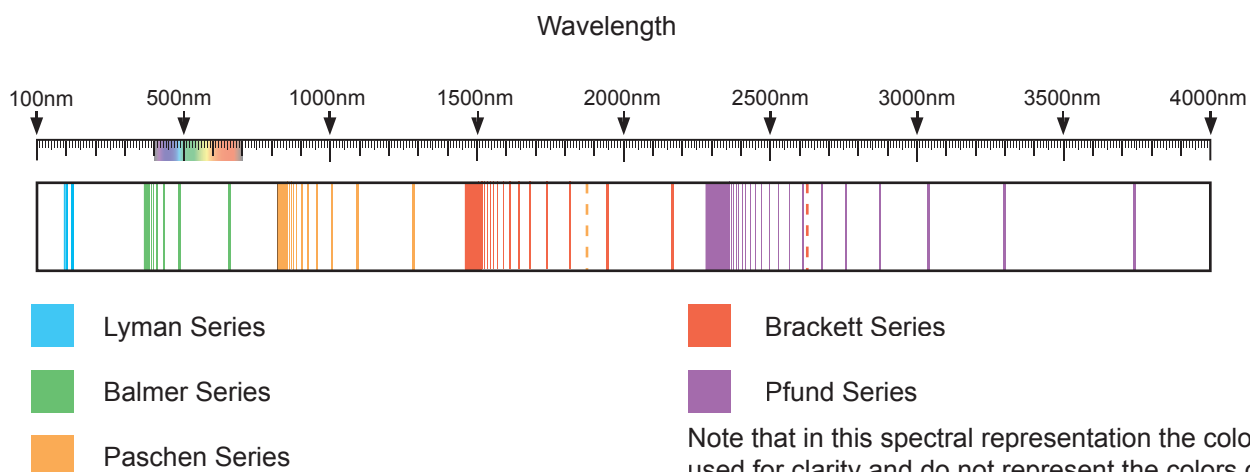
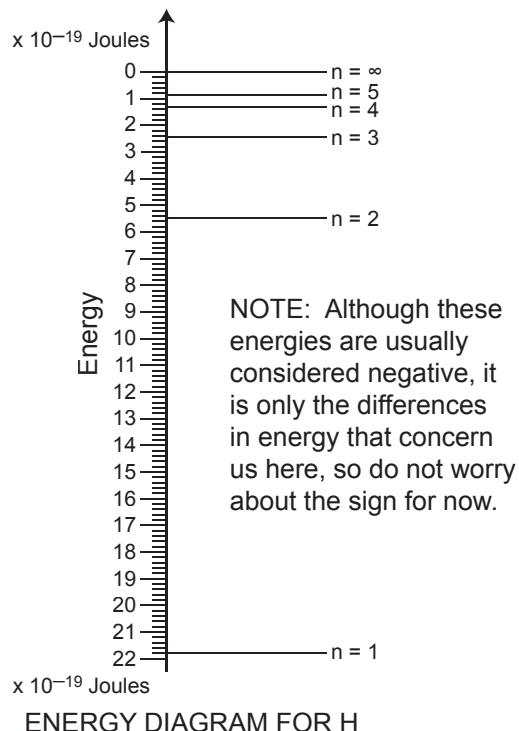
STEP FIVE: Measure the wavelengths of the left edge of each of the five series. Calculate the energy for each of those wavelengths.

STEP SIX: Find and mark the five energies you calculated in Step Five on the Energy Diagram for H.

STEP SEVEN: Interpret and discuss your results.

For further practice:

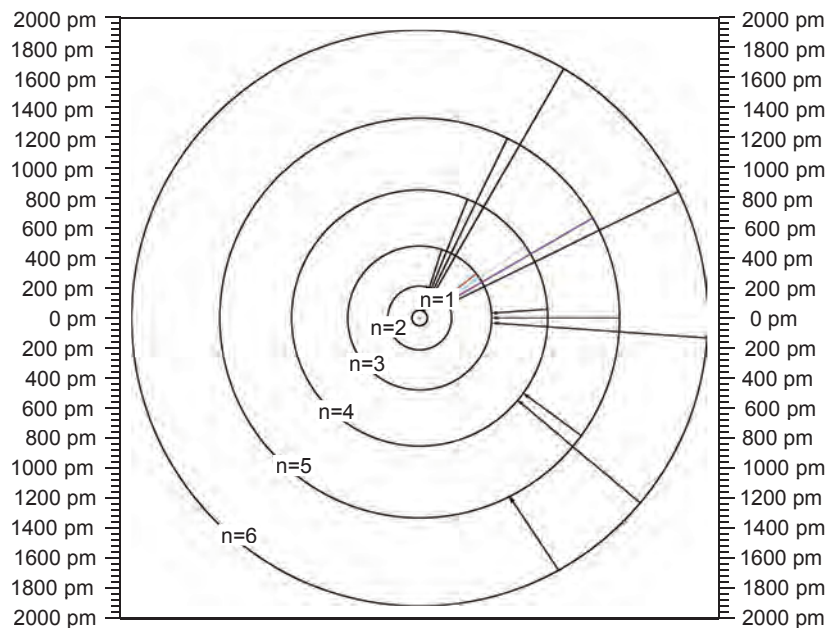
1. Use the Energy Diagram for H to find the difference in energy between $n = 5$ and $n = 3$. Calculate the wavelength of the electromagnetic radiation that would have this energy and locate it on the Spectral Chart for H.
2. Using the third longest wavelength line in the Balmer series, calculate its energy and find two energy levels on the Energy Chart for H whose difference would produce light of that wavelength.



Note that in this spectral representation the colors are used for clarity and do not represent the colors of the actual lines, most of which are invisible.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

H-RADII OF ENERGY LEVELS AND TRANSITIONS



The scale for orbital radii is given in picometers (pm).
 $1.00\text{pm} = 1.00 \times 10^{-12}\text{m}$
 The radius of the nucleus is less than $6.00 \times 10^{-3}\text{pm}$.

This is a correct presentation of the relative radii of the first six orbitals of hydrogen, from $n = 1$ to $n = 6$.

A hydrogen atom consists of a negatively charged electron with a probability of being in a region of space around a tiny, positively charged nucleus, which in the case of hydrogen is just a single proton. The probability of finding the electron always peaks at the nucleus and always descends as we look farther and farther away from the nucleus. But how rapidly that probability descends away from the nucleus and in what directions it descends less or more depends upon the quantum state of the atom. In any case, the shape and extent of that region within which we can expect to find the electron (usually with a 95% probability) is called an orbital. In the simplest cases (those with no angular momentum) the orbital is spherical and depends for its size upon the energy of the atom. That energy is described by the quantum number n .

The energy is lowest for $n = 1$, which also has the smallest orbital. Both the energy and the radius of the orbital rise as the square of n .

Using the scale given beside the chart, measure the radii of the first six orbitals of hydrogen.

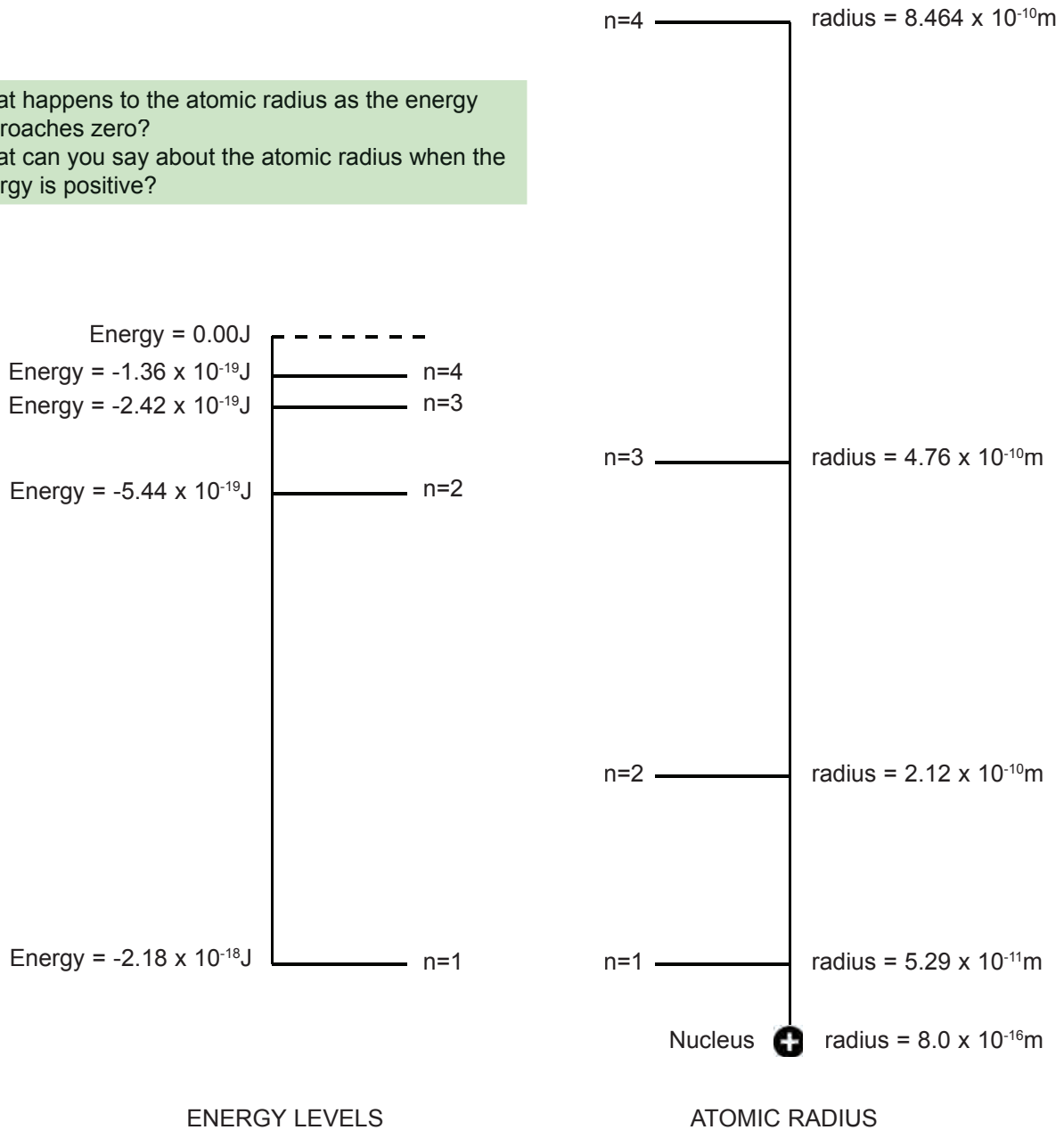
Convert your answers for the radii from picometers to meters.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

HYDROGEN ENERGY STATES

ENERGY LEVELS COMPARED TO ATOMIC RADIUS

What happens to the atomic radius as the energy approaches zero?
 What can you say about the atomic radius when the energy is positive?



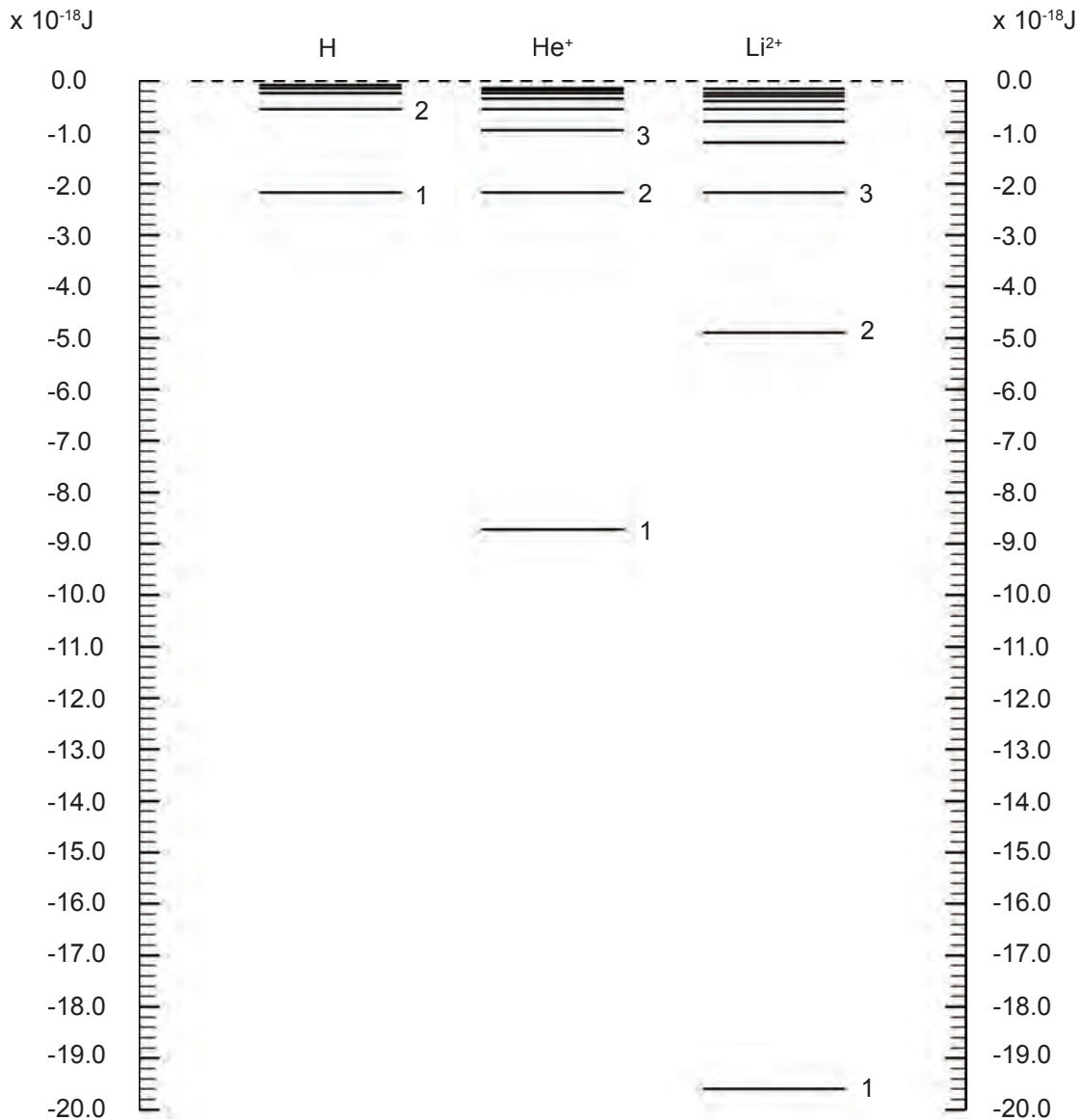
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ENERGY LEVELS OF ONE ELECTRON SPECIES

The Rydberg equation shows the wavelength, λ , of the photon emitted when a single electron atom of nuclear charge Z falls from energy level n_1 to energy level n_2 .
 R is the Rydberg constant.
 $R = 1.096776 \times 10^7 \text{ m}^{-1}$

Rydberg equation

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$



Qualitatively describe the difference between the energy levels of H, He⁺, and Li²⁺.
 What is the cause of these differences?

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

THE QUANTUM NUMBER l

When the excited hydrogen atom is in a magnetic field, something new happens. The spectral lines are **SPLIT!**

In order to explain these observations we introduce another quantum number, l , which is called the azimuthal quantum number or the angular momentum quantum number.

For all atoms with more than one electron the spectral lines are split by l even without a magnetic field, due to the interaction of the excited electron with the other electrons in the atom.

For hydrogen we have pictured the orbitals as circular. Circular orbitals correspond to the case where $l = 0$.

From quantum mechanics it is known that l can take on any integral value between 0 and $n-1$, for the principle quantum number n . Now we can make a table of quantum states for n and l .

n	l
1	0
2	0
2	1
3	0
3	1
3	2
4	0
etc	

Finish the table for $n = 4$ and extend it through $n = 5$.

We have shown hydrogen orbitals as circles in this module. These correspond to the $l = 0$ states. For the other states it is best to represent the orbitals in three dimensions, as we do in our module Chemical Bonding.

Chemists and other spectroscopists also have a special system of naming the orbitals corresponding to the different l values

$l = 0$ is called an s state.

$l = 1$ is called a p state.

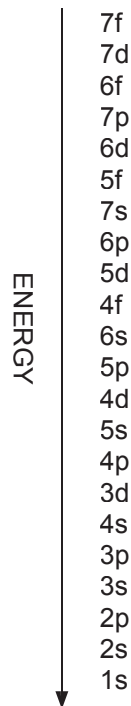
$l = 2$ is called a d state.

$l = 3$ is called an f state.

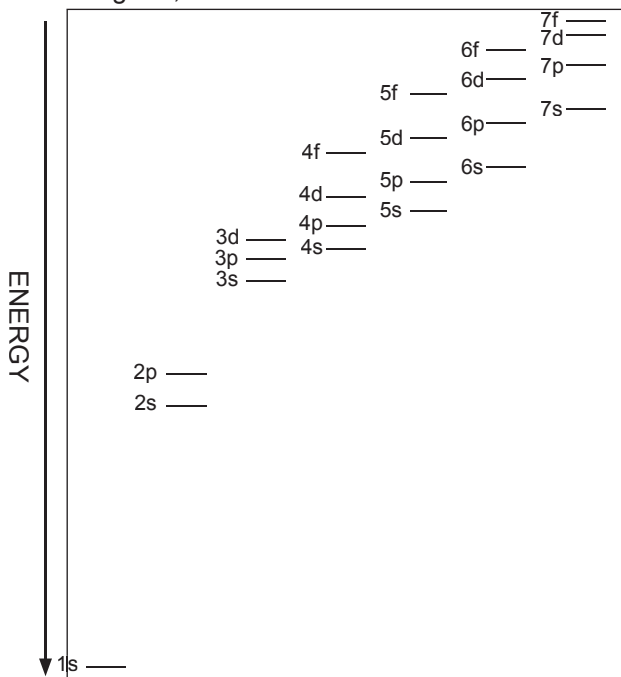
Thus, for example, an state with $n = 3$ and $l = 2$ would be called a 3d state.

A basic principle is that, except for one electron atoms, for a given principle quantum number n the energy of a state increases with increasing l .

Chemists use spectroscopic studies to determine the energy differences between the various states, from which they can determine the actual energy levels of the states. In general, the energy states are ordered as follows, with 1s being the lowest (most strongly bound) and 7f the highest (least strongly bound) energy states.

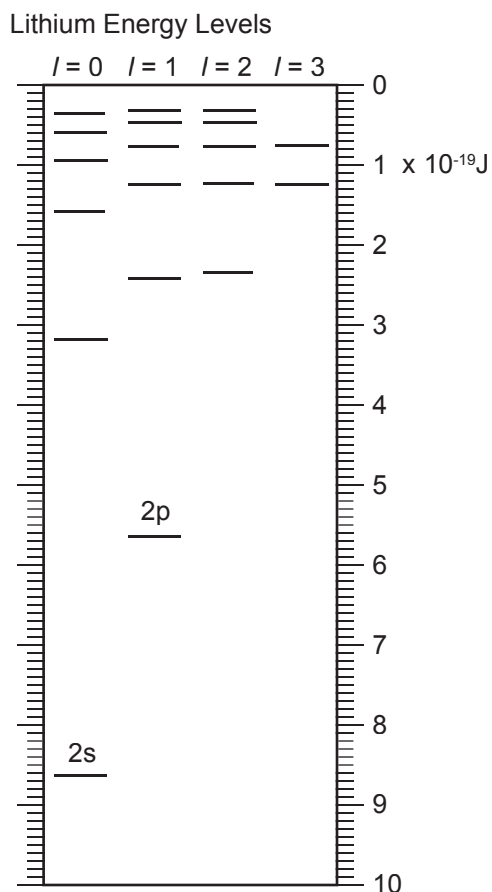


It is more common, because useful, to separate the different n levels horizontally and make what is called a term diagram, such as:



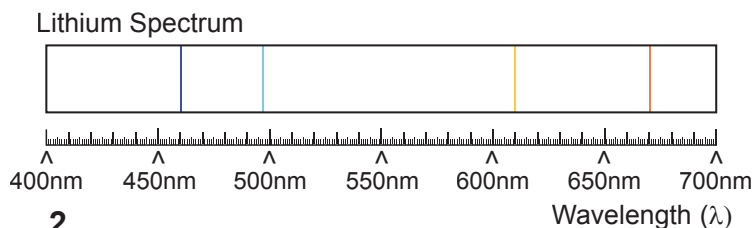
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

LITHIUM



1

Picture 1 shows the some of the lower energy levels for lithium. The 2s and 2p levels are labeled, you label the rest of the levels. Draw in all of the transitions between levels which involve a change in l of plus or minus 1.



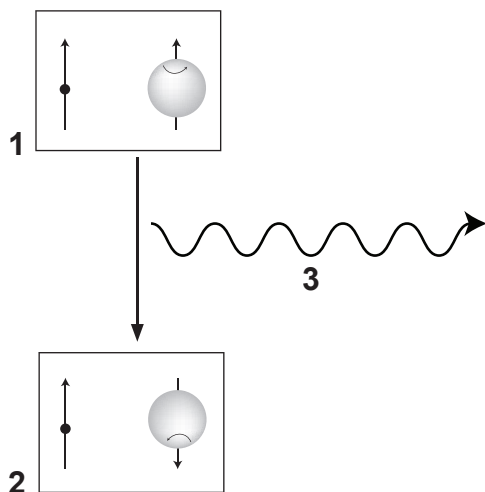
2

Measure the wavelength of each of the lines shown in the lithium spectrum (picture 2). In picture 1, find the energy of the 2p–2s transition. Would this transition produce one of the lines in the lithium spectrum shown in picture 2? Which one?

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ELECTRON SPIN AND THE UNIVERSE

ELECTRON SPIN



In picture 1 the magnetic fields of the electron and the nucleus of a hydrogen atom are shown parallel. In picture 2 the magnetic fields are shown antiparallel. Recalling the experiment with bar magnets, you know that the parallel state has a higher energy than the antiparallel state.

The wavelength of electromagnetic radiation given off when the hydrogen atoms drops from the parallel state to the antiparallel state is 21 cm. What is the frequency of the 21 cm photon? What is the difference in energy between the hydrogen atom in the parallel state and in the antiparallel state? What happens if a 21 cm photon is absorbed by a hydrogen atom in the antiparallel state?

It is known from experiment and from quantum mechanics that the magnetic field of an electron can have only two directions, up and down, and nothing in between. For historical reasons this property of electrons has been named 'spin' and assigned the letter m_s .

For spin up $m_s = +\frac{1}{2}$

For spin down $m_s = -\frac{1}{2}$

The proton has the same spin property as the electron.

What is the total spin of the hydrogen atom in the parallel state?
What is the total spin of the hydrogen atom in the antiparallel state?

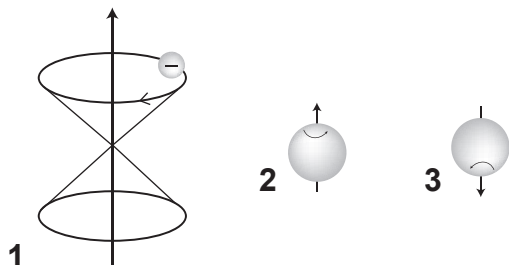
THE UNIVERSE

In the 1930's astronomers trying to map our galaxy were frustrated by the vast lanes of dust blocking our vision of the inner galaxy. In the early 1940's the Dutch astronomers Oort and van Hulst proposed using the 21 cm hydrogen line to explore the galaxy and beyond. Eventually the technology to do this was developed and now this is a major probe of the universe, since most of the universe is made of hydrogen.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

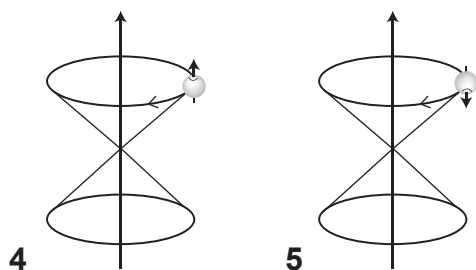
SPECTROSCOPIC LINE SPLITTING

Since the electron is a moving charged particle when $l \neq 0$, it has a magnetic field, as indicated by the vertical arrow in picture 1.



The electrons themselves also have their own magnetic fields, as shown in pictures 2 and 3.

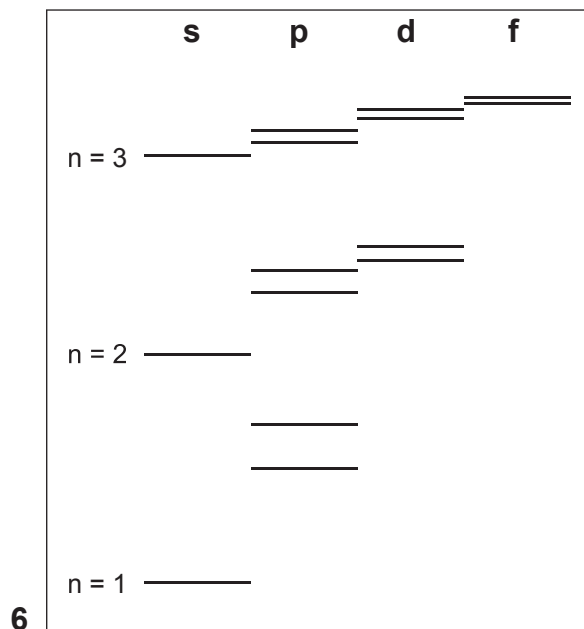
Obtain two bar magnets with their north and south poles labeled. Align the magnets parallel to each other with their north poles pointing in the same direction. Hold onto one magnet while you let the other one go. Then align the magnets parallel so that the south pole of one magnet is aligned with the north pole of the other magnet, then let go. Compare the two situations. Which one, N-N or N-S has the higher energy? Which one is more stable. Explain the relationship between energy and stability.



We call the magnetic effect of an electron by the name 'spin' because it is what would be produced by a spinning charge. According to quantum mechanics the direction of the electron spin can only have two values, one aligned with the magnetic field it is in and one opposite. Having done the experiment with bar magnets above, explain which arrangement, either picture 4 or picture 5, would have the higher energy.

The electron shown in picture 2 has spin $s = +\frac{1}{2}$
 The electron shown in picture 3 has spin $s = -\frac{1}{2}$

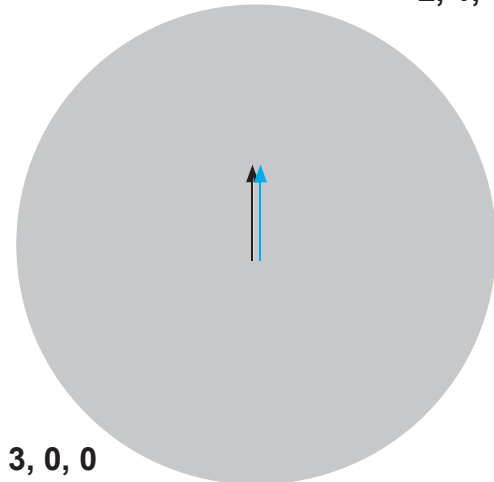
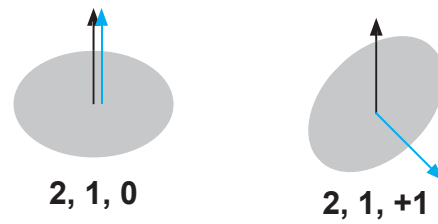
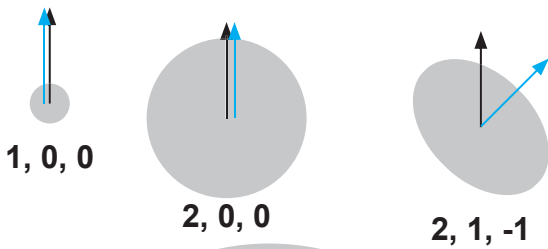
Many energy levels are actually split by the interaction between the magnetic field of the electron (spin) and the magnetic field of the charged electron moving in its orbital. This is called the fine structure.



Picture 6 shows the fine structure of an alkali atom (solid horizontal lines). The principle quantum number, n , is shown next to the state for which $l = 0$.

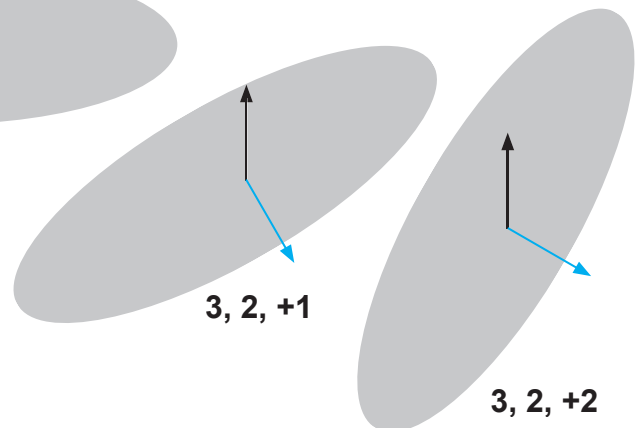
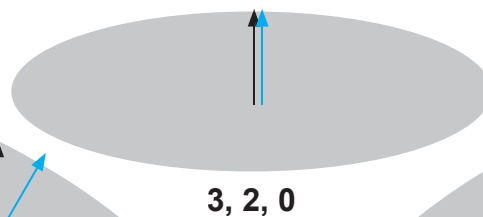
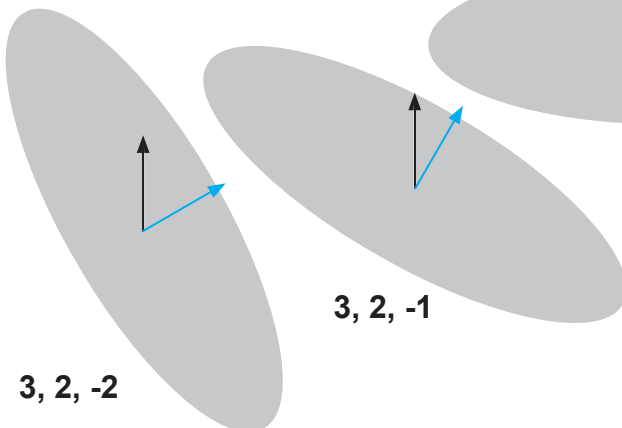
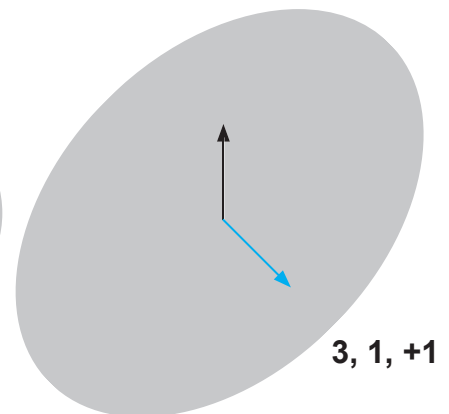
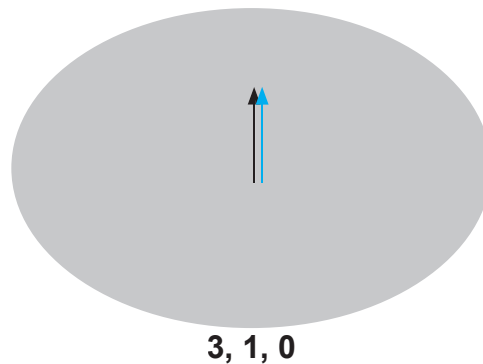
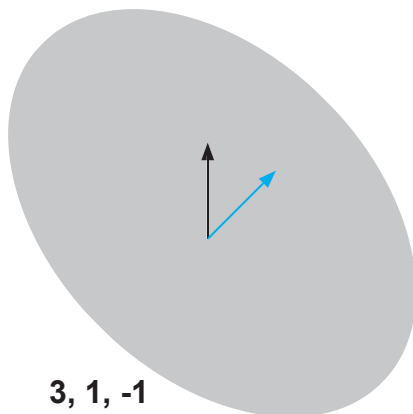
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

n, l, m orbitals



This page shows all of the orbital sizes and shapes for the hydrogen atom through $n = 3$. The n quantum number determines the radius of the orbital for $l = 0$, which is the same as the semimajor elliptical axis for $l \neq 0$. The m , quantum number is represented by the angle between the external and internal magnetic fields.

In all of the orbital diagrams on this page, the same external magnetic field is shown by the vertical black arrow. The magnetic field of the electron in its orbital is shown by the blue arrow. Assuming, for simplicity, that all of the orbital magnetic fields are of equal strength (not necessarily true), list the orbitals from lowest energy state to highest energy state.



SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

THE PAULI EXCLUSION PRINCIPLE

Each orbital is determined by three quantum numbers. They are

n , the principle quantum number,

which can take any positive integer

l , the azimuthal quantum number,

which can take any value $0 \leq l \leq n-1$

m , the magnetic quantum number,

which can take any value $-l \leq m \leq l$.

In addition, each electron has its spin quantum number s , where either $s = +\frac{1}{2}$ or $s = -\frac{1}{2}$.

The PAULI EXCLUSION PRINCIPLE says that no two electrons (in the same atom) can have the same set of quantum numbers.

1	$n = 1$	$l = 0$	$m = 0$
	$n = 2$	$l = 0$	$m = 0$
		$l = 1$	$m = -1$
$l = 1$		$m = 0$	
		$l = 1$	$m = +1$
$n = 3$	$l = 0$	$m = 0$	
	$l = 1$	$m = -1$	
	$l = 1$	$m = 0$	
	$l = 1$	$m = +1$	
	$l = 2$	$m = -2$	
	$l = 2$	$m = -1$	
	$l = 2$	$m = 0$	
	$l = 2$	$m = +1$	
	$l = 2$	$m = +2$	
	$n = 4$		

As done in the above chart, write out all of the sets of quantum numbers with principle quantum number $n = 4$.

AUFBAU

With each increase of one in the atomic number, one more electron has to be added to the atom to balance the nuclear charge. In the ground state, this electron will be added to the lowest energy unoccupied orbital, with a maximum of two electrons per orbital. The following diagram is a useful aid to help remember in which order the electrons are added, going along the path of each arrow from top down.

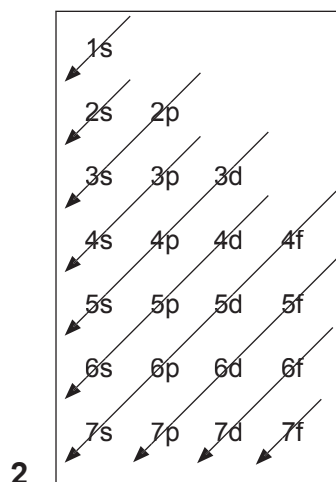
The orbitals are named according to the following system. First comes the principle quantum number, n . This is followed by a letter representing the l value, according to the following rules:

For $l = 0$ we have s orbitals.

For $l = 1$ we have p orbitals.

For $l = 2$ we have d orbitals.

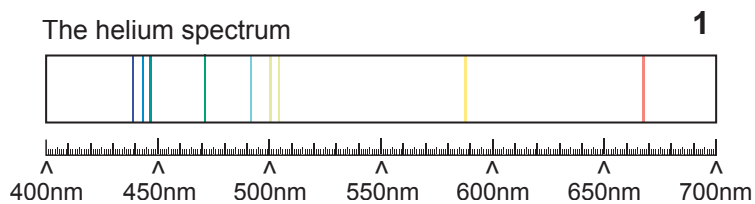
For $l = 3$ we have f orbitals.



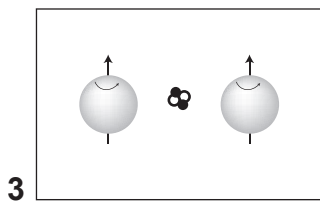
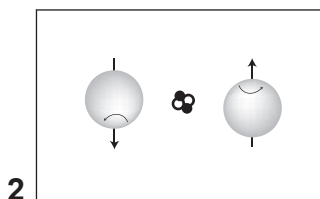
Using the Pauli exclusion principle and the fact that electrons can have either of two spin states, calculate how many electrons can be in each orbital.

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

HELIUM



The helium atom has two forms, which are illustrated in pictures 2 and 3. Describe the difference between the forms as shown in the pictures.

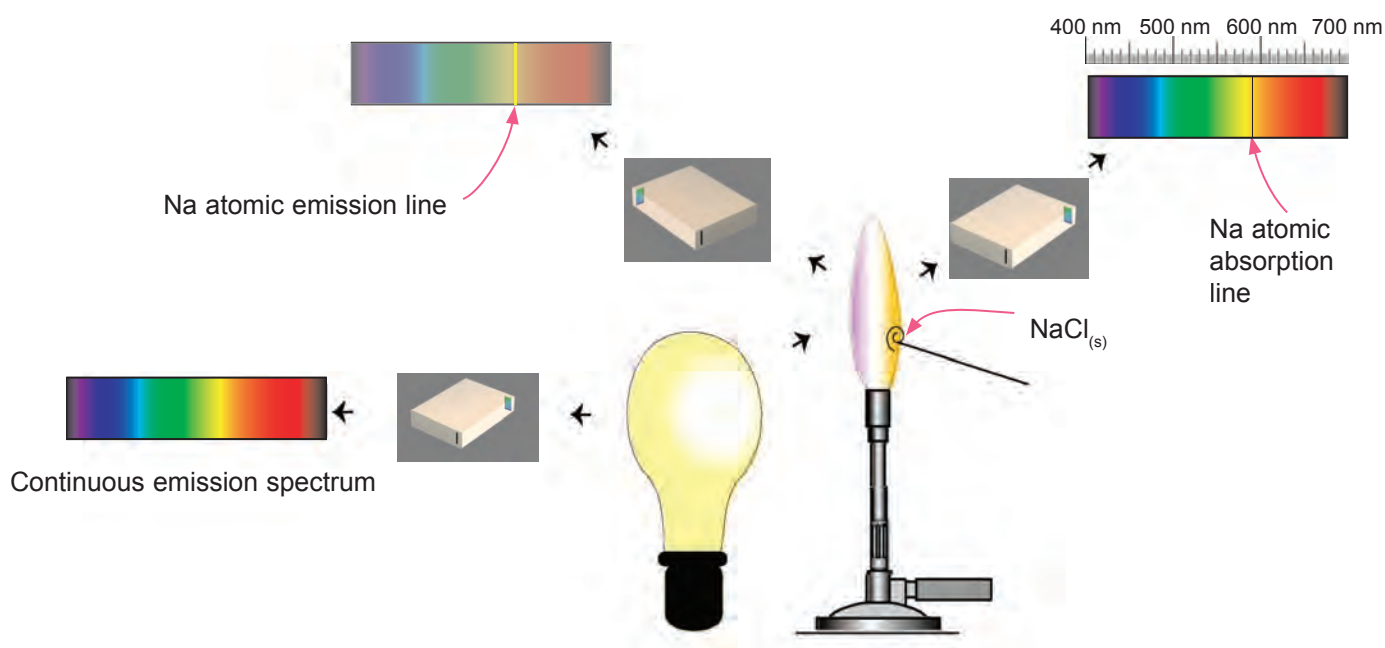


The form shown in picture 2 is called parahelium and the form shown in picture 3 is called orthohelium. The visible helium spectrum shown in picture 1 arises from orthohelium.

Using the spin assignments given on the previous page, what is the total spin of the parahelium atom? What is the total spin of the orthohelium atom? (You can ignore the nucleus for these questions.)

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

SODIUM EMISSION AND ABSORPTION EXPERIMENT

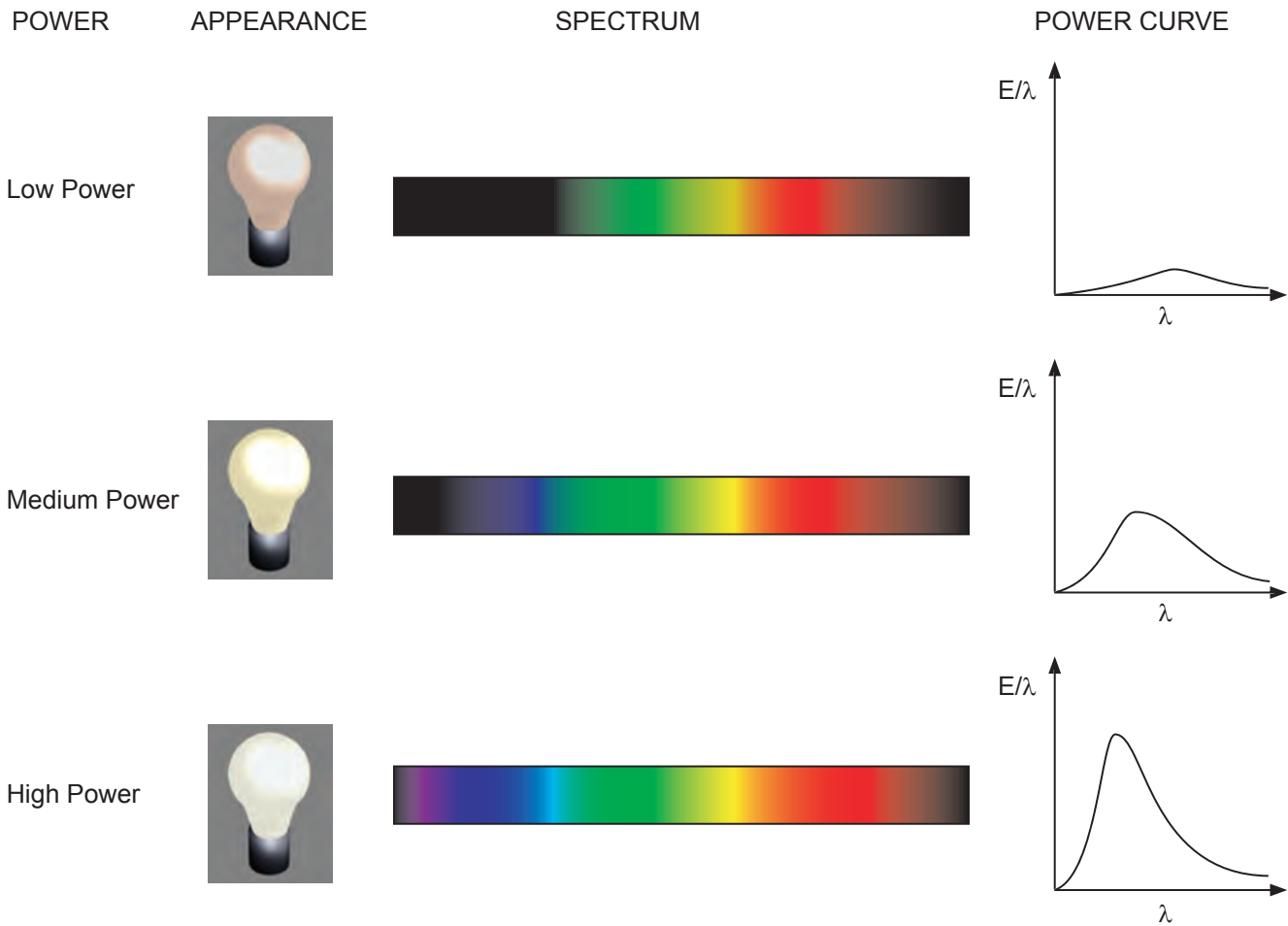


1. When the spectroscope is pointed at a Bunsen burner flame with $\text{NaCl}_{(s)}$ held in the flame a single yellow line appears. Explain.
2. The same flame viewed against a 100 Watt incandescent bulb shows a **dark** line at the **same** wavelength as the bright yellow line. Explain.
3. What is the wavelength of the dark line?

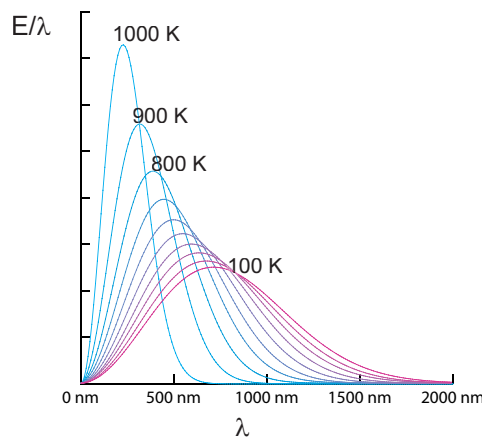
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

BLACK BODY RADIATION

When a light bulb is connected to a variable resistor we observe the following sequence of events as the power is gradually increased.



The curves shown on the right are mathematically generated to show the amount of relative emission power at different wavelengths from a source at temperatures from 100K to 1000K. Something which emits electromagnetic radiation according to this law is called a black body.



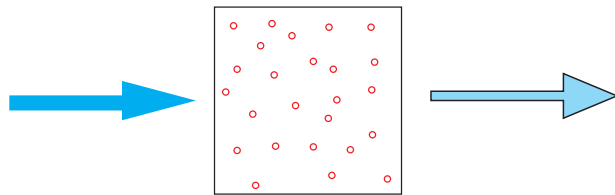
E/λ means the amount of light energy produced at the wavelength λ .

SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

LAMBERT-BOUGER-BEER LAW

PICTURES FOR CONCENTRATION AND PATH LENGTH EFFECTS

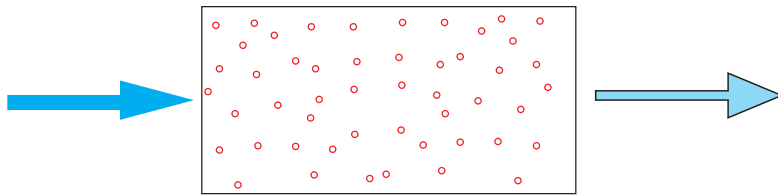
Original Solution



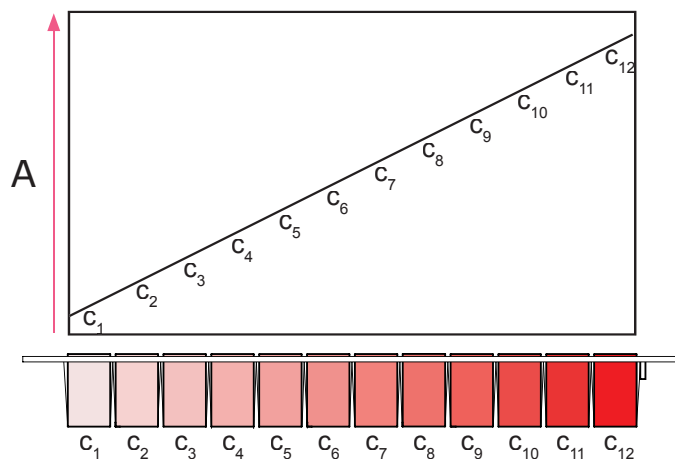
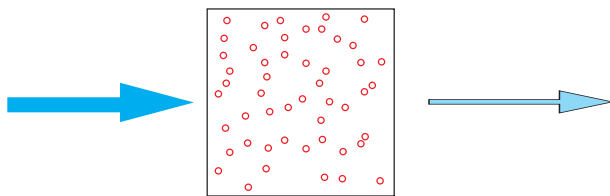
$$A = a \times b \times c$$

A = absorption
a = absorptivity
b = path length
c = concentration

Path Length Effect

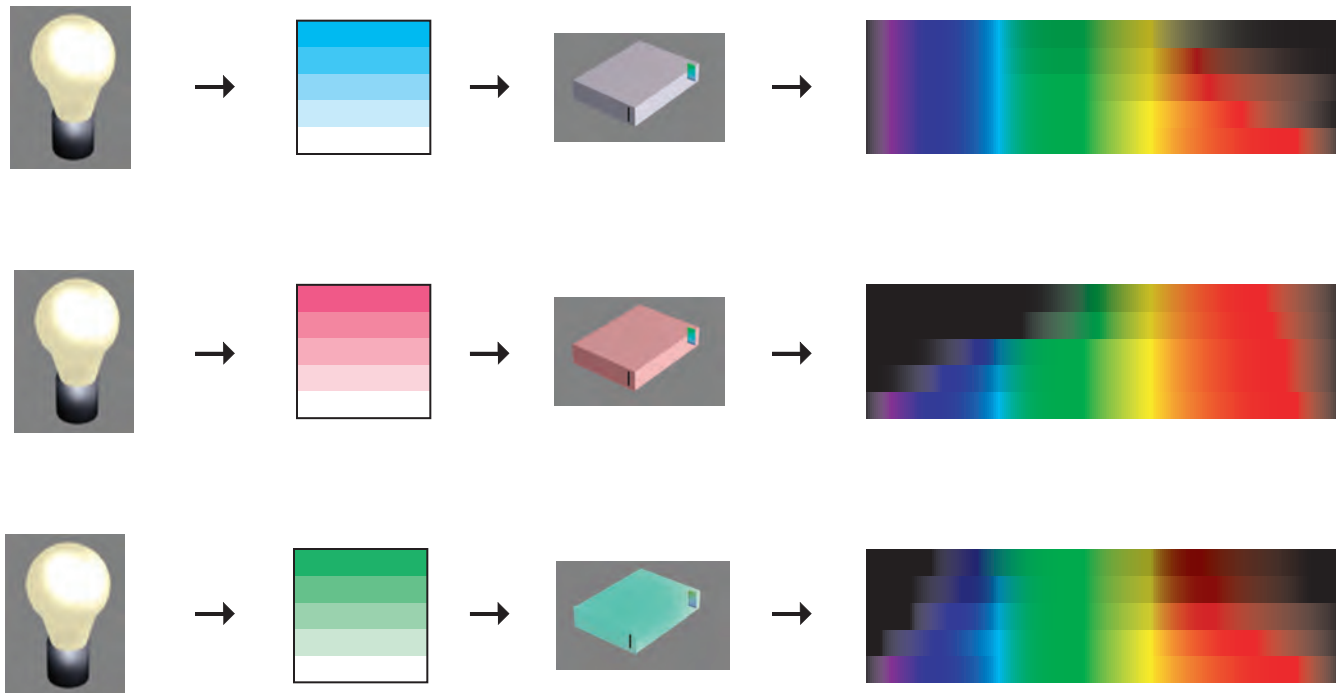


Concentration Effect



SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ABSORPTION SPECTRA FROM LIQUIDS AND SOLIDS WITH DIFFERENT CONCENTRATIONS OF DYE



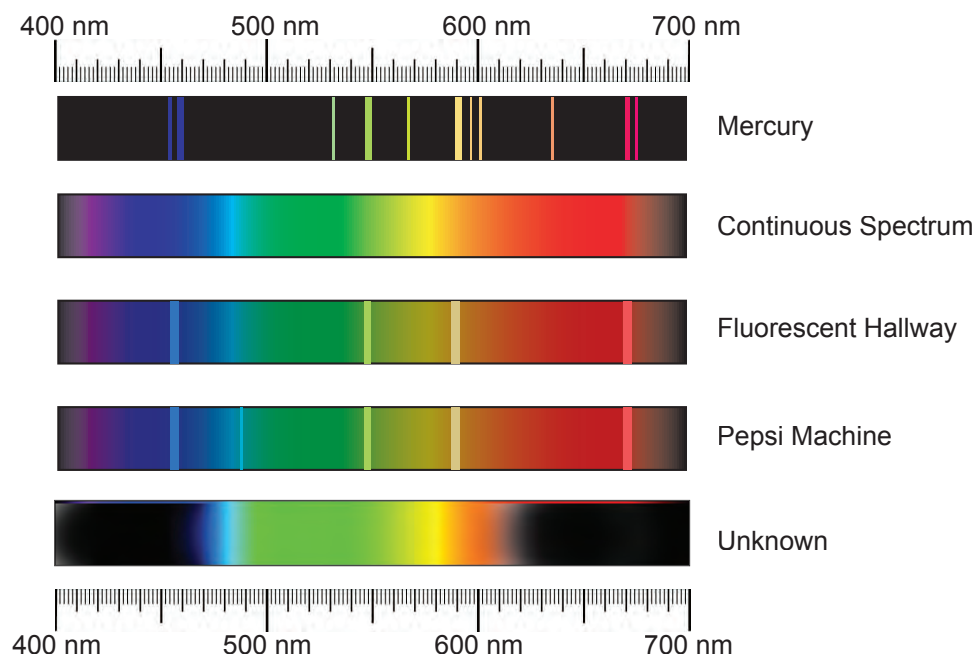
Principles behind Lambert-Bouger-Beer Law

- Particular kinds of molecules absorb light in particular wavelength regions.
- More molecules absorb more light.
- More molecules absorb more light.

Explain what is happening to produce each of the three spectral sequences above. Be particular. Explain the differences between the spectral sequences and explain how and why the spectra are changing in each spectral sequence.

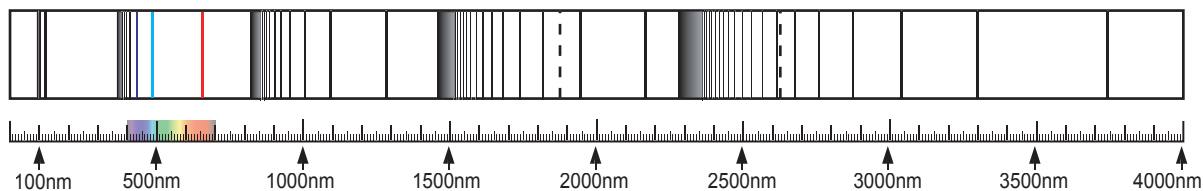
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

ASSESSMENT

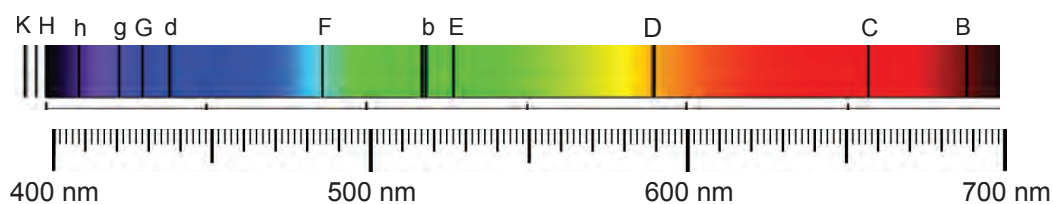


Describe the spectra shown on this page; e.g., tell everything you can about it including the wavelengths and energies associated with its emission and/or absorption regions and lines, the type and state of matter which produced it, whether it is an emission or absorption spectrum or both, and everything else you can observe or think of.

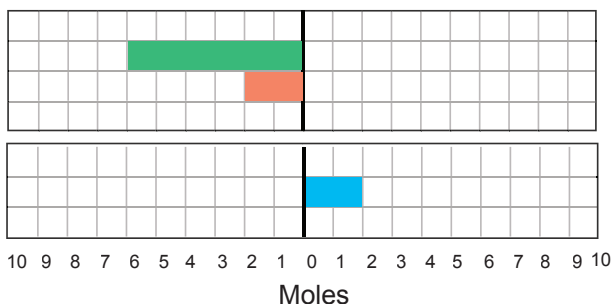
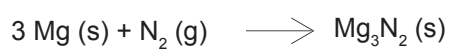
Hydrogen



Sun



STOICHIOMETRY via ChemLog



by

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The contents of this module were developed under grant award # P116B-001338 from the Fund for the Improvement of Postsecondary Education (FIPSE), United States Department of Education. However, those contents do not necessarily represent the policy of FIPSE and the Department of Education, and you should not assume endorsement by the Federal government.

ChemLog STOICHIOMETRY

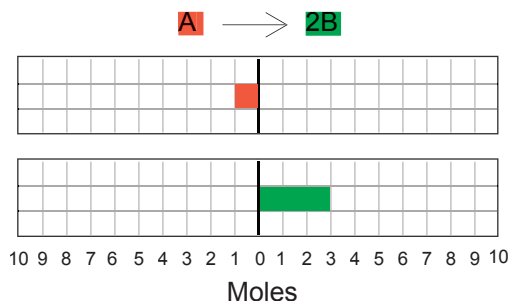
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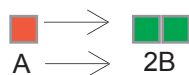
ChemLog STOICHIOMETRY

CHEMICAL REACTIONS

In the following reaction, one mole of reactant A goes to 2 moles of product B.



This can also be shown using “blocks” from the ChemLog.



► From the ChemLog, how many moles of B are formed for each mole of A that reacts? To answer this question, fill in the appropriate numbers in this sentence: _____ mole(s) of A react(s) to form _____ mole(s) of B.

► From the ChemLog, how many moles of A are needed to decompose for each mole of B produced? To answer this question, fill in the appropriate number in this sentence: For every _____ mole(s) of B that is formed, _____ mole(s) of A decomposed.

Another way to say this is that the ratio of moles of A to B is 1 to 2.



The ratio of moles of B to A is 2 to 1.

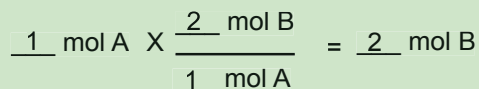


► We can use this ratio to answer the following question: when starting with one mole of A, how many moles of B will you obtain? Let's set this up mathematically.

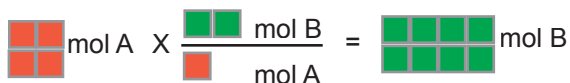


You might be wondering why we chose this ratio (with moles of B on top) rather than the other ratio. The trick is to remember to put the units you want (in our case, we want to get to moles of B) on top. In this example, moles of A cancels, and we're left with moles of B.

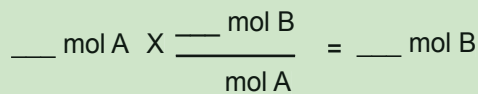
► We can answer this question simply by using numbers also. Notice that we get the same answer.



► Now try this one, when starting with four moles of A, how many moles of B will you obtain?



► Fill in the appropriate numbers for this reaction.



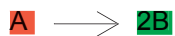
► Now try this one, when starting with 3 moles of A, how many moles of B will you obtain?

► When starting with one half a mole of A, how many moles of B will you obtain?

ChemLog STOICHIOMETRY

CHEMICAL REACTIONS

Let's continue working with the following reaction.



► Here's a slightly different, but similar question: when you get 2 moles of B from this reaction, how many moles of A did you start with? We'll go about answering it in the same manner.

$$2 \text{ mol B} \times \frac{1 \text{ mol A}}{2 \text{ mol B}} = 1 \text{ mol A}$$

Notice that we're using a different ratio here. Our answer needs to be in units of "mol A", so we use the appropriate ratio with moles of A on top.

► Fill in the appropriate numbers for this reaction.

$$\underline{\quad} \text{ mol B} \times \frac{\underline{\quad} \text{ mol A}}{\underline{\quad} \text{ mol B}} = \underline{\quad} \text{ mol A}$$

► When you get 6 moles of B from this reaction, how many moles of A did you start with?

$$6 \text{ mol B} \times \frac{1 \text{ mol A}}{2 \text{ mol B}} = 3 \text{ mol A}$$

► Fill in the appropriate numbers for this reaction.

$$\underline{\quad} \text{ mol B} \times \frac{\underline{\quad} \text{ mol A}}{\underline{\quad} \text{ mol B}} = \underline{\quad} \text{ mol A}$$

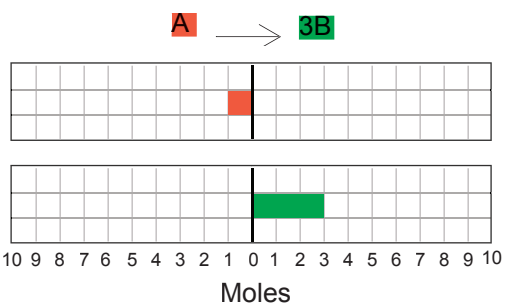
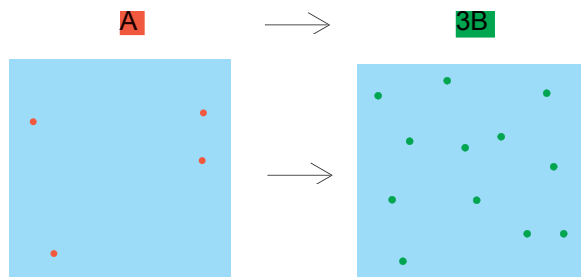
► When you get 3 moles of B from this reaction, how many moles of A did you start with?

► How many moles of B are produced in this reaction when you start with 3 moles of A?

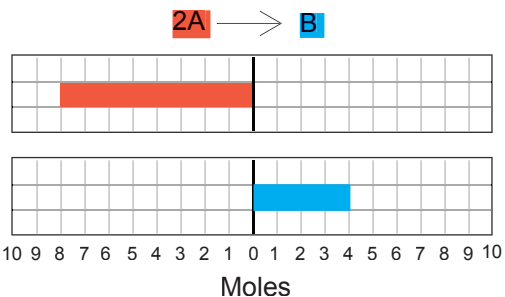
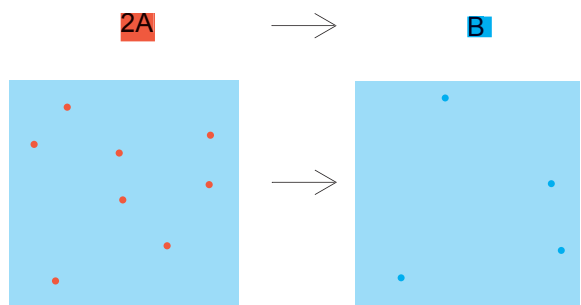
ChemLog STOICHIOMETRY

CHEMICAL REACTIONS

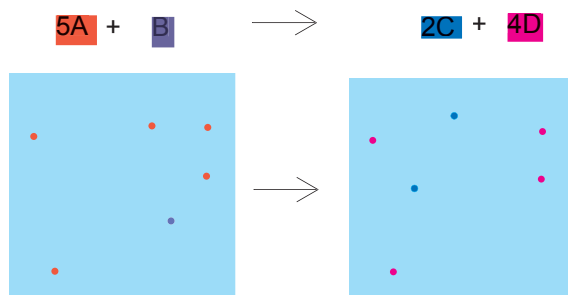
Here are some more practice questions.



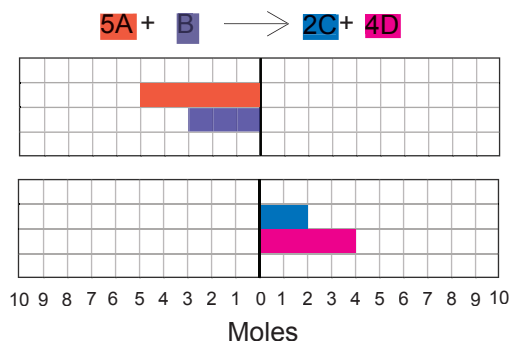
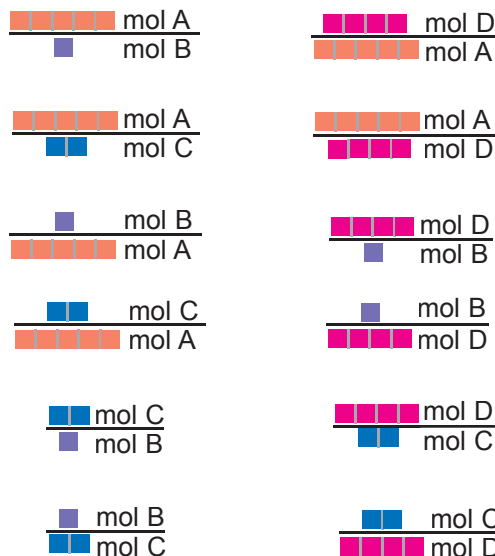
► How many moles of A will react to give 6 moles of B? Five moles of B?



► How much of the reactant is left after the reaction?
When 7 moles of A react, how many moles of product will be obtained? Three moles of B?



To help with answering the following questions, all the possible ratios are given.



► How much of the reactant(s) is left after the reaction?
When 2 moles of C are formed, how many moles of D are formed?
How many moles of C will form from 10 moles of A and 2 moles of B?
Challenge: How many moles of C will form from 10 moles of A and 1 mole of B?

ChemLog STOICHIOMETRY

MASS PERCENT

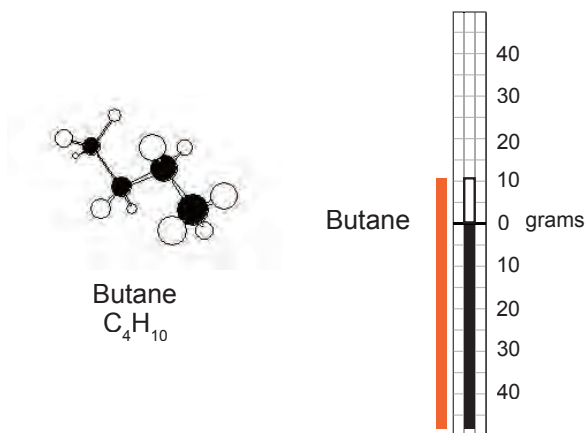
Determining the mass percent composition of a compound refers to the proportion of one element expressed as a percentage of the total mass of the compound.

Knowing the mass percent composition of a compound can help determine environmental effects from that compound. For example, carbon dioxide (CO₂) from burning fossil fuels may contribute to global warming. Methane (CH₄) and butane (C₄H₁₀) are both fossil fuels that, when burned, produce CO₂. Which one will produce less CO₂? Well, it's the one that contains the least amount of carbon as a percentage of the total compound. Let's use mass percent calculations to determine this.

$$\text{Mass Percent of Carbon (C)} = \frac{\text{Mass of Carbon (C)}}{\text{Total Mass of Compound}} \times 100 \%$$

First, let us determine the mass percent composition of carbon in butane.

█ total mass of butane
 mass of hydrogen in butane
 mass of carbon in butane



$$\text{Mass Percent of Carbon (C)} = \frac{4 \times 12.011 \text{ g C}}{(4 \times 12.011 \text{ g C}) + (10 \times 1.008 \text{ g H})} \times 100 \%$$

$$= \frac{48.044 \text{ g C}}{48.044 \text{ g C} + 10.080 \text{ g H}} \times 100 \%$$

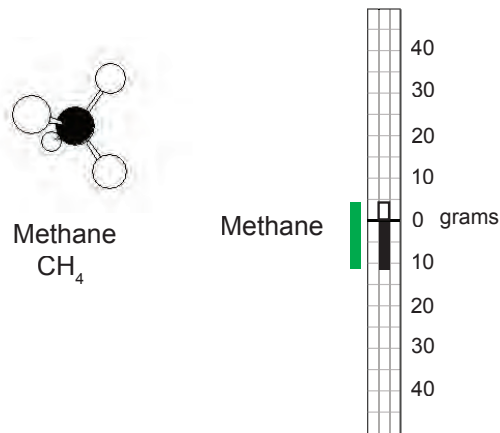
$$= \frac{48.044 \text{ g C}}{58.124 \text{ g C}_4\text{H}_{10}} \times 100 \%$$

$$= \frac{48.044 \text{ g C}}{58.124 \text{ g C}_4\text{H}_{10}} \times 100 \%$$

$$= 82.66 \%$$

Now, let's consider methane.

█ total mass of methane
 mass of hydrogen in methane
 mass of carbon in methane



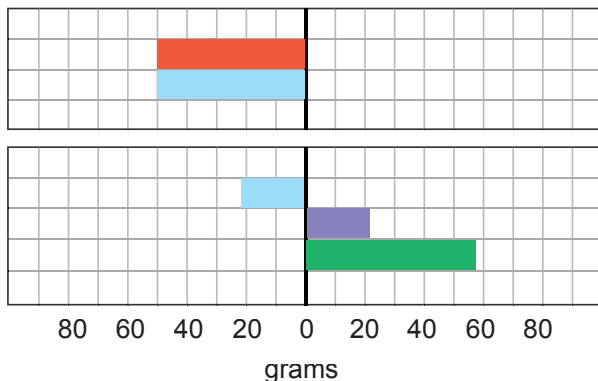
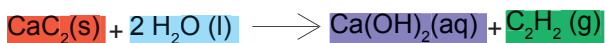
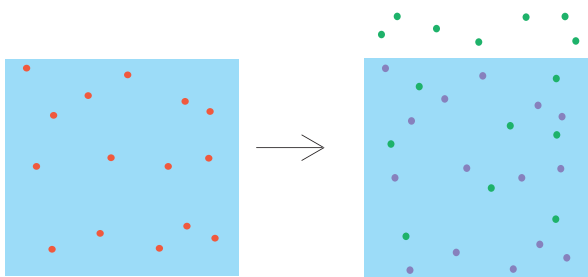
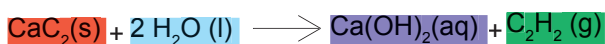
► Use the same technique to calculate the mass percent of carbon in methane.

► Which compound, methane or butane, contains a higher mass percent of carbon?
Which one will produce more CO₂ when burned?

ChemLog STOICHIOMETRY

LIMITING REACTANTS

When carrying out a chemical reaction, we may use the exact amount of each reactant needed. Or, we may use an excess of some reactants and a limited amount of others. We may do this if one reactant is very expensive and others are inexpensive so that we can use all of the expensive compound. It can be more cost effective, even if we are wasting money on the excess reactants. The reactant that governs the maximum yield of a product is the limiting reactant.



► Which is the limiting reactant when 100 g of water reacts with 100 g of calcium carbide?

First, determine the moles of each reactant that we start with.

$$\begin{aligned} \text{Moles of CaC}_2(\text{s}) &= 100 \text{ g CaC}_2(\text{s}) \times \frac{1 \text{ mol CaC}_2(\text{s})}{64.10 \text{ g CaC}_2(\text{s})} \\ &= 1.56 \text{ mol CaC}_2(\text{s}) \end{aligned}$$

$$\begin{aligned} \text{Moles of H}_2\text{O}(\text{l}) &= 100 \text{ g H}_2\text{O}(\text{l}) \times \frac{1 \text{ mol H}_2\text{O}(\text{l})}{18.02 \text{ g H}_2\text{O}(\text{l})} \\ &= 5.55 \text{ mol H}_2\text{O}(\text{l}) \end{aligned}$$

► How many moles of H₂O react with 1 mole CaC₂ in this reaction?

► Next, what is the amount of CaC₂ that is needed to react with 100 g of H₂O? Convert moles to grams.

$$5.55 \text{ mol H}_2\text{O}(\text{l}) \times \frac{1 \text{ mol CaC}_2(\text{s})}{2 \text{ mol H}_2\text{O}(\text{l})} = 2.78 \text{ mol CaC}_2(\text{s})$$

► Compare this answer with what we actually start with.

$$2.78 \text{ mol CaC}_2(\text{s}) > 1.56 \text{ mol CaC}_2(\text{s})$$

► What is the amount of H₂O that is needed to react with 100 g of CaC₂? Convert moles to grams.

$$1.56 \text{ mol CaC}_2(\text{s}) \times \frac{2 \text{ mol H}_2\text{O}(\text{l})}{1 \text{ mol CaC}_2(\text{s})} = 3.12 \text{ mol H}_2\text{O}(\text{l})$$

► Compare this answer with what we actually start with.

$$3.12 \text{ mol H}_2\text{O}(\text{l}) < 5.55 \text{ mol H}_2\text{O}(\text{l})$$

Because 3.12 mol H₂O is required and 5.55 mol H₂O is supplied, there is an excess of H₂O. So CaC₂(s) is the limiting reactant and all of it can react.

► Why is it always important to work in the unit of moles when determining limiting reactants? Why not grams or milliliters?

ChemLog STOICHIOMETRY

LIMITING REACTANTS

There's another way to determine the limiting reactant using the number of moles of a product that can be made from each reactant.

► How many moles of C_2H_2 is formed from one mole of CaC_2 ? How many moles of C_2H_2 is formed from one mole of H_2O ? Use this information to determine the number of moles of product that can be made from our starting quantities.

$$\begin{aligned} \text{Moles of } C_2H_2(\text{aq}) \text{ from } CaC_2(\text{s}) &= \\ 1.56 \text{ mol } CaC_2(\text{s}) \times \frac{1 \text{ mol } C_2H_2(\text{aq})}{1 \text{ mol } CaC_2(\text{s})} &= 1.56 \text{ mol } C_2H_2 \end{aligned}$$

$$\begin{aligned} \text{Moles of } C_2H_2(\text{aq}) \text{ from } H_2O(\text{l}) &= \\ 5.55 \text{ mol } H_2O(\text{l}) \times \frac{1 \text{ mol } C_2H_2(\text{aq})}{2 \text{ mol } H_2O(\text{l})} &= 2.78 \text{ mol } C_2H_2 \end{aligned}$$

► From this calculation, which reactant is the limiting reactant? Why?
Is it the limiting reactant that was determined previously?

► Determine which reactant is the limiting reactant when 40 g of magnesium and 20 g of nitrogen react in the following reaction:



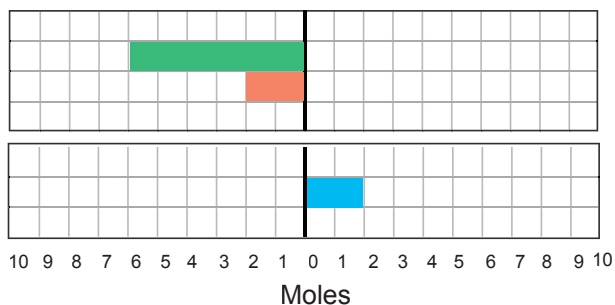
► How many moles of the limiting reactant are consumed by the reaction?
How many grams of the excess reactant are left after the reaction?

ChemLog STOICHIOMETRY

YIELDS

The theoretical yield is the maximum product that can be obtained from the amount (mass, moles, volume) of reactant(s) used. Calculate the maximum number of moles of product that can be obtained from the following reaction, when 13.45 g of N_2 reacts with 35 g of Mg.

*Always remember to check for limiting reactants!



The actual yield of a reaction is the amount (moles, volume, mass) of product obtained at the end of the reaction.

The percentage yield can be calculated by:

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

► In the reaction that forms magnesium nitride, the actual yield was 39.8 g. The theoretical yield was not obtained because the Mg was impure, meaning that when 35 g was weighed out, it was not all Mg (s). What is the percentage yield for this reaction?

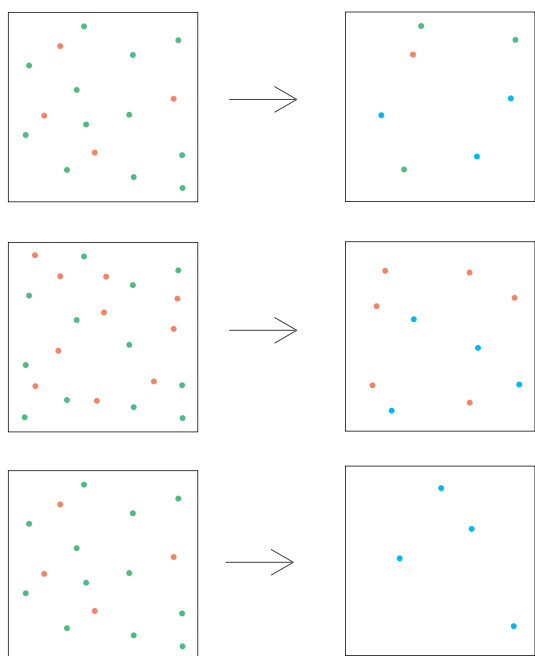
► Name three reasons that a chemist could obtain a yield less than the theoretical yield.

► Determine the theoretical yield for the reaction magnesium nitride reaction when 35 g of Mg reacts with 16 g of N_2 .

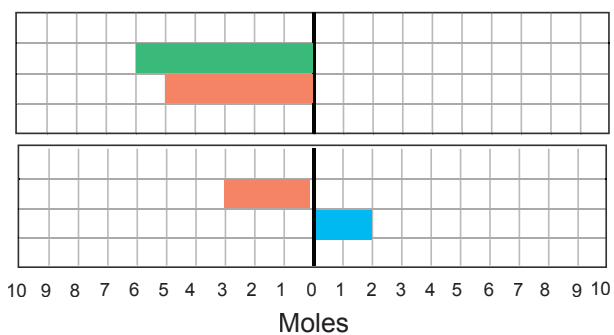
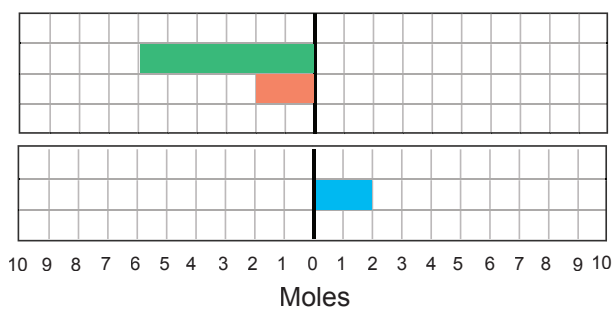
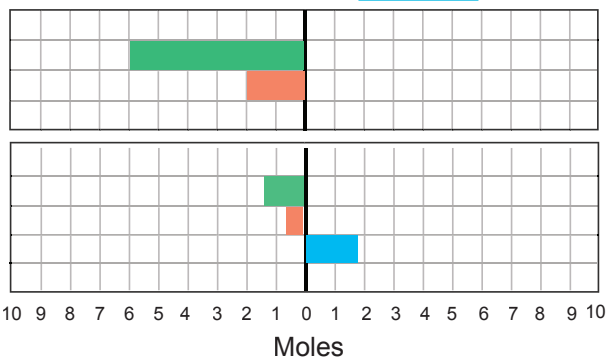
ChemLog STOICHIOMETRY

YIELDS

► Mark each set of pictures and each ChemLog as either showing a reaction that proceeded to the theoretical yield, the reaction which shows an actual yield, or the reaction which shows there was a limiting reactant.



► Connect the reaction pictures above with the ChemLog that each refers to.



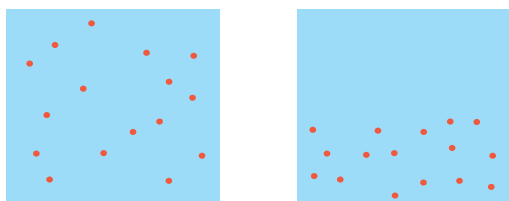
ChemLog STOICHIOMETRY

MOLARITY

A solution is a homogeneous (uniform in composition) mixture of two chemicals. The solute in a solution is the substance that is being dissolved. The solvent in a solution is the substance doing the dissolving.

Supposed we poured **sugar** into **water** to form a solution.

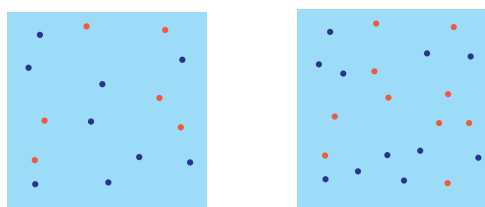
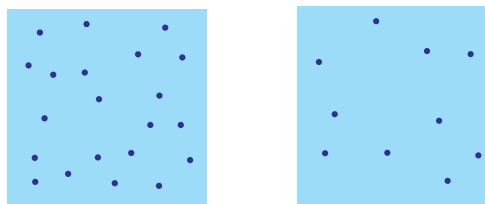
► Which of the following pictures would be an accurate representation of the sugar solution? Circle the solution



Chemists talk about the concentrations of solutions. The concentration of solution is the amount of solute per solvent. One way to state the concentration of a liquid solution is to state its molarity. Molarity is defined as the number of moles of solute per liter of solvent.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solvent}}$$

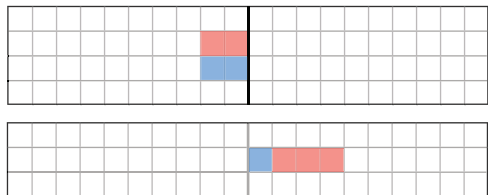
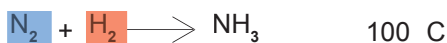
► Of the following pairs of pictures. Circle the picture which is most concentrated (the picture with the highest molarity).



ChemLog STOICHIOMETRY

BALANCING CHEMICAL REACTIONS

The numbers to the left of entire chemical formulas in a reaction are called the stoichiometric coefficients. A coefficient of one, as seen in the reaction below, is not written explicitly but is implied. When the number of atoms of each element on each side of the arrow are the same, the reaction is said to be balanced.



► Each block in ChemLog designates an element. Count the number of red elements before the reaction. Count the number of red elements after the reaction. Count the number of blue elements before the reaction. Count the number of blue elements after the reaction. Compare the number of red elements before and after the reaction. Compare the number of blue elements before and after the reaction.

Before Reaction

2

2

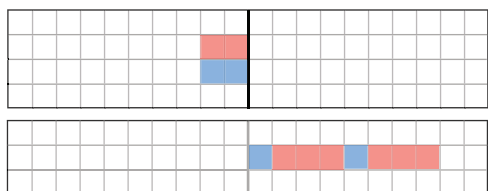
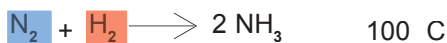
After Reaction

1

3

In order to balance the chemical reaction, we must make the number of blue elements before the reaction equal to the number of blue elements after the reaction. The same must be done for the red elements. Let's first begin with the products of the reaction. In order to make the number of blue blocks before and after the reaction equal, we need to double the blue blocks after the reaction. In doing that, we double the red blocks too.

► Notice that the amount of product has been doubled. Complete the following table using the ChemLog below.



Before Reaction

2

2

=

After Reaction

2 x 1

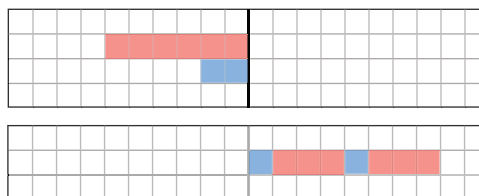
6



Notice the number in front of the product; this is called a stoichiometric coefficient. Since we doubled the number amount of product, we must show this in the chemical reaction using coefficients.

► The number of blue elements before and after the reaction is now equal. What can we do to make the number of red elements equal before and after the reaction?

Complete the following table using the ChemLog below.



Before Reaction

2

2 x 3

After Reaction

2

6

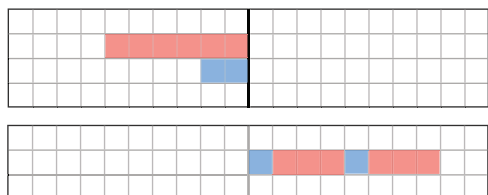


Notice that the coefficients are the numbers we multiplied by in order to gain the same number of blue boxes before and after the reaction and the same number of red boxes before and after the reaction.

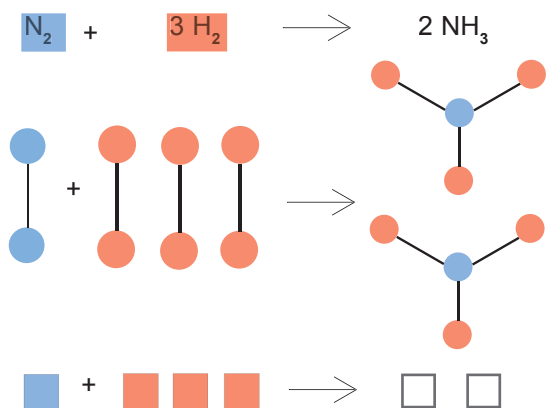
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MOLE-TO-MOLE CALCULATIONS

Using the chemical reaction we balanced previously, let's do some simple calculations with that information.

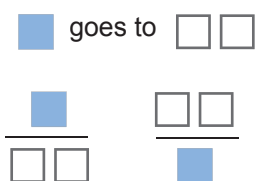


Here are a few ways to think about and visualize this reaction.



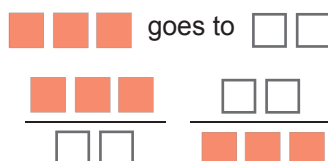
► How many moles of product can come from one mole of N_2 ?

To answer, just look at the fact given in the reaction. One mole of N_2 (along with something not important to answer the question) goes to two moles of NH_3 , the product.



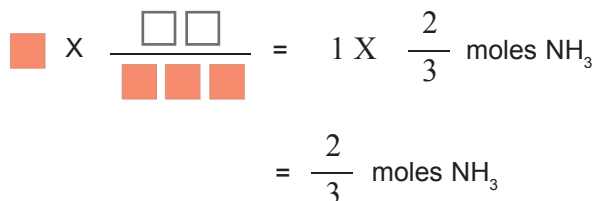
So, 2 moles of product can come from 1 mole of N_2 .

► How many moles of product can come from three moles of H_2 ?



► How many moles of product can come from one mole of H_2 ?

Since this question is more difficult and cannot be answered just by looking at the reaction, we'll use some simple math to figure it out.



Hint: Remember that the ratio we use has the number of moles of product (the thing we need to answer the question) on the top.

► How many moles of NH_3 can be made from four moles of N_2 ?

► Why must moles be used instead of molecules when answering this question? Try to figure out the number of molecules of product you would make when starting with one molecule of H_2 . Explain your answer.

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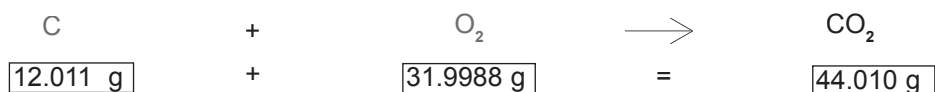
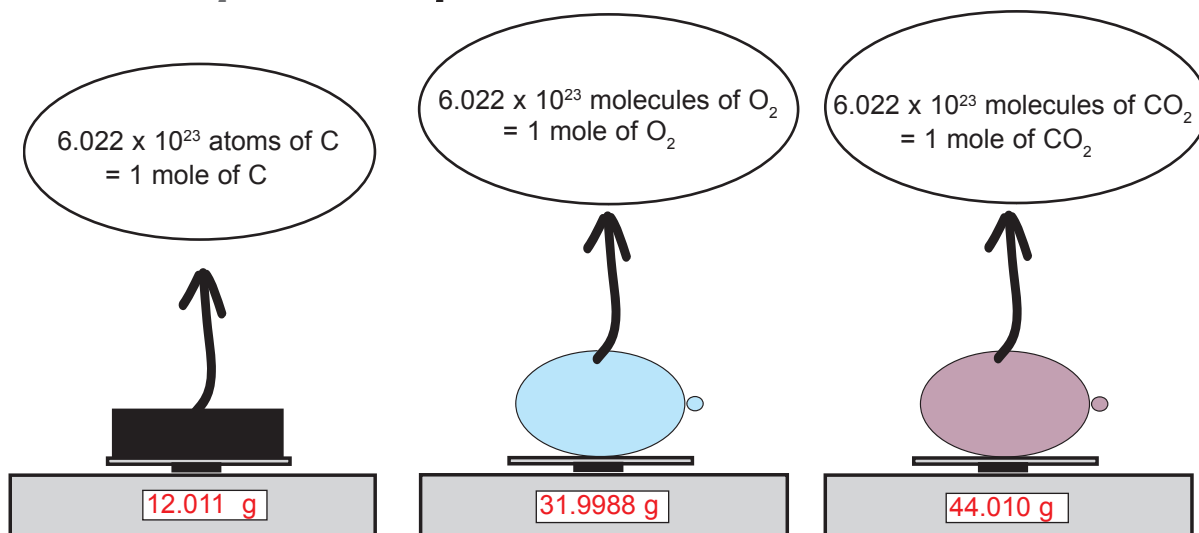
AVOGADRO'S NUMBER

Avogadro's number is the number of particles of substance in a mole. Just as 1 dozen means 12 of something, regardless of what it is - eggs, diamonds, molecules, 1 mole means 6.022×10^{23} of something. There are Avogadro's number, 6.022×10^{23} , of particles in every mole. That's a lot!

► How many atoms are in a mole of atoms?
How many molecules are in a mole of molecules?

► Since there are the same number of items in a mole, does a mole have a specific mass, say 5 grams? Why or why not?

Let's look at the following reaction of carbon oxygen to form carbon dioxide.



► What is the mass of 2 moles of C?
What is the mass of 0.5 moles of CO₂?
What is the mass of 1 mole of ozone, O₃?

You may be wondering, how scientists came up with Avogadro's number - 6.022×10^{23} isn't a number one normally thinks of off the top of one's head! Well, Amadeo Avogadro was not the first scientist who realized this number. However, he was the first scientist to sense the significance of the mole, so the number is named after him. Technically, a mole is an amount of substance that contains as many elementary entities as there are atoms in exactly 12 g of the carbon - 12 isotope.