INTERMEDIATE PHYSICAL ORGANIC (MORSCH)

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Morsch Intermediate Physical Organic

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CHAPTER OVERVIEW

1: Models of Chemical Bonding

SECTION OVERVIEW

1.1: Atomic and Molecular Properties

The atomic and molecular properties are the intrinsic features associated with the system at the atomic and sub-atomic level.

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1.1.1: Atomic and Ionic Radius

Atomic radii is useful for determining many aspects of chemistry such as various physical and chemical properties. The periodic table greatly assists in determining atomic radius and presents a number of trends.

Definition

Atomic radius is generally stated as being the total distance from an atom’s nucleus to the outermost orbital of electron. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change.

The effective nuclear charge Z_{eff} of an atom is the net positive charge felt by the valence electron. Some positive charge is shielded by the core electrons therefore the total positive charge is not felt by the valence electron. A detailed description of shielding and effective nuclear charge can be found here. Z_{eff} greatly affects the atomic size of an atom. So as the Z_{eff} decreases, the atomic radius will grow as a result because there is more screening of the electrons from the nucleus, which decreases the attraction between the nucleus and the electron. Since Z_{eff} decreases going down a group and right to left across the periodic table, the atomic radius will *increase* going down a group and right to left across the periodic table.

Types of Radius with Respect to Types of Bonds

Determining the atomic radii is rather difficult because there is an uncertainty in the position of the outermost electron – we do not know exactly where the electron is. This phenomenon can be explained by the Heisenberg Uncertainty Principle. To get a precise measurement of the radius, but still not an entirely correct measurement, we determine the radius based on the distance between the nuclei of two bonded atoms. The radii of atoms are therefore determined by the bonds they form. An atom will have different radii depending on the bond it forms; so there is no fixed radius of an atom.

Covalent Radius

When a covalent bond is present between two atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, but you want the radius which is half the diameter.

> Covalent radii will increase in the same pattern as atomic radii. The reason for this trend is that the bigger the radii, the further the distance between the two nuclei. See explanation for Z_{eff} for more details.

The covalent radius depicted below in Figure 1 will be the same for both atoms because they are of the same element as shown by X.

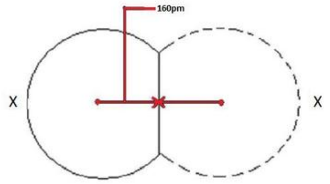


Figure 1: *Covalent radii*

Ionic Radius

The ionic radius is the radius of an atom forming ionic bond or an ion. The radius of each atom in an ionic bond will be different than that in a covalent bond. This is an important concept. The reason for the variability in radius is due to the fact that the atoms in an ionic bond are of greatly different size. One of the atoms is a cation, which is smaller in size, and the other atom is an anion which is a lot larger in size. So in order to account for this difference, one most get the total distance between the two nuclei and divide the distance according to atomic size. The bigger the atomic size, the larger radius it will have. This is depicted in Figure 2 as shown below where the cation is displayed on the left as X+, and clearly has a smaller radius than the anion, which is depicted as Y- on the right.

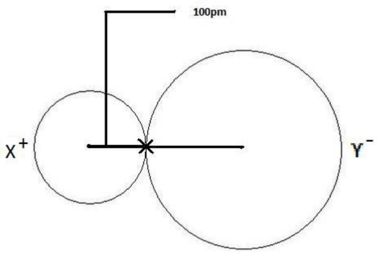


Figure 2: *Ionic radii*

Example 1: Cadmium Sulfide

If we were able to determine the atomic radius of an atom from experimentation, say Se, which had an atomic radius of 178 pm, then we could determine the atomic radius of any other atom bonded to Se by subtracting the size of the atomic radius of Se from the total distance between the two nuclei. So, if we had the compound CaSe, which had a total distance of 278 pm between the nucleus of the Ca atom and Se atom, then the atomic radius of the Ca atom will be 278 pm (total distance) - 178 pm (distance of Se), or 100 pm. This process can be applied to other examples of ionic radius.

Cations have **smaller** ionic radii than their neutral atoms. In contrast, anions have **bigger** ionic radii than their corresponding neutral atoms.

A detailed explanation is given below:

- The cation, which is an ion with a positive charge, by definition has fewer electrons than protons. The loss in an electron will consequently result in a change in atomic radii in comparison to the neutral atom of interest (no charge).
- The loss of an electron means that there are now more protons than electrons in the atom, which is stated above. This will cause a *decrease* in atomic size because there are now fewer electrons for the protons to pull towards the nucleus and will result in a stronger pull of the electrons towards the nucleus. It will also decrease because there are now less electrons in the outer shell, which will decrease the radius size.
- An analogy to this can be of a magnet and a metallic object. If ten magnets and ten metallic objects represent a neutral atom where the magnets are protons and the metallic objects are electrons, then removing one metallic object, which is like removing an electron, will cause the magnet to pull the metallic objects closer because of a decrease in number of the metallic objects. This can similarly be said about the protons pulling the electrons closer to the nucleus, which as a result *decreases* atomic size.

Figure 3 below depicts this process. A neutral atom X is shown here to have a bond length of 180 pm and then the cation X^+ is smaller with a bond length of 100 pm.

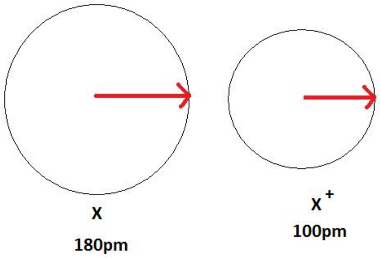


Figure 3: The ionic radius decreases for the generation of positive ions.

An **anion**, on the other hand, will be bigger in size than that of the atom it was made from because of a gain of an electron. This can be seen in the Figure 4 below. The gain of an electron adds more electrons to the outermost shell which *increases* the radius because there are now more electrons further away from the nucleus and there are more electrons to pull towards the nucleus so the pull becomes slightly weaker than of the neutral atom and causes an *increase* in atomic radius.

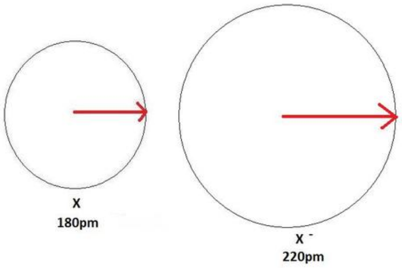


Figure 4: The ionic radius increases for the generation of negative ions.

Metallic Radius

The metallic radius is the radius of an atom joined by metallic bond. The metallic radius is half of the total distance between the nuclei of two adjacent atoms in a metallic cluster. Since a metal will be a group of atoms of the same element, the distance of each atom will be the same (Figure 5).

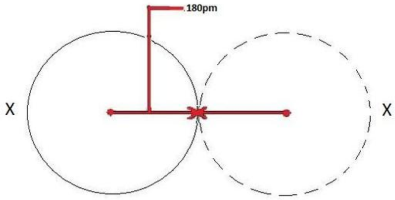


Figure 5: Metallic radii from metallic bonding

Periodic Trends of Atomic Radius

- An atom gets larger as the number of electronic shells increase; therefore the radius of atoms increases as you go down a certain group in the periodic table of elements.
- In general, the size of an atom will decrease as you move from left to the right of a certain period.

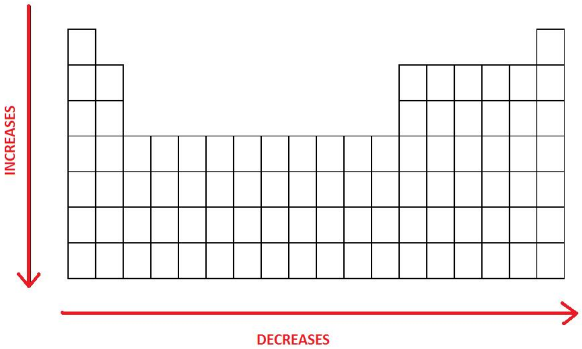
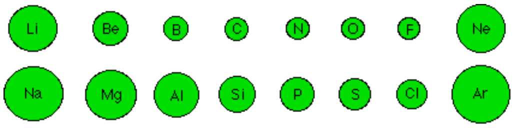


Figure 6: *Periodic Trend in atomic radii*

The exact pattern you get depends on which measure of atomic radius you use - but the trends are still valid. The following diagram uses metallic radii for metallic elements, covalent radii for elements that form covalent bonds, and van der Waals radii for those (like the noble gases) which don't form bonds.

Trends in atomic radius in Periods 2 and 3



Trends in atomic radius down a group

It is fairly obvious that the atoms get bigger as you go down groups. The reason is equally obvious - you are adding extra layers of electrons.

Trends in atomic radius across periods

You have to ignore the noble gas at the end of each period. Because neon and argon don't form bonds, you can only measure their van der Waals radius - a case where the atom is pretty well "unsquashed". All the other atoms are being measured where their atomic radius is being lessened by strong attractions. You aren't comparing like with like if you include the noble gases.

Leaving the noble gases out, atoms get smaller as you go across a period. If you think about it, the metallic or covalent radius is going to be a measure of the distance from the nucleus to the electrons which make up the bond. (Look back to the left-hand side of the first diagram on this page if you aren't sure, and picture the bonding electrons as being half way between the two nuclei.)

From lithium to fluorine, those electrons are all in the 2-level, being screened by the $1s^2$ electrons. The increasing number of protons in the nucleus as you go across the period pulls the electrons in more tightly. The amount of screening is constant for all of these elements.

In the period from sodium to chlorine, the same thing happens. The size of the atom is controlled by the 3-level bonding electrons being pulled closer to the nucleus by increasing numbers of protons - in each case, screened by the 1- and 2-level electrons.

Trends in the transition elements

Although there is a slight contraction at the beginning of the series, the atoms are all much the same size. The size is determined by the 4s electrons. The pull of the increasing number of protons in the nucleus is more or less offset by the extra screening due to the increasing number of 3d electrons.

Vertical Trend

The radius of atoms increases as you go down a certain group.

Horizontal Trend

The size of an atom will decrease as you move from left to the right of a period.

Ionic Radius

Ionic radii are difficult to measure with any degree of certainty, and vary according to the environment of the ion. For example, it matters what the co-ordination of the ion is (how many oppositely charged ions are touching it), and what those ions are. There are several different measures of ionic radii in use, and these all differ from each other by varying amounts. It means that if you are going to make reliable comparisons using ionic radii, they have to come from the same source.

What you have to remember is that there are quite big uncertainties in the use of ionic radii, and that trying to explain things in fine detail is made difficult by those uncertainties. What follows will be adequate for UK A level (and its various equivalents), but detailed explanations are too complicated for this level.

Trends in ionic radius in the Periodic Table

Trends in ionic radius down a group: This is the easy bit! As you add extra layers of electrons as you go down a group, the ions are bound to get bigger. The two tables below show this effect in Groups 1 and 7.

	electronic structure of ion	ionic radius (nm)
Li^+	2	0.076
Na^+	2, 8	0.102
K^+	2, 8, 8	0.138
Rb^+	2, 8, 18, 8	0.152
Cs^+	2, 8, 18, 18, 8	0.167

	electronic structure of ion	ionic radius (nm)
F^-	2, 8	0.133
Cl^-	2, 8, 8	0.181
Br^-	2, 8, 18, 8	0.196
I^-	2, 8, 18, 18, 8	0.220

Trends in ionic radius across a period

Let's look at the radii of the simple ions formed by elements as you go across Period 3 of the Periodic Table - the elements from Na to Cl.

	Na^+	Mg^{2+}	Al^{3+}		P^{3-}	S^{2-}	Cl^-
no of protons	11	12	13		15	16	17
electronic structure of ion	2,8	2,8	2,8		2,8,8	2,8,8	2,8,8
ionic radius (nm)	0.102	0.072	0.054		(0.212)	0.184	0.181

The table misses out silicon which does not form a simple ion. The phosphide ion radius is in brackets because it comes from a different data source, and I am not sure whether it is safe to compare it. The values for the oxide and chloride ions agree in the different source, so it is probably OK. The values are again for 6-co-ordination, although I can't guarantee that for the phosphide figure.

First of all, notice the big jump in ionic radius as soon as you get into the negative ions. Is this surprising? Not at all - you have just added a whole extra layer of electrons. Notice that, within the series of positive ions, and the series of negative ions, that the ionic radii fall as you go across the period. We need to look at the positive and negative ions separately.

- **The positive ions**: In each case, the ions have exactly the same electronic structure - they are said to be **isoelectronic**. However, the number of protons in the nucleus of the ions is increasing. That will tend to pull the electrons more and more towards the center of the ion - causing the ionic radii to fall. That is pretty obvious!
- **The negative ions:** Exactly the same thing is happening here, except that you have an extra layer of electrons. What needs commenting on, though is how similar in size the sulphide ion and the chloride ion are. The additional proton here is making hardly any difference.

The difference between the size of similar pairs of ions actually gets even smaller as you go down Groups 6 and 7. For example, the Te^{2-} ion is only 0.001 nm bigger than the I^- ion.

As far as I am aware there is no simple explanation for this - certainly not one which can be used at this level. This is a good illustration of what I said earlier - explaining things involving ionic radii in detail is sometimes very difficult.

Trends in ionic radius for some more isoelectronic ions

This is only really a variation on what we have just been talking about, but fits negative and positive isoelectronic ions into the same series of results. Remember that isoelectronic ions all have exactly the same electron arrangement.

	N^{3-}	O^{2-}	F^-		Na^+	Mg^{2+}	Al^{3+}
no of protons	7	8	9		11	12	13
electronic structure of ion	2, 8	2, 8	2, 8		2, 8	2, 8	2, 8
ionic radius (nm)	(0.171)	0.140	0.133		0.102	0.072	0.054

Note: The nitride ion value is in brackets because it came from a different source, and I don't know for certain whether it relates to the same 6-co-ordination as the rest of the ions. This matters. My main source only gave a 4-coordinated value for the nitride ion, and that was 0.146 nm.

You might also be curious as to how the neutral neon atom fits into this sequence. Its van der Waals radius is 0.154 or 0.160 nm (depending on which source you look the value up in) - bigger than the fluoride ion. You can't really sensibly compare a van der Waals radius with the radius of a bonded atom or ion.

References

1. Pauling, Linus. Atomic Radii and Interatomic Distances in Metal, *Journal of the American Chemical Society* 194769 (3), 542-553
2. Petrucci, Ralph H., William S. Harwood, Geoffery F. Herring, and Jeffry D. Madura. General Chemistry. 9th ed. New Jersey: Pearsin Prentice Hall, 2007.

Problems

1. Which atom is larger: K or Br?
2. Which atom is larger: Na or Cl?
3. Which atom is smaller: Be or Ba?
4. Which atom is larger: K^+ or K?
5. Put in order of largest to smallest: F, Ar, Sr, Cs.
6. Which has a bigger atomic radius: Sr^{2+} or Se^{2-}?
7. If Br has an ionic radius of 100 pm and the total distance between K and Br in KBr is 150 pm, then what is the ionic radius of K?
8. Which has a smaller atomic radius: Cs^+ or Xe?
9. If the distance between the nuclei of two atoms in a metallic bond is 180 pm, what is the atomic radius of one atom?
10. If Z effective is increasing, is the atomic radius also increasing?

Hint When solving a radius-bond problem, identify the bond first and then use the standard method of finding the radius for that particular bond. Also remember the trend for the atomic radii.

Answers

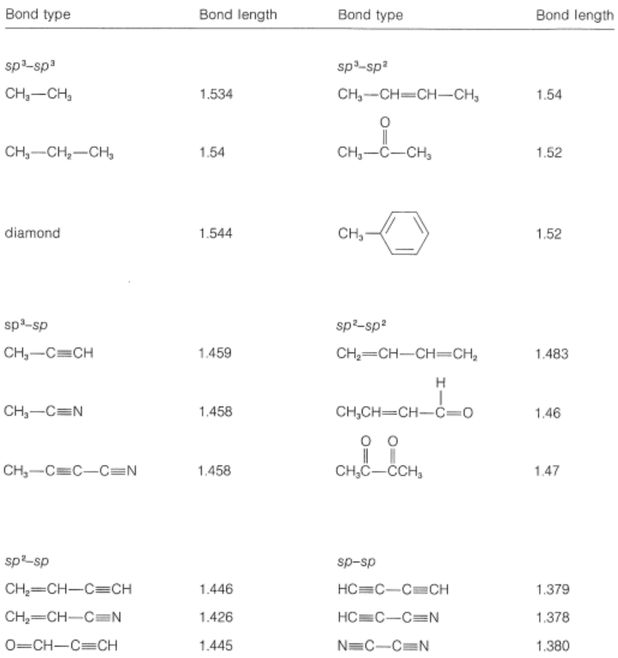
1. K
2. Na
3. Be
4. K
5. Cs, Sr, Ar, F
6. Se^{2-}
7. 50 pm
8. Cs^+
9. 90 pm

10. No

1.1.2: Bond Lengths and Double-Bond Character

Bond lengths frequently are cited as evidence for, or against, electron delocalization, although some caution should be exercised in this respect. For instance, if the hybrid structure of benzene is considered to be represented by the two possible Kekule structures, then each carbon-carbon bond should be halfway between a single bond and a double bond. In other words, each should possess 50% *double-bond character*. We then may expect the carbon-carbon bond lengths for benzene to be the average of single- and double-bond lengths. However, the average of the $C-C$ bond in ethane $(1.534\ \text{Å})$ and in ethene $(1.337\ \text{Å})$ is $1.436\ \text{Å}$, which does not agree well with the measured $C-C$ bond distance for benzene of $1.397\ \text{Å}$. The discrepancy lies largely in the assumption inherent in this crude calculation that, in the absence of resonance, all $C-C$ single bonds are equal to $1.534\ \text{Å}$. Clearly, this is not a valid assumption because, as we have seen, bond energies depend upon environment, and because the energy of a bond depends upon its length (see Figure 21-1), bond lengths also must vary with environment. This can be seen from the data in Table 21-3, which gives the carbon-carbon *single* bond lengths for several compounds. The single bonds shorten as the other bonds to carbon become progressively unsaturated, that is, as the hybridization of carbon changes from sp^3 to sp. Admittedly, some of this shortening may be ascribed to resonance, but not all.

Table 21-3: *Carbon-Carbon Single-Bond Distances (Å)*



Bond type	Bond length	Bond type	Bond length
sp^3–sp^3		sp^3–sp^2	
CH_3-CH_3	1.534	$CH_3-CH=CH-CH_3$	1.54
$CH_3-CH_2-CH_3$	1.54	$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	1.52
diamond	1.544	CH_3-	1.52
sp^3–sp		sp^2–sp^2	
$CH_3-C\equiv CH$	1.459	$CH_2=CH-CH=CH_2$	1.483
$CH_3-C\equiv N$	1.458	$CH_3CH=CH-\overset{H}{\overset{\vert}{C}}=O$	1.46
$CH_3-C\equiv C-C\equiv N$	1.458	$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3$	1.47
sp^2–sp		sp–sp	
$CH_2=CH-C\equiv CH$	1.446	$HC\equiv C-C\equiv CH$	1.379
$CH_2=CH-C\equiv N$	1.426	$HC\equiv C-C\equiv N$	1.378
$O=CH-C\equiv CH$	1.445	$N\equiv C-C\equiv N$	1.380

If we take $1.48\ \text{Å}$ as a reasonable $C-C$ bond distance between two sp^2-hybridized carbons and $1.34\ \text{Å}$ for $C=C$ bonds (see Table 2-1), the average is $1.41\ \text{Å}$, which is not much different from the $1.40\ \text{Å}$ for the carbon-carbon bonds in benzene.

1.1.2.1: Contributors and Attributions

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

1.1.3: Dipole Moments

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\,m$). The dipole moment of a molecule can be calculated by Equation 1.1.3.1:

$$\vec{\mu} = \sum_i q_i\,\vec{r}_i \tag{1.1.3.1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the i^{th} charge, and
- $\vec{r}_i$ is the vector representing the position of i^{th} charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is H_2O. Because of the lone pair on oxygen, the structure of H_2O is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

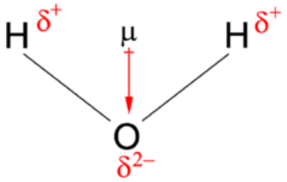


Figure 1.1.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 1.1.3.2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 1.1.3.2).

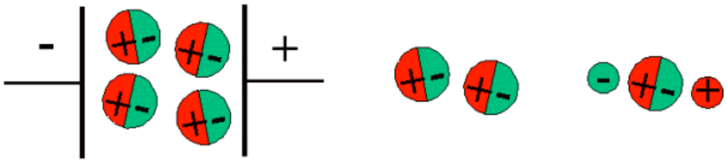


Figure 1.1.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 1.1.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{1.1.3.2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 1.1.3.2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\, C \cdot m) \left(\frac{1\ D}{3.336 \times 10^{-30}\, C \cdot m} \right) \\ &= 4.80\ D \end{aligned}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\, D \tag{1.1.3.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\, D \tag{1.1.3.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\, D \tag{1.1.3.5}$$

✓ Example 1.1.3.1: Water

The water molecule in Figure 1.1.3.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

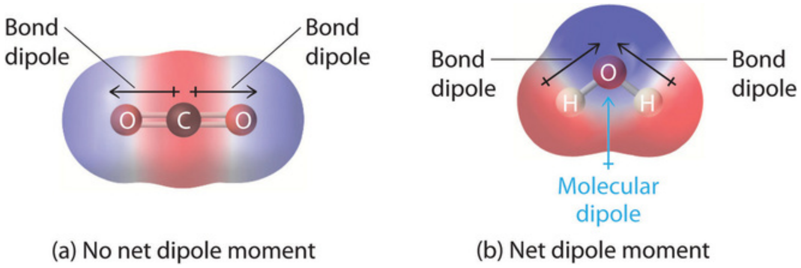


Figure 1.1.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure $1.1.3.3a$). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

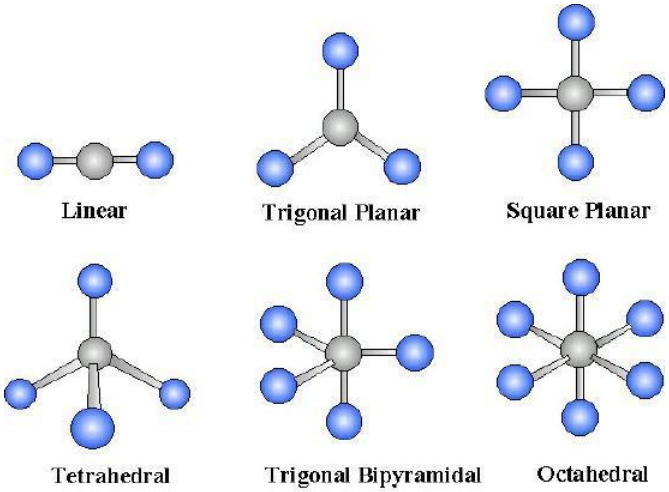
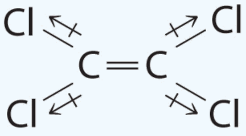


Figure 1.1.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

✓ Example 1.1.3.3: C_2Cl_4

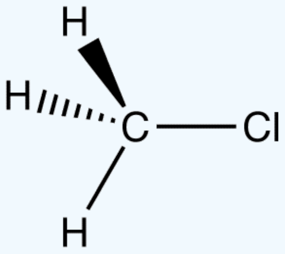
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 1.1.3.3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\begin{aligned}\mu &= \frac{178}{100}(4.80\ D)\\ &= 8.54\ D\end{aligned}$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table 1.1.3.1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

1. *Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)*
2. *Tro, Nivaldo J. Chemistry: A Molecular Approach. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)*

1.1.4: Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used.

Linus Pauling described electronegativity as “the power of an atom in a molecule to attract electrons to itself.” Basically, the electronegativity of an atom is a relative value of that atom's ability to attract election density toward itself when it bonds to another atom. The higher the electronegativity of an element, the more that atom will attempt to pull electrons towards itself and away from any atom it bonds to. The main properties of an atom dictate it's electronegativity are it's atomic number as well as its atomic radius. The trend for electronegativity is to increase as you move from left to right and bottom to top across the periodic table. This means that the most electronegative atom is Fluorine and the least electronegative is Francium. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to Cesium and Francium which are the least electronegative at 0.7.

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms:

To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules. **Note:** It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

What if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.

That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.

If B is a lot more electronegative than A, then the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. The bond is then an ionic bond rather than a covalent bond.

A "spectrum" of bonds

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Example 1: Polar Bonds vs. Polar Molecules

In a simple diatomic molecule like HCl, if the bond is polar, then the whole molecule is polar. What about more complicated molecules?

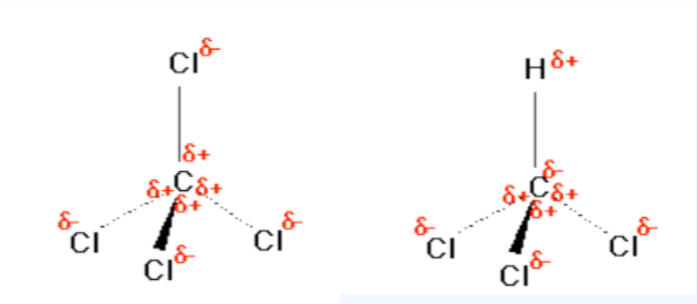


Figure 1.1.4.1: (left) CCl_4 (right) $CHCl_3$

Consider CCl_4, (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Patterns of electronegativity in the Periodic Table

The distance of the electrons from the nucleus remains relatively constant in a periodic table row, but not in a periodic table column. The force between two charges is given by Coulomb's law.

$$F = k\frac{Q_1Q_2}{r^2} \tag{1.1.4.1}$$

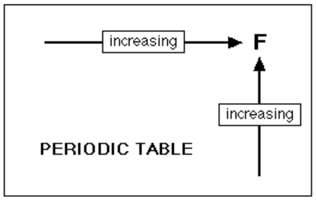
In this expression, Q represents a charge, k represents a constant and r is the distance between the charges. When r = 2, then r^2= 4. When r = 3, then r^2 = 9. When r = 4, then r^2 = 16. It is readily seen from these numbers that, as the distance between the charges increases, the force decreases very rapidly. This is called a quadratic change.

The result of this change is that electronegativity increases from bottom to top in a column in the periodic table even though there are more protons in the elements at the bottom of the column. Elements at the top of a column have greater electronegativities than elements at the bottom of a given column.

The overall trend for electronegativity in the periodic table is diagonal from the lower left corner to the upper right corner. Since the electronegativity of some of the important elements cannot be determined by these trends (they lie in the wrong diagonal), we have to memorize the following order of electronegativity for some of these common elements.

F > O > Cl > N > Br > I > S > C > H > metals

The most electronegative element is fluorine. If you remember that fact, everything becomes easy, because electronegativity must always increase towards fluorine in the Periodic Table.

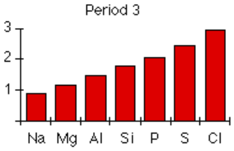


Note

This simplification ignores the noble gases. Historically this is because they were believed not to form bonds - and if they do not form bonds, they cannot have an electronegativity value. Even now that we know that some of them do form bonds, data sources still do not quote electronegativity values for them.

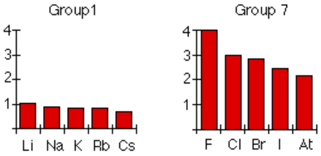
Trends in electronegativity across a period

The positively charged protons in the nucleus attract the negatively charged electrons. As the number of protons in the nucleus increases, the electronegativity or attraction will increase. Therefore electronegativity **increases** from **left to right** in a row in the periodic table. This effect only holds true for a row in the periodic table because the attraction between charges falls off rapidly with distance. The chart shows electronegativities from sodium to chlorine (ignoring argon since it does not does not form bonds).



Trends in electronegativity down a group

As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.



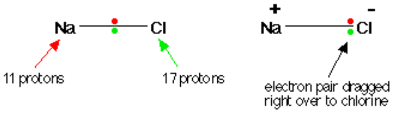
Explaining the patterns in electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Why does electronegativity increase across a period?

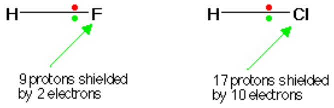
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.



Both sodium and chlorine have their bonding electrons in the 3-level. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed. Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

Why does electronegativity fall as you go down a group?

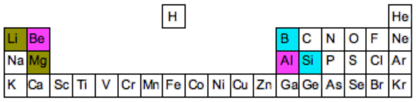
As you go **down** a group, electronegativity **decreases** because the bonding pair of electrons is increasingly distant from the attraction of the nucleus. Consider the hydrogen fluoride and hydrogen chloride molecules:



The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^22s^22p^6$ electrons. In each case there is a net pull from the center of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather than the 3-level as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

Diagonal relationships in the Periodic Table

At the beginning of periods 2 and 3 of the Periodic Table, there are several cases where an element at the top of one group has some similarities with an element in the next group. Three examples are shown in the diagram below. Notice that the similarities occur in elements which are diagonal to each other - not side-by-side.



For example, boron is a non-metal with some properties rather like silicon. Unlike the rest of Group 2, beryllium has some properties resembling aluminum. And lithium has some properties which differ from the other elements in Group 1, and in some ways resembles magnesium. There is said to be a diagonal relationship between these elements. There are several reasons for this, but each depends on the way atomic properties like electronegativity vary around the Periodic Table. So we will have a quick look at this with regard to electronegativity - which is probably the simplest to explain.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. So, for example, the electronegativities of beryllium and boron are:

Be	1.5
B	2.0

Electronegativity falls as you go down the Periodic Table. So, for example, the electronegativities of boron and aluminum are:

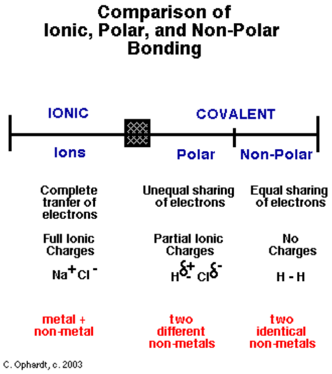
B	2.0
Al	1.5

So, comparing Be and Al, you find the values are (by chance) exactly the same. The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminum. Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8). In these cases, the electronegativities are not exactly the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry. You may well come across examples of this later on in your course.

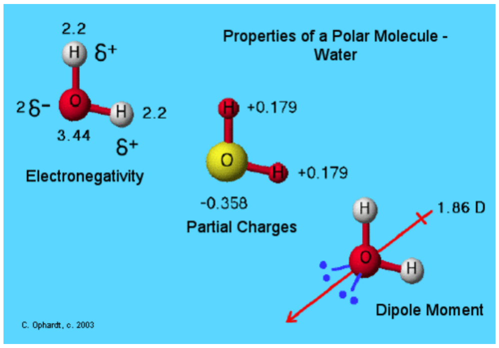
1.1.5: Molecular Polarity

Polarity is a physical property of compounds which relates other physical properties such as melting and boiling points, solubility, and intermolecular interactions between molecules. For the most part, there is a direct correlation between the polarity of a molecule and number and types of polar or non-polar covalent bonds which are present. In a few cases, a molecule may have polar bonds, but in a symmetrical arrangement which then gives rise to a non-polar molecule such as carbon dioxide.



Polarity - Dipole

Polarity results from the uneven partial charge distribution between various atoms in a compound. Atoms, such as nitrogen, oxygen, and halogens, that are more electronegative have a tendency to have partial negative charges. Atoms, such as carbon and hydrogen, have a tendency to be more neutral or have partial positive charges. Electrons in a polar covalent bond are unequally shared between the two bonded atoms, which results in partial positive and negative charges. The separation of the partial charges creates a dipole. The word dipole means two poles: the separated partial positive and negative charges. A polar molecule results when a molecule contains polar bonds in an unsymmetrical arrangement.



Nonpolar molecules are of two types. Molecules whose atoms have equal or nearly equal electronegativities have zero or very small dipole moments. A second type of nonpolar molecule has polar bonds, but the molecular geometry is symmetrical allowing the bond dipoles to cancel each other out.

Let's go back to that first ion pair which was formed when the positive ion and the negative ion came together. If the electronegativities of the elements are sufficiently different (like an alkali metal and a halide), the charges on the paired ions will not change appreciably - there will be a full electron charge on the blue ion and a full positive charge on the red ion. The bond formed by the attraction of these opposite charges is called an ionic bond. If the difference in electronegativity is not so great, however, there will be some degree of sharing of the electrons between the two atoms. The result is the same whether two ions come together or two atoms come together:

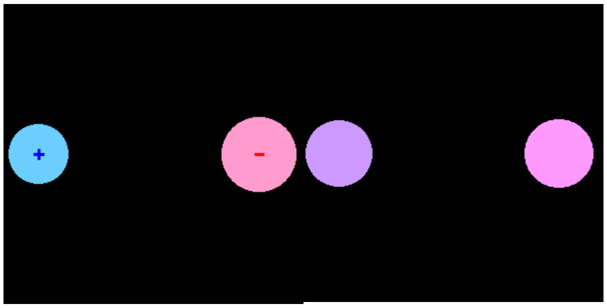


Figure 1.1.5.1: Polar Molecule

The combination of atoms or ions is no longer a pair of ions, but rather a polar molecule which has a measureable dipole moment. The dipole moment (D) is defined as if there were a positive (+q) and a negative (-q) charge separated by a distance (r):

$$D = qr \tag{1.1.5.1}$$

If there is no difference in electronegativity between the atoms (as in a diatomic molecule such as O_2 or F_2) there is no difference in charge and no dipole moment. The bond is called a covalent bond, the molecule has no dipole moment, and the molecule is said to be non-polar. Bonds between different atoms have different degrees of ionicity depending on the difference in the electronegativities of the atoms. The degree of ionicity may range from zero (for a covalent bond between two atoms with the same electronegativity) to one (for an ionic bond in which one atom has the full charge of an electron and the other atom has the opposite charge).

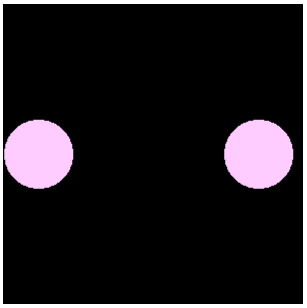


Figure 1.1.5.1: Non-polar Molecule

In some cases, two or more partially ionic bonds arranged symmetrically around a central atom may mutually cancel each other's polarity, resulting in a non-polar molecule. An example of this is seen in the carbon tetrachloride (CCl_4) molecule. There is a substantial difference between the electronegativities of carbon (2.55) and chlorine (3.16), but the four chlorine atoms are arranged symmetrically about the carbon atom in a tetrahedral configuration, and the molecule has zero dipole moment. Saturated hydrocarbons (C_nH_{n+2}) are non-polar molecules because of the small difference in the electronegativities of carbon and hydrogen plus the near symmetry about each carbon atom.

Contributors and Attributions

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1.2: Intermolecular Forces - Introduction and London Dispersion

Intermolecular forces are forces between molecules. Depending on its strength, intermolecular forces cause the forming of three physical states: solid, liquid and gas. The physical properties of melting point, boiling point, vapor pressure, evaporation, viscosity, surface tension, and solubility are related to the strength of attractive forces between molecules. These attractive forces are called Intermolecular Forces or Van der Waals forces.

Introduction

There are four types of intermolecular forces. The weakest of these are induced dipole forces (London Dispersion Forces). Most of the intermolecular forces are similar to bonding between atoms in a single molecule. Intermolecular forces just extend the thinking to forces between molecules and follows the patterns already set by the bonding within molecules.

Induced Dipole - London Dispersion Forces

London Dispersion Force is the weakest intermolecular force. It is the only attractive interaction between two nonpolar molecules.

The chance that an electron of an atom is in a certain area in the electron cloud at a specific time is called the "electron charge density." Since there is no way of knowing exactly where the electron is located and since they do not all stay in the same area 100 percent of the time, if the electrons all go to the same area at once, a dipole is formed momentarily. Even if a molecule is nonpolar, this displacement of electrons causes a nonpolar molecule to become polar for a moment, this is called an instantaneous dipole.

Since the molecule is now polar, this means that all the electrons are concentrated at one end and the molecule is partially negatively charged on that end. This negative end makes the surrounding molecules have an instantaneous dipole also, attracting the surrounding molecules' positive ends. This process is known as the London Dispersion Force of attraction.

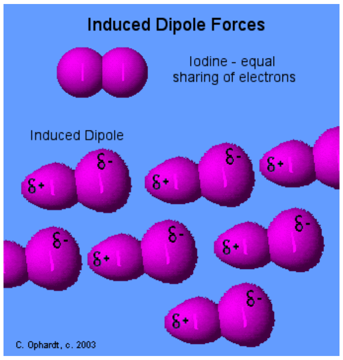


Figure 1: Induced dipoles between iodine molecules.

The ability of a molecule to become polar and displace its electrons is known as the molecule's "polarizability." The more electrons a molecule contains, the higher its ability to become polar. Polarizability increases in the periodic table from the top of a group to the bottom and from right to left within periods. This is because the higher the molecular mass, the more electrons an atom has. With more electrons, the outer electrons are easily displaced because the inner electrons shield the nucleus' positive charge from the outer electrons..

When the molecules become polar, the melting and boiling points are raised because it takes more heat and energy to break these intermolecular forces. Therefore, the greater the mass, the more electrons present, and the more electrons present, the higher the melting and boiling points of these substances.

London dispersion forces are stronger in those molecules that are not compact, but long chains of elements. This is because these molecules have greater surface area and therefore have more points of contact to interact with other molecules.

We can calculate the potential energy between the two identical nonpolar molecules using the following formula:

$$V = -\frac{3}{4}\frac{\alpha^2 I}{r^6} \tag{2}$$

- α is the polarizability of nonpolar molecule.

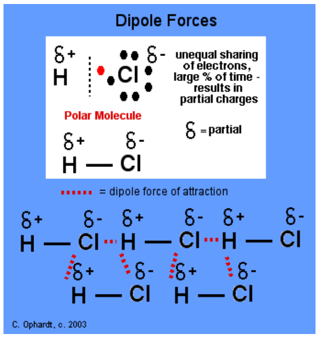
- r is the distance between the two molecule.
- I = the first ionization energy of the molecule.

Negative sign indicates the attractive interaction.

Dipole Forces

Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule. Those atoms that are more electronegative pull the bonded electrons closer to themselves. The buildup of electron density around an atom or discreet region of a molecule can result in a molecular dipole in which one side of the molecule possesses a partially negative charge and the other side a partially positive charge. Molecules with dipoles that are not canceled by their molecular geometry are said to be polar.

In the figure below, hydrochloric acid is a polar molecule with the partial positive charge on the hydrogen and the partial negative charge on the chlorine. A network of partial + and - charges attract molecules to each other.



$$V = -\frac{3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{r^6} \tag{3}$$

Dipole-Dipole Interactions

When a polar molecule encounters another polar molecule, the positive end of one molecule is attracted to the negative end of the other polar molecule. Many molecules have dipoles, and their interaction occur by dipole-dipole interaction. For example: $SO_2 \leftrightarrow SO_2$. (approximate energy: 15 kJ/mol). Polar molecules have permanent dipole moments, so in this case, we consider the electrostatic interaction between the two dipoles:

$$V = -\frac{2}{3}\frac{\mu_1^2 \mu_2^2}{(4\pi\epsilon_0)^2 r^6} \tag{4}$$

μ is the permanent dipole moment of the molecule 1 and 2.

Ion-Dipole Interactions

Ion-Dipole interaction is the interaction between an ion and polar molecules. For example, the sodium ion/water cluster interaction is approximately 50 KJ/mol.

$$Na^+ \leftrightarrow (OH_2)_n \tag{5}$$

Because the interaction involves in the charge of the ion and the dipole moment of the polar molecules, we can calculate the potential energy of interaction between them using the following formula:

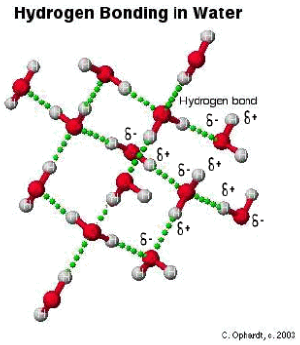
$$V = -\frac{q\mu}{(4\pi\epsilon_0)r^2} \tag{6}$$

- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- μ is the permanent dipole moment of the polar molecule.

Hydrogen Bonding

The hydrogen bond is really a special case of dipole forces. A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine. In other words - The hydrogen on one molecule attached to O or N that is attracted to an O or N of a different molecule.

In the graphic below, the hydrogen is partially positive and attracted to the partially negative charge on the oxygen or nitrogen. Because oxygen has two lone pairs, two different hydrogen bonds can be made to each oxygen. This is a very specific bond as indicated. Some combinations that are not hydrogen bonds include: hydrogen to another hydrogen or hydrogen to a carbon.



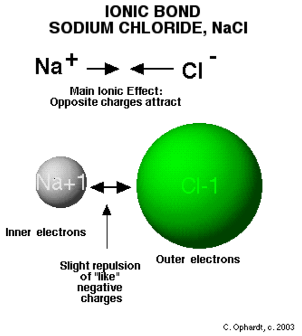
Coulombic Forces

The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. Ionic forces hold many ions in a crystal lattice structure. According to Coulomb's law:

$$V = -\frac{q_1 q_2}{4\pi\epsilon r} \tag{1}$$

- q is the charges.
- r is the distance of separation.

Based on Coulomb's law, we can find the potential energy between different types of molecules.



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SECTION OVERVIEW

1.2.1: Specific Interactions

Intermolecular forces are forces of attraction or repulsion which act between neighboring particles (atoms, molecules or ions). They are weak compared to the intramolecular forces, which keep a molecule together (e.g., covalent and ionic bonding).

Topic hierarchy

1.2.2: Hydrogen Bonding

A hydrogen bond is a special type of dipole-dipole attraction which occurs when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. These bonds are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

Introduction

For a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is the atom to which the hydrogen atom participating in the hydrogen bond is covalently bonded, and is usually a strongly electronegative atom such as N, O, or F. The hydrogen acceptor is the neighboring electronegative ion or molecule, and must posses a lone electron pair in order to form a hydrogen bond.

Since the hydrogen donor is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor, and the lone electron pair on the acceptor.

Types of hydrogen bonds

Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules.

- **Intramolecular hydrogen bonds**: Intramolecular hydrogen bonds are those which occur within one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor an acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.
- **Intermolecular hydrogen bonds**: Intermolecular hydrogen bonds occur between separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present an in positions in which they can interact. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.

Properties and effects of hydrogen bonds

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces. Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

We see that H_2O, HF, and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O, HF, and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF, but partakes in more hydrogen bonds per molecule, so its boiling point is consequently higher.

Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the viscosity of certain substances. Those substances which are capable of forming hydrogen bonds tend to have a higher viscosity than those that do not. Substances which have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

- **Electronegativity**: Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3, which no not partake in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammmonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, no dipole moment occurs. This prevents the hydrogen bonding from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule (see Polarizability)
- **Atom Size**: The size of donors and acceptors can also effect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve

close proximity when they interact, resulting in a weak interaction.

Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the unusual properties of water. In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain which comprises the wall of plant cells. This creates a sort of capillary tube which allows for capillary action to occur since the vessel is relatively small. This mechanism allows plants to pull water up into their roots. Furthermore,hydrogen bonding can create a long chain of water molecules which can overcome the force of gravity and travel up to the high altitudes of leaves.

Proteins

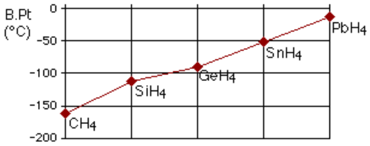
Hydrogen bonding is present abundantly in the secondary structure of proteins, and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain Nitrogen-Hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and visa-versa. Though they are relatively weak,these bonds offer great stability to secondary protein structure because they repeat a great number of times.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe and further reinforce conformation.

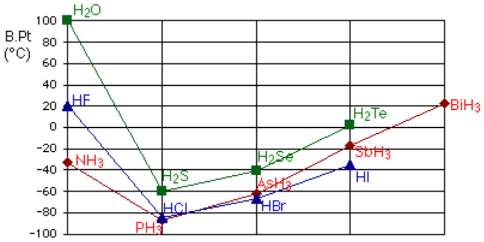
This page explains the origin of hydrogen bonding - a relatively strong form of intermolecular attraction.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the Group 4 elements with hydrogen, you find that the boiling points increase as you go down the group.



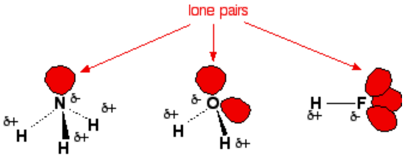
The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in Groups 5, 6 and 7 with hydrogen, something odd happens.



Although for the most part the trend is exactly the same as in group 4 (for exactly the same reasons), the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break. These relatively powerful intermolecular forces are described as hydrogen bonds.

The origin of hydrogen bonding

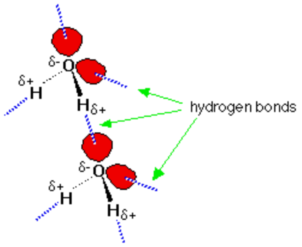
The molecules which have this extra bonding are:



The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you. Notice that in each of these molecules:

- The hydrogen is attached directly to one of the most electronegative elements, causing the hydrogen to acquire a significant amount of positive charge.
- Each of the elements to which the hydrogen is attached is not only significantly negative, but also has at least one "active" lone pair.
- Lone pairs at the 2-level have the electrons contained in a relatively small volume of space which therefore has a high density of negative charge. Lone pairs at higher levels are more diffuse and not so attractive to positive things.

Consider two water molecules coming close together.

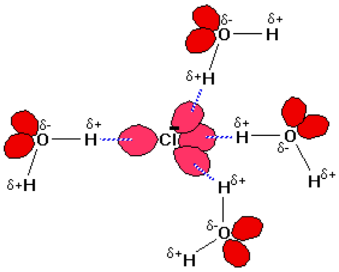


The $\delta+$ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are being constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water as a "perfect" example of hydrogen bonding

Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules. There are exactly the right numbers of $\delta+$ hydrogens and lone pairs so that every one of them can be involved in hydrogen bonding. This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there aren't enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, there are exactly the right number of each. Water could be considered as the "perfect" hydrogen bonded system.

The diagram shows the potential hydrogen bonds formed to a chloride ion, Cl^-. Although the lone pairs in the chloride ion are at the 3-level and wouldn't normally be active enough to form hydrogen bonds, in this case they are made more attractive by the full negative charge on the chlorine.

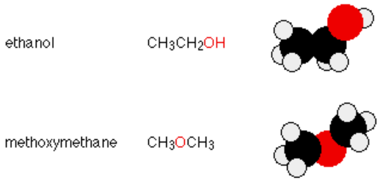


However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -O-H group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Such molecules will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier", and more heat is necessary to separate them.

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.



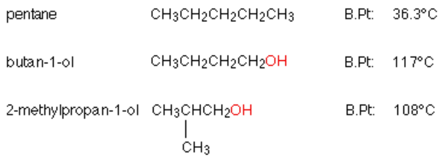
They have the same number of electrons, and a similar length to the molecule. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be much the same. However, ethanol has a hydrogen atom attached directly to an oxygen - and that oxygen still has exactly the same two lone pairs as in a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient δ+ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens aren't sufficiently δ+ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)		78.5°C
methoxymethane (without hydrogen bonding)		-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C.

It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two are much the same length. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



pentane	$CH_3CH_2CH_2CH_2CH_3$	B.Pt:	36.3°C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	B.Pt:	117°C
2-methylpropan-1-ol	CH_3CHCH_2OH | CH_3	B.Pt:	108°C

Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding due to the hydrogen attached directly to the oxygen - but they are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

Hydrogen bonding in nitrogen containing organic molecules

Hydrogen bonding also occurs in organic molecules containing N-H groups - in the same sort of way that it occurs in ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

References

1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
3. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

1.2.3: Dipole-Dipole Interactions

Dipole-Dipole interactions result when two dipolar molecules interact with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. This type of interaction between molecules accounts for many physically and biologically significant phenomena such as the elevated boiling point of water.

Definition of a Dipole

Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule. Those atoms that are more electronegative pull the bonded electrons closer to themselves. The buildup of electron density around an atom or discreet region of a molecule can result in a molecular dipole in which one side of the molecule possesses a partially negative charge and the other side a partially positive charge. Molecules with dipoles that are not canceled by their molecular geometry are said to be polar.

✓ Example 1.2.3.1: Carbon Dioxide and Hydrogen Flouride

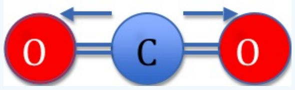


Figure 1.2.3.1.

In Figure 1 above, the more electronegative Oxygen atoms pull electron density towards themselves as demonstrated by the arrows. Carbon Dioxide is not polar however because of its linear geometry. A molecule's overall dipole is directional, and is given by the vector sum of the dipoles between the atoms. If we imagined the Carbon Dioxide molecule centered at 0 in the XY coordinate plane, the molecule's overall dipole would be given by the following equation:

$$\mu \cos(0) + -\mu \cos(0) = 0. \tag{1.2.3.1}$$

Where μ is the dipole moment of the bond (given by μ=Q x r where Q is the charge and r is the distance of separation). Therefore, the two dipoles cancel each other out to yield a molecule with no net dipole.

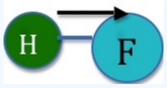


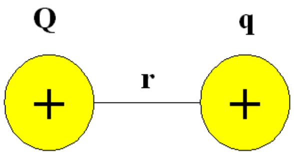
Figure 1.2.3.2.

In contrast, figure 2 demonstrates a situation where a molecular dipole does result. There is no opposing dipole moment to cancel out the one that is shown above. If we were to imagine the hydrogen flouride molecule placed so that the Hydrogen sat at the origin in the XY coordinate plane, the dipole would be given by $\mu \cos(0) = \mu$.

Potential Energy of Dipole Interaction

Potential energy is the maximum energy that is available for an object to do work. In physics, work is a quantity that describes the energy expended as a force operates over a distance. Potential energy is positional because it depends on the forces acting on an object at its position in space. For instance, we could say that an object held above the ground has a potential energy equal to its mass x acceleration due to gravity x its height above the ground (i.e., mgh). This potential energy that an object has as a result of its position can be used to do work. For instance we could use a pulley system with a large weight held above the ground to hoist a smaller weight into the air. As we drop the large weight it converts its potential energy to kinetic energy and does work on the rope which lifts the smaller weight into the air. It is important to remember that due to the second law of thermodynamics, the amount of work done by an object can never exceed (and is often considerably less) than the objects potential energy.

On a subatomic level, charged atoms have an electric potential which allows them to interact with each other. Electric potential refers to the energy held by a charged particle as a result of it's position relative to a second charged particle. Electric potential depends on charge polarity, charge strength and distance. Molecules with the same charge will repel each other as they come closer together while molecules with opposite charges will attract.



For two positively charged particles interacting at a distance r, the potential energy possessed by the system can be defined using Coulomb's Law:

$$V = \frac{kQq}{r} \tag{1.2.3.2}$$

where

- k is the Coulomb constant and
- Q and q refer to the magnitude of the charge for each particle in Coulombs.

The above equation can also be used to calculate the distance between two charged particles (r) if we know the potential energy of the system. While Coulomb's law is important, it only gives the potential energy between two point particles. Since molecules are much larger than point particles and have charge concentrated over a larger area, we have to come up with a new equation.

The potential energy possessed by two polar atoms interacting with each other depends on the dipole moment, μ, of each molecule, the distance apart, r, and the orientation in which the two molecules interact. For the case in which the partially positive area of one molecule interacts only with the partially negative area of the other molecule, the potential energy is given by:

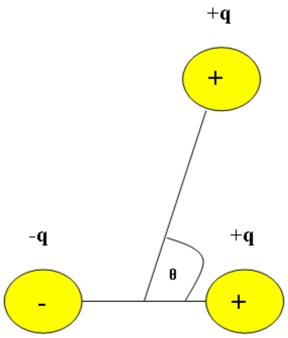
$$V(r) = -\frac{2\mu_1\mu_2}{4\pi\epsilon_o r^3} \tag{1.2.3.3}$$

where ϵ_o is the permeability of space. If it is not the case that the molecular dipoles interact in this straight end to end manor, we have to account mathematically for the change in potential energy due to the angle between the dipoles. We can add an angular term to the above equation to account for this new parameter of the system:

$$V(r) = -\frac{\mu_1\mu_2}{4\pi\epsilon_0 r_{12}^3}(\cos\theta_{12} - 3\cos\theta_1\cos\theta_2) \tag{1.2.3.4}$$

In this formula θ_{12} is the angle made by the two oppositely charged dipoles, and r_{12} is the distance between the two molecules. Also, θ_1 and θ_2 are the angles formed by the two dipoles with respect to the line connecting their centers.

It is also important to find the potential energy of the dipole moment for more than two interacting molecules. An important concept to keep in mind when dealing with multiple charged molecules interacting is that like charges repel and opposite charges attract. So for a system in which three charged molecules (2 positively charged molecules and 1 negatively charged molecule) are interacting, we need to consider the angle between the attractive and repellant forces.



The potential energy for the dipole interaction between multiple charged molecules is:

$$V = \frac{kp\cos\theta}{r^2} \tag{1.2.3.5}$$

where

- k is the Coulomb constant, and
- r is the distance between the molecules.

Figure 1.2.3.3: Dipole-Dipole Interaction in the Gas Phase. image used with permission (Gary L Bertrand).

Example 1.2.3.2

Calculate the potential energy of the dipole-dipole interaction between 2 HF molecules oriented along the x axis in an XY coordinate plane whose area of positive charge is separated by 5.00 Angstroms from the area of negative charge of the adjacent molecule:

Solution

The Dipole moment of the HF molecules can be found in many tables, μ=1.92 D. Assume the molecules exist in a vacuum such that $\epsilon_0 = 8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2}$

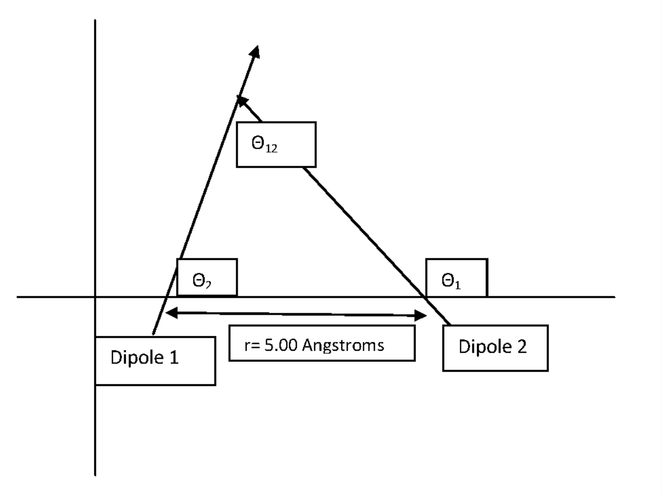
$$\mu = 1.92 D \times 3.3356 \times 10^{-30} \frac{Cm}{D} = 6.4044 \times 10^{-30} Cm \tag{1.2.3.6}$$

Now use Equation 1.2.3.3to calculate the interaction energy

$$\begin{aligned} V &= -\frac{2(6.4044 \times 10^{-30} Cm)^2}{4(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2})(5.0 \times 10^{-10})^3} \\ &= 1.4745 \times 10^{-19} Nm \end{aligned}$$

Example 1.2.3.3

Now imagine the same two HF molecules in the following orientation:



Given: $\theta_1 = \frac{3\pi}{4}$, $\theta_2 = \frac{\pi}{3}$ and $\theta_{12} = \frac{5\pi}{12}$

Solution

$$\begin{aligned} V &= -\frac{(6.4044 \times 10^{-30} Cm)^2}{4\pi(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2}(5.00 \times 10^{-10} m)^3}(\cos\frac{5\pi}{12} - 3\cos\frac{3\pi}{4}\cos\frac{\pi}{3}) \\ &= -9.73 \times 10^{-20} Nm = 9.73 \times 10^{-20} J \end{aligned}$$

Dipole-Dipole Interactions in Macroscopic Systems

It would seem, based on the above discussion, that in a system composed of a large number of dipolar molecules randomly interacting with one another, V should go to zero because the molecules adopt all possible orientations. Thus the negative potential energy of two molecular dipoles participating in a favorable interaction would be cancelled out by the positive energy of two molecular dipoles participating in a high potential energy interaction. Contrary to our assumption, in bulk systems, it is more probable for dipolar molecules to interact in such a way as to minimize their potential energy (i.e., dipoles form less energetic, more probable configurations in accordance with the Boltzmann's Distribution). For instance, the partially positive area of a molecular dipole being held next to the partially positive area of a second molecular dipole is a high potential energy configuration and few molecules in the system will have sufficient energy to adopt it at room temperature. Generally, the higher potential energy configurations are only able to be populated at elevated temperatures. Therefore, the interactions of dipoles in a bulk Solution are not random, and instead adopt more probable, lower energy configurations. The following equation takes this into account:

$$V = -\frac{2\mu_A^2\mu_B^2}{3(4\pi\epsilon_0)^2 r^6}\frac{1}{k_B T} \tag{1.2.3.7}$$

✓ Example 1.2.3.4

Looking at Equation 1.2.3.7, what happens to the potential energy of the interaction as temperature increases.

Solution

The potential energy of the dipole-dipole interaction decreases as T increases. This can be seen from the form of the above equation, but an explanation for this observation is relatively simple to come by. As the temperature of the system increases, more molecules have sufficient energy to occupy the less favorable configurations. The higher, less favorable, configurations are those that give less favorable interactions between the dipoles (i.e., higher potential energy configurations).

✓ Example 1.2.3.5

Calculate the average energy of HF molecules interacting with one another in a bulk Solution assuming that the molecules are 4.00 Angstroms apart in room temperature Solution.

Solution

Using Equation 1.2.3.7to calculate the bulk potential energy:

$$\begin{aligned} V &= -\frac{2}{3}\frac{(6.4044 \times 10^{-30} Cm)^4}{(4\pi(8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2})^2(4.00 \times 10^{-10} m)^6}\frac{1}{(1.381 \times 10^{-23} Jk^{-1})(298k)} \\ &= -5.46 \times 10^{-21} J \end{aligned}$$

✓ Example 1.2.3.6

What is the amount of energy stabilization that is provided to the system when 1 mole of HF atoms interact through dipole-dipole interactions.

Solution

Since we have already calculated above the average potential energy of the HF dipole-dipole interaction this problem can be easily solved.

$$\begin{aligned} V &= -5.46 \times 10^{-21} J \times (6.022 \times 10^{23} mol^{-1}) \\ &= -3288\frac{J}{mol} = 3.29\frac{kJ}{mol} \end{aligned}$$

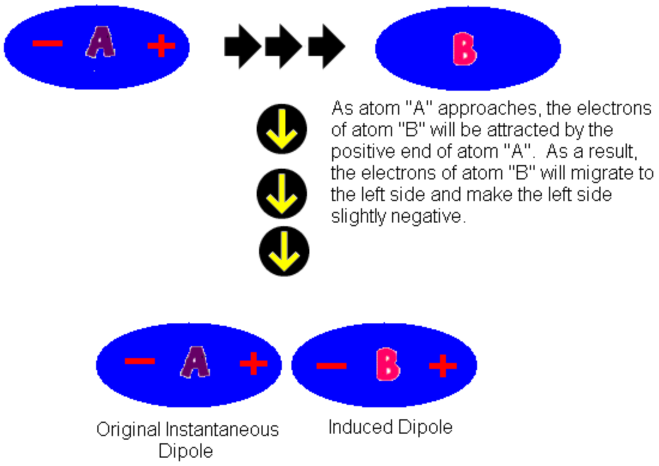
Biological Importance of Dipole Interactions

The potential energy from dipole interactions is important for living organisms. The biggest impact dipole interactions have on living organisms is seen with protein folding. Every process of protein formation, from the binding of individual amino acids to secondary structures to tertiary structures and even the formation of quaternary structures is dependent on dipole-dipole interactions.

A prime example of quaternary dipole interaction that is vital to human health is the formation of erythrocytes. Erythrocytes, commonly known as red blood cells are the cell type responsible for the gas exchange (i.e. respiration). Inside the erythrocytes, the molecule involved in this crucial process, is 'hemoglobin', formed by four protein subunits and a heme group'. For an heme to form properly, multiple steps must occur, all of which involve dipole interactions. The four protein subunits—two alpha chains, two beta chains—and the heme group, interact with each other through a series of dipole-dipole interactions which allow the erythrocyte to take its final shape. Any mutation that destroys these dipole-dipole interactions prevents the erythrocyte from forming properly, and impairs their ability to carry oxygen to the tissues of the body. So we can see that without the dipole-dipole interactions, proteins would not be able to fold properly and all life as we know it would cease to exist.

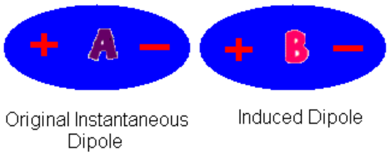
Induced Dipoles

An induced dipole moment is a temporary condition during which a neutral nonpolar atom (i.e. Helium) undergo a separation of charges due to the environment. When an instantaneous dipole atom approaches a neighboring atom, it can cause that atom to also produce dipoles. The neighboring atom is then considered to have an induced dipole moment.



As atom "A" approaches, the electrons of atom "B" will be attracted by the positive end of atom "A". As a result, the electrons of atom "B" will migrate to the left side and make the left side slightly negative.

Even though these two atoms are interacting with each other, their dipoles may still fluctuate. However, they must fluctuate in synchrony in order to maintain their dipoles and stay interacted with each other. Result of synchronizing fluctuation of dipoles:



The potential energy representing the dipole-induced dipole interaction is:

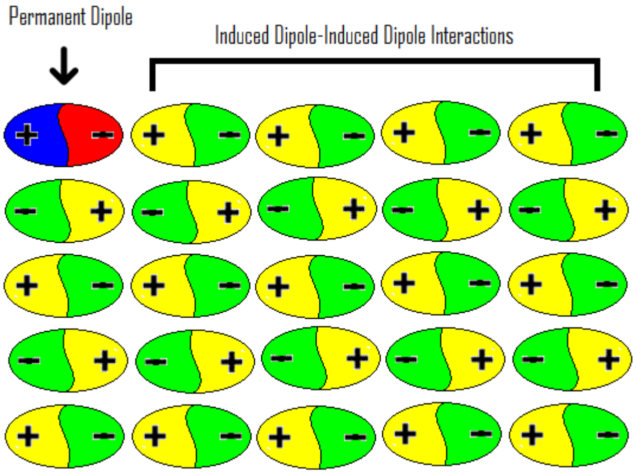
$$V = -\frac{\alpha\mu^2}{4\pi\epsilon_o r^6} \tag{4}$$

- α = polarizability of the nonpolar molecule

Polarizability defines how easy the electron density of an atom or a molecule can be distorted by an external electric field.

Spontaneous Dipole-Induced Dipole Interaction

Spontaneous dipole-induced dipole interactions are also known as **dispersion** or **London forces** (name after the German physicist Fritz London). They are large networks of intermolecular forces between nonpolar and non-charged molecules and atoms (i.e. alkanes, noble gases, and halogens). Molecules that have induced dipoles may also induce neighboring molecules to have dipole moments, so a large network of induced dipole-induced dipole interactions may exist. The image below illustrates a network of induced dipole-induced dipole interactions.



The potential energy of an induced dipole-induced dipole interaction is represented by this equation:

$$V = -\frac{3}{2}\frac{I_a I_b}{I_a + I_b}\frac{\alpha_a \alpha_b}{r^6} \tag{5}$$

- I = The first ionization energy of the molecule

The radius is a huge determinant of how large the potential energy is since the potential energy is inversely proportional to r^6. A small increase in the radius, would greatly decrease the potential energy of the interaction.

References

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Contributors and Attributions

- Justin Than (UCD)

1.2.4: Polarizability

The term **polarizability** refers to the tendency of molecules to generate induced electric dipole moments when subjected to an electric field. It originates from the fact that nuclei and electrons are generally not fixed in space and that when molecules are subject to an electric field, the negatively charged electrons and positively charged atomic nuclei are subject to opposite forces and undergo charge separation. Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments.

Introduction

Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted (Figure 1.2.4.1). The ease of this distortion is the polarizability of the atom or molecule. The created distortion of the electron cloud causes the originally nonpolar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom and the strength of the electric field by the following equation:

$$\mu_{ind} = \alpha E \tag{1.2.4.1}$$

where E denotes the strength of the electric field and α is the polarizability of the atom or molecule with units of C m^2V^{-1}.

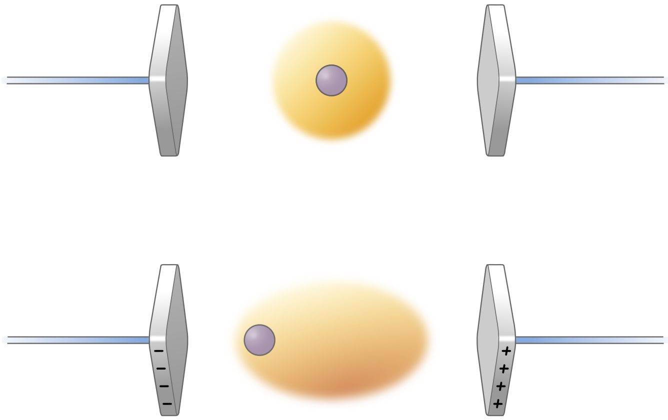

Figure 1.2.4.1: A neutral nonpolar species's electron cloud is distorted by an externally applied electric field. (top) Before the electric field is turned on the electron cloud is isotropically distributed. (bottom) Once the electric field is turned on, an induced dipole moment is generated. If we turn off the electric field, the dipole moment goes away (not shown). (CC BY-NC 4.0; Ümit Kaya via LibreTexts).

In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with fewer electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with fewer electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields. In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizability (labeled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labeled Orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron-dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

Polarizability Influences Dispersion Forces

The dispersion force is the weakest intermolecular force. It is an attractive force that arises from surrounding temporary dipole moments in nonpolar molecules or species. These temporary dipole moments arise when there are instantaneous deviations in the electron clouds of the nonpolar species. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created (Figure 1.2.4.2).

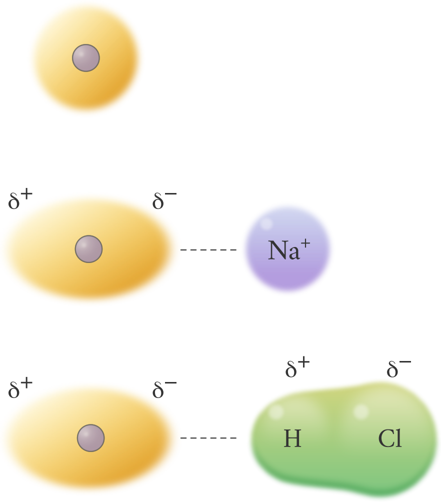

Figure 1.2.4.2: A neutral nonpolar species's electron cloud (yellow) can be distorted by the electric field of a nearby ion (e.g., sodium cation) or polar molecule (e.g., hydrogen chloride) to induce a dipole moment. (CC BY-NC 4.0; Ümit Kaya via LibreTexts).

These cumulative dipole-induced dipole interactions create attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough.

Polarizability affects dispersion forces in the following ways:

- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *strongly* and melting and boiling points of covalent substances *increase* with *larger* molecular mass.
- Polarizability also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules with electrons that are delocalized (e.g., with double or triple bonds) will have some of those electrons easily shifted over a greater distance. This is manifested in an greater polarizability and thus greater dispersion forces.

Structure Dependence to Dispersion Forces

The influence of polarizability on the strength of the dispersion forces is also modulated by the 3-D structure of the molecules. For example, neo-pentane and n-pentane (Figure 1.2.4.3) exhibit comparable polarizabilities, but have different boiling points. The lack of polar bonding in both indicates that dispersion is the dominant interaction responsible in both substances. The higher boiling point of n-pentane indicates there are stronger intermolecular interactions.

Table 1.2.4.3: Properties of neopentane and n-pentane

molecule	Boiling Points (ºC)	α (Å^3)

molecule	Boiling Points (°C)	α (Å^3)
neopentane	9.5	10.24
n-pentane	36.0	9.879

Both neopentane and n-pentane would be expected to exhibits comparable dispersion forces since they have comparable polarizabilities. However, the structure of the n-pentane molecule facilitates greater dispersion forces due to more contacts between n-pentane molecules. In contrast, neopentane has a smaller dispersion force since the interactions between neopentane are reduced since neopentane is more compact and symmetrical.

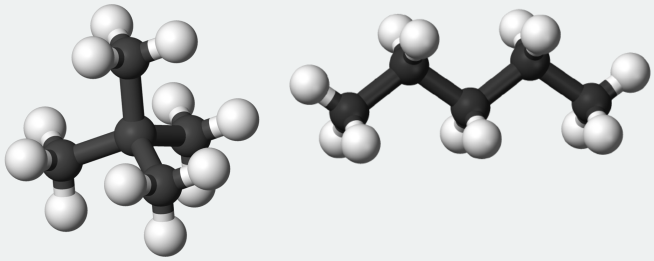

Figure 1.2.4.3: (left) Neopentane, an isomer of n-pentane, is an example of a more compact and less polarizable molecule. (right) n-Pentane is an example of an elongated molecule that is more easily polarized.

The relationship between polarizability and dispersion forces can be seen in the following equation, which can be used to quantify the interaction between two like nonpolar atoms or molecules (e.g., A with A):

$$V(r) = \frac{-3}{4}\frac{\alpha^2 I}{r^6} \tag{1.2.4.2}$$

where r is the distance between the atoms or molecules, I is the **first ionization energy** of the atom or molecule, and α is the polarizability constant expressed in units of m^3.

This expression of α is related to α' by the following equation:

$$\alpha' = \frac{\alpha}{4\pi\epsilon_o} \tag{1.2.4.3}$$

To quantify the interaction between unlike atoms or molecules (A and B), Equation 1.2.4.2becomes:

$$V(r) = \frac{-3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{r^6} \tag{1.2.4.4}$$

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1.3: Overview of Valence Bond Theory

Molecular bonding occurs due to an energy minimum that occurs as electrons are shared between 2 nuclei. The potential energy is approximated as a harmonic potentia depending on the displacement, R, of the nuclei from their equilibrium positions.

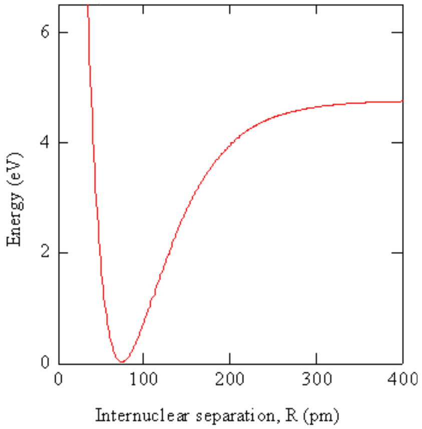

Figure 1.3.1 : The potential energy function for a diatomic molecule.

The graph in Figure 1.3.1 shows the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This shows the energy advantage of chemical bonding but doesn't describe anything about molecular shapes or numbers of bonds that an atom will form.

Valence Bond (VB) Theory looks at the interaction between atoms to explain chemical bonds. It is one of the two common theories that helps describe the bonding between atoms. The other theory is Molecular Orbital Theory. Take note that these are theories and should be treated as such; they are not always perfect.

Introduction

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule* in which he suggested that bonding results from sharing of electron pairs between two atoms. Walter Heitler and Fritz London brought a quantum mechanical foundation to explain this type of bonding and added the ideas that resonance and wavefunctions contributed to chemical bonds. Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of atomic orbital overlap, hybridization, resonance, and covalent-ionic superposition to describe chemical bonds.

Atomic Orbital Overlap

Valence bond theory describes that bonds are formed between atoms because the atomic orbitals overlap and the electrons in those orbitals are localized within the area of that overlap. They have a higher probability of being found within that bond; we will return to this statement when we talk about wavefunctions. Dihydrogen (H_2) is a simple diatomic gas that has been used to illustrate this idea; however, let's look at Cl_2 as a simple example. Chlorine has seven valence electrons. From its Lewis structure, one can see that Cl has a radical. That sole radical indicates that Cl can bond once. As a general rule, the number of unpaired electrons denotes how many bonds that atom can make. Since there is only one unpaired electron in each Cl, those electrons interact to bond. In this case, the 3p orbitals overlap. Lone pairs can be seen as the orbitals not interacting with each other. The idea of atomic orbitals overlapping works well for simple molecules, such as diatomic gases, but more complex molecules cannot be explained simply by the overlap of atomic orbitals, especially if they defy the octet rule when drawing out Lewis structures and if they bond beyond their predicted amount.

Atomic Orbital Hybridization

Consider phosphorus pentafluoride (PF_5). P, the central atom, has five valence electrons, with 2 electrons paired in the 3s orbital and three unpaired electrons in the 3p orbital. Thus, P should only be able to form three bonds based on its ground state atomic orbitals. However, since PF_5 exists with phosphorus as the central atom, P must be able to bond five times. This requires orbital hybridization which creates degenerate hybrid orbitals that allow atoms to bond well beyond their normal amount. Orbitals involved in hybridization are the s, p, and d atomic orbitals. There are certain principles for hybrid orbitals:

1. The number of orbitals mixed must match the number of resulting hybrid orbitals.
2. Hybrid orbitals are more directional than atomic orbitals and lead to greater overlap (which makes stronger bonds)

Hybrid orbitals consist of sp, sp^2, sp^3, sp^2d, sp^3d, and sp^3d^2 (3). Returning back to PF_5, let's see how hybrid orbitals can describe its bonds. Remember that P can only bond three times, but we need it to bond five times. In order to bond five times, five orbitals must be singularly filled (one electron in each). Bonds occur when orbitals with only one electron are spin paired with the electron from another atom. The five orbitals can be acquired by sp^3d orbital hybridization. Starting off with a total of five atomic orbitals will result in five hybrid orbitals. Note that since P is in period 3, it has d orbitals in the same energy level. Thus, 3d orbitals can be used to hybridize, even though electrons do not occupy it in the ground state. The process is outlined in the figure below. Remember to follow the aufbau principle, Hund's rule, and the Pauli exclusion principle when assigning electrons to their orbitals. Note that only valence electrons are involved in hybridization and bonding.

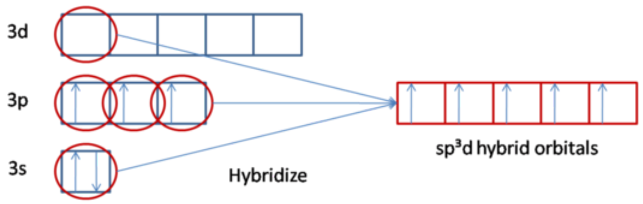

Figure1: Depiction of sp^3d hybridization.
Author: Tony Chhom

Now, P has five hybrid orbitals. Remember that P has five valence electrons. Electrons too are not lost or gained, so those electrons transfer over to the hybrid orbitals. Fill them in accordingly, following Hund's rule and the Pauli exclusion principle. Note that the hybrid orbitals are now degenerate, so the aufbau principle doesn't apply for this case. From sp^3d hybridization, P has five unpaired electrons and can now bond with five fluorine atoms.

The number of hybrid orbitals ends up equal to the number of electron groups surrounding the atom. This includes lone pairs as well as bond pairs. In the example, PF_5, there are no lone pairs. The type of hybrid orbitals also corresponds to the molecular shape. In the case of PF_5, its shape as defined by VSEPR is trigonal bypyramidal. The shape can also be determined by the type of hybridization. With the following common shapes related to hybridization:

- sp linear
- sp^2 trigonal planar
- sp^3 tetrahedral
- sp^3d trigonal bipyramidal

Wavefunctions in VB Theory

The wavefunction is a solution to the Schrödinger equation (a quantum mechanical solution for electrons) describes the state of an electron. From the name of the function, one can derive that the electron can behave like a wave. This wave-like behavior of the electrons defines the shapes of the orbitals. Thus, it makes sense that wavefunctions are related to Valence Bond Theory. If orbitals overlap to create bonds, and orbital shapes and the state of an electron is described by the wavefunction, then it makes sense that the overlap of orbitals (the bonds) can be described by wavefunctions as well. Thus, covalent and ionic bonds can be described by wavefunctions. Covalent and ionic representations of a bond represent the same bond, but they differ in how the electrons are placed. This is called resonance. Different intermolecular interactions give rise to different wavefunctions. Recall from Hund's Rule and the Pauli exclusion principle that electrons must be spin paired when the right conditions are met. Due to this, there are two separate ways to represent a covalent bond in terms of electron spin, which is related to the wavefunction. The figure shows the two different cases for two electrons in a bond. Thus, it is possible to write two different wavefunctions that describe each case, which can be superimposed to describe the overall covalent bond (2). The superposition of the covalent bond and ionic bond wavefunctions will result in an overall wavefunction that describes the state of the molecule. Due to this module being an overview of Valence Bond Theory, the full details will not be covered.

Figure 2: A) The electron from one undetermined atom to the left has an upward spin while the electron from another undetermined atom to the right has a downward spin. B) The spins are now reversed. Author: Tony Chhom

While the wavefunction doesn't have any direct physical significance, the wavefunction squared will result in a probability density of where the electrons are located relative to the nucleus. These give rise to the common shapes of s, p, d and f orbitals. Recall that when atomic orbitals overlap, the electrons are localized and more likely to be found within that overlap. In terms of electrostatic interactions, this bond will result in some form of equilibrium between all of the electrostatic forces (between the electrons and the electrons with each nucleus) (1). If the overlap is too far in, there is a net repulsion force; the electrons will also be forced apart. If the atomic orbital overlap is too small, the net attraction force is very small; the electron will have a smaller chance of remaining in the overlap since they will be more attracted to their own nucleus. If the overlap is just right, then the electrons are attracted to both nuclei and more likely to stay in the overlapped area. Thus, wavefunctions and electrostatic forces can both explain why electrons are localized within their bonds.

Reliability of Valence Bond Theory and Uses

Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnitism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also, sp^2d and sp^3 both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or tetrahedral (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape of some molecules.

Problems

Exercise 1.3.1

Draw the Lewis structures HF, CO_2, and C_2H_2. Which orbitals are involved with bonding for HF? Now, use hybridization to explain the bonds of CO_2 and C_2H_2. Can you account for the single, double, and triple bonds via orbitals overlapping and hybridization? It is not required to draw the hybridization process, but it might help you in your thinking.

Answer

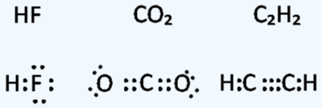

Figure 3: Lewis structures of HF, CO_2, and C_2H_2. Author: Tony Chhom

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HF: Hydrogen has one electron in the 1s orbital. Flourine has two electrons in the 2s orbital, and five in the 2p orbitals. These can be derived from the electron configurations. We are only interested in the valence electrons, so the lower shell can be ignored. Remember to fill in the orbitals accordingly. The orbitals available to bond are Hydrogen's 1s orbital and one of Flourine's 2p orbitals. Thus, the bond must take place between these two orbitals. This is a sigma bond. A bond of this type, or one of similar orientation, such as two s orbitals, are the bonds associated with hybrid orbitals when hybridization takes place.

CO_2: C has four valence electrons; two are in 2s and two are in 2p. O has six valence electrons; two in 2s and four in 2p. Notice that there is a double bond. Now, hybridize to explain the bonds. When determining the coordinate number, double bonds and triple bonds count as one bond. Thus, the coordinate number of C is 2 and the corresponding hybridization is sp. The diagram below shows the sp hybridization process for C. Notice that two 2p orbital remains unhybridized. We fill in the hybrid orbitals with two of C's electrons so that C has space available to bond with the two O's. The hybrid orbitals describes two sigma bonds between C and the O's; one 2p orbital from each O is used in this process. Two electrons remain for C, which are allocated to the unhybridized orbitals. Now, C can form the other two bonds for a total of four which is what is expected due to the presence of two double bonds. The unhybridized orbitals overlap O's 2p orbitals and forms what is called a pi bond. There is one pi bond and one sigma bond between C and each O. The lone pairs of the O's are the filled 2s orbital and the final and filled 2p orbital. Thus, a double bond is explained by one sigma bond associated with the hybrid orbitals and a pi bond associated with unhybridized p orbitals.

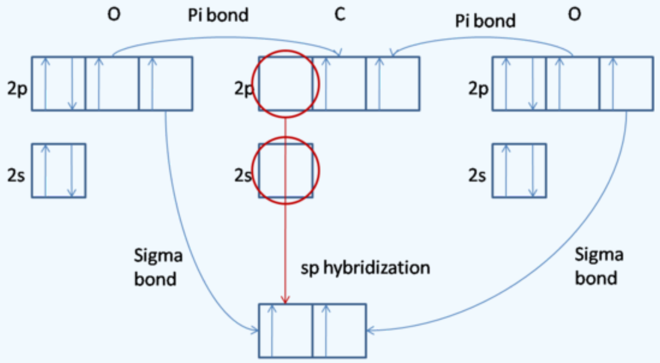

Figure 4: sp hybridization and types of bonds.
Author: Tony Chhom

C_2H_2: C has four valence electrons (two in 2s and two in 2p) and H has one (one in 1s). There is a total of ten valence electrons. From the Lewis structure, one can see that there is a triple bond between the two C's. For each C, one can explain the bonds through sp hybridization (a triple bond and one single bond). This process is similar to CO_2. However, in this case, C's available unhybridized 2p orbitals bond together with the unhybridized p orbitals of the other C. Now, there are two pi bonds and one sigma bond between the C's; there is one sigma bond between each C and H bond. Thus, a triple bond is explained by one sigma bond associated with the hybrid orbitals and two pi bonds associated with unhybridized p orbitals.

? Exercise 1.3.2

Using VSEPR, one can derive that IBr_5 has an octahedral parent shape. Now, use Valence Bond Theory to account for all of the bonds and verify that the parent shape is indeed an octahedral. Why can you determine the parent shape of a molecule based on Valence Bond Theory? Show your work.

Answer

I is the central atom. Usually, the least electronegative atom is the central atom. Drawing the Lewis structure reveals that I can only form one bond. However, with the use of hybridization, I can form more bonds. Showing that is the goal. First, find out how many valence electrons IBr_5 has. This is simply derived by adding all of the valence electrons from each atom; all have 7 valence electrons, so (6)(7)=42. Then, use Lewis structure and allocate all of the electrons into the correct places. You will find that the Lewis structure looks like the picture below.

Figure 5: Lewis dot structure of IBr_5. Author: Tony Chhom

Notice that there is a lone pair. Remember that the number of hybrid orbitals needed is the summation of lone pairs and bonds. This is a total of six; thus a sp^3d^2 hybridization is needed. This process is shown below. Take note that the lone pair is the only spin paired electrons in the hybrid orbitals. Since the coordinate number is six, then the family shape of this molecule is an octahedral shape. Even the lone pairs are accounted for when hybridization takes place. It is because we used the coordinate number (determined by using Lewis dot structure first) to determiine the type of hybridization that hybridization does indeed give the correct family shape. There are of course exceptions, such as sp^2d and sp^3. We cannot predict the shape based on hybridization alone for these.

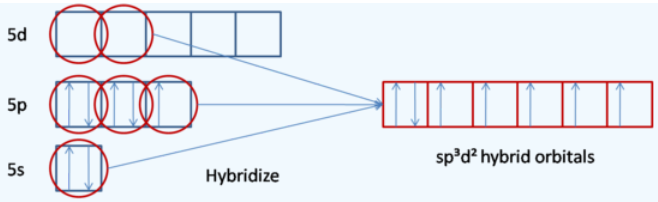

Figure 6: Original depiction of sp^3d^2 hybridization.
Author: Tony Chhom

Exercise 1.3.3

Determine the family shapes correlated with the sp^3, sp^3d, and sp^3d^2 hybridization. Does this mean that all molecules with the respectable hybridization will have the same shape? Explain.

Answer

The shapes are tetrahedral, trigonal bypyramidal, and octahedral respectively. Not all molecules will have the shape associated with the hybridization type because lone pairs must be taken into account as well. For example, look at problem number two. The coordinate number is six. That tells you that the *parent shape* is an octahedral. However, the shape of IBr_5 will only be that shape if the lone pair was another atom. The parent shape will not always match the actual shape of the molecule. It gives you a place to start and is only true if lone pairs do not exist. "Removing" one bond away from the octahedral shape will give the result of the square-base pyramidal shape.

Exercise 1.3.4

Predict which of these atoms/molecules is diamagnetic using Valence Bond Theory: H, H_2, and NO.

Answer

One can solve this problem simply by counting the valence electrons. H has only one electron; it is not paired with any other electron and thus must be paramagnetic. H_2 has two valence electrons; thus, those electrons are spin paired and H_2 is diamagnetic. NO has eleven valence electrons; it is paramagnetic. In general, if an atom/molecule has an odd number of electrons, then that atom/molecule is paramagnetic. It is diamagnetic if it has an even number of electrons; however, like the case of O_2, this does not always work.

Exercise 1.3.5

Briefly summarize Valence Bond Theory. Is it always reliable?

Answer

Valence Bond Theory looks at the interaction between orbitals to describe bonds. It can also be used to derive the shape of the molecule in question, as well as determining whether or not an atom/molecule is diamagnetic or paramagnetic; however Valence Bond Theory is not always reliable. It fails in some cases. One must always remember that this is a theory.

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1.3.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

Learning Objectives

- Understand the need to introduce an approximation like the Born-Oppenheimer approximation to solve multi-electron systems
- Understand the basis of parameterization involved in using the Born-Oppenheimer approximation

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

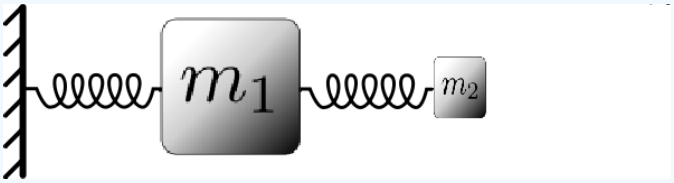
1.3.1.1: The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

✓ Example 9.1.1 : Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:



(CC BY-SA 3.0 Unported; Jim.belk via Wikipedia).

Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{1.3.1.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{1.3.1.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i}\frac{1}{r_{ij}}\right) \tag{1.3.1.3}$$

In Equation 1.3.1.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

? Exercise 9.1.1

Define all the symbols in Equations 1.3.1.1through 1.3.1.3.

Answer

$$\begin{aligned}
\hat{H}(r,R) &= \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_o}\frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r,R)}_{\text{Hamiltonian for electrons}} \\
\hat{T}_{nuc}(R) &= \underbrace{\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b}\nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}} \\
\hat{H}_{elec}(\vec{r},\vec{R}) &= \underbrace{\frac{-\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} \\
&+ \frac{e^2}{4\pi\epsilon_o}\left(- \underbrace{\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} - \underbrace{\sum_i \frac{Z_B}{R_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i}\frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}}\right)
\end{aligned}$$

where, $Z_x$is the charge of particle x, m_x is the mass of particle x and r_{xz} is the distance between particle x and z.

? Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 1.3.1.3.

Answer

The 1/2 term is there to make sure we do not double count the potential energies via the two summations. Otherwise, we would independently add the potential energy of electron 1 with electron 2 and the potential energy of electron 2 with electron 1. These are the same and hence one has to be removed.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 1.3.1.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r, R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r, R)\varphi_e(r, R) = E_e(R)\varphi_e(r, R) \tag{1.3.1.4}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R. As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r, R) = X_{ne}(R)\varphi_e(r, R) \tag{1.3.1.5}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction, which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function, $\varphi_e(r, R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation 1.3.1.5to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, R is set equal to R_o, the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei (i.e., the nuclei never move). The electronic energy, $E_e(R)$, in Equation 1.3.1.4combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure 9.1.1 .

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{1.3.1.6}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \tag{1.3.1.7}$$

1.3.1.2: Potential Energy Curves and Surfaces

Previously, the potential energy was approximated as a harmonic potential or Morse potential depending on the displacement, R, of the nuclei from their equilibrium positions.

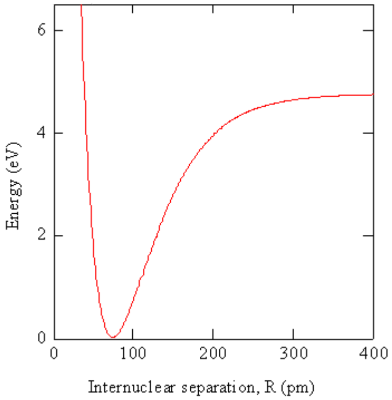


Figure 9.1.1 : The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r, R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure 9.1.1 .

The graph in Figure 9.1.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

? Exercise 9.1.3

Relate Equation 1.3.1.7to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure 9.1.1), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with 3N-6 (or 3N-5 for linear molecule) dimensions for the number of internal degrees of freedom.

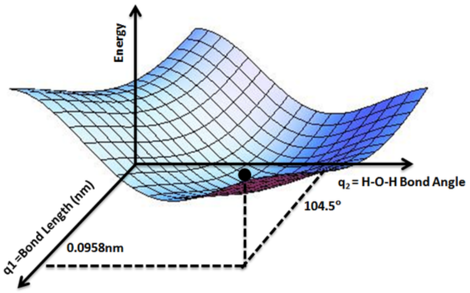


Figure 9.1.2 : The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

? Exercise 9.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

1.3.1.3: Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Contributors and Attributions

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

1.3.2: Covalent Bonding and Orbital Overlap

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

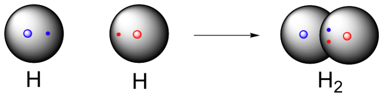
Introduction

As we have talked about using Lewis structures to depict the bonding in organic compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in organic molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

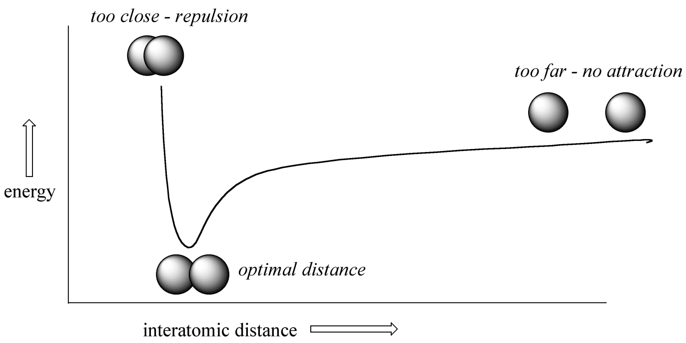
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

It is not accurate, however, to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure $1.3.2.1$). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure $1.3.2.1$).

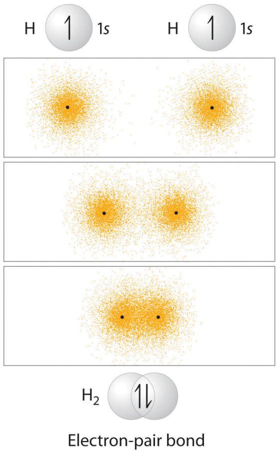


Figure **1.3.2.1** *: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in* H_2*. The formation of* H_2 *from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an* H_2 *molecule increases the electron density in the region between the two positively charged nuclei.*

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 1.3.2.2shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where *n* = 2. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

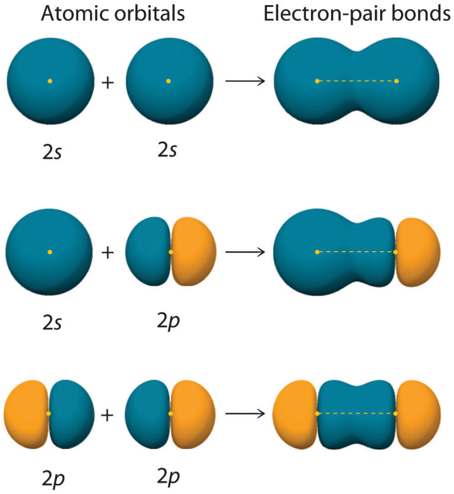


Figure **1.3.2.2** *: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.*

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

1.3.3: Hybrid Orbitals

The localized **valence bonding theory** uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 1.3.3.1.

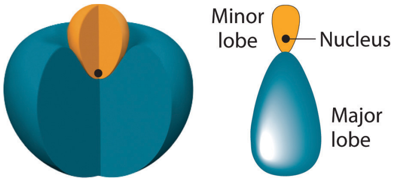


Figure **1.3.3.1**: *The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.*

Because the difference A − B can also be written as A + (−B), in Figure 1.3.3.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation 9.5.1, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{1.3.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{1.3.3.2}$$

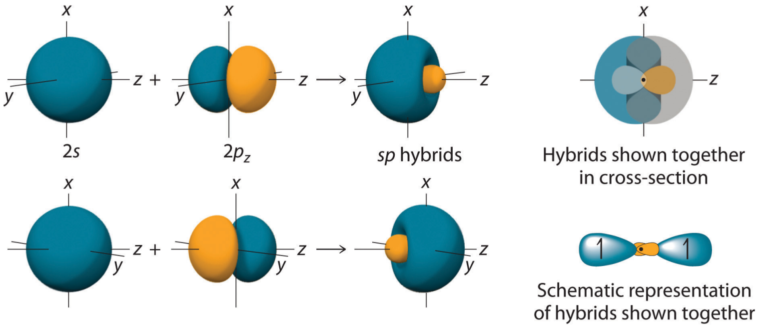


Figure 1.3.3.2: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

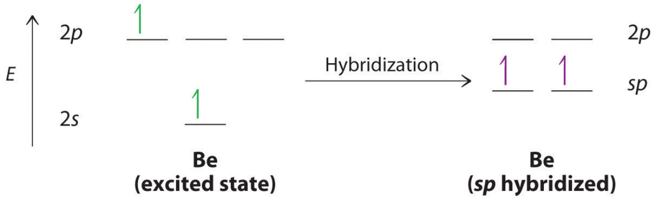


Figure 9.5.2, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

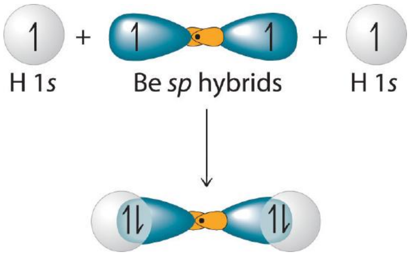


Figure 1.3.3.3: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 1.3.3.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

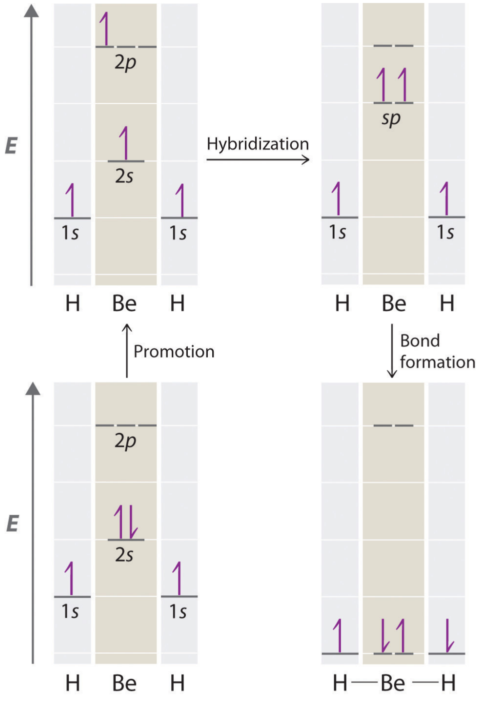


Figure 1.3.3.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

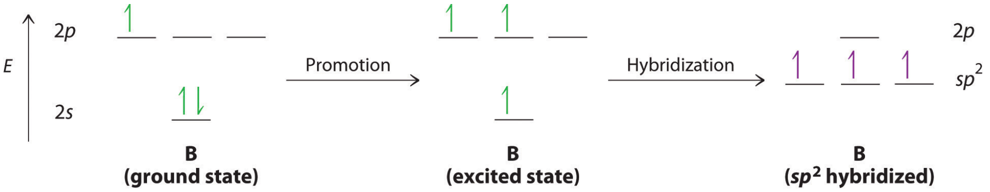


Figure 1.3.3.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

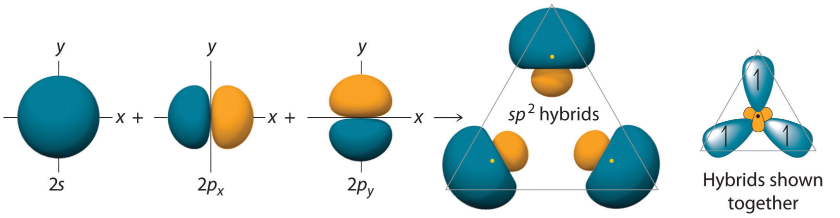
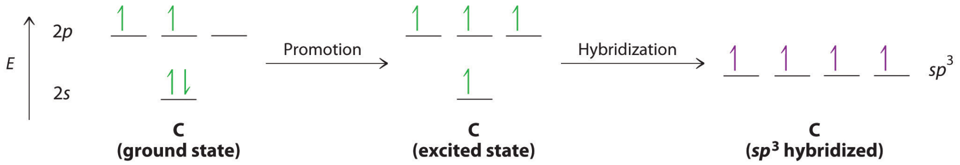


Figure 1.3.3.5: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 1.3.3.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

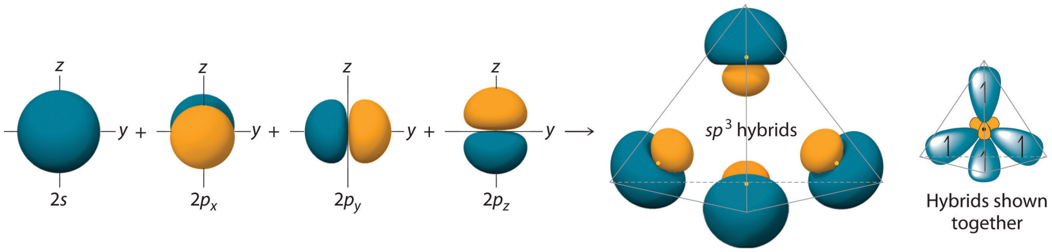


Figure 1.3.3.6: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^22p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:

The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

Example 1.3.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VPSER approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^23p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^22p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 1.3.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer

a. B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

b. Each N atom is *sp*^{3} hybridized and uses one *sp*^{3} hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

> The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled *ns*^{2} subshell to an empty *np* or ($n - 1$)*d* valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent ***sp*^{2} hybrids** or four equivalent ***sp*^{3} hybrids**, respectively.

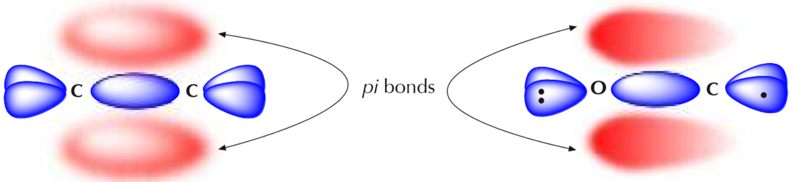
1.3.4: Delocalization of Electrons

Learning Objectives

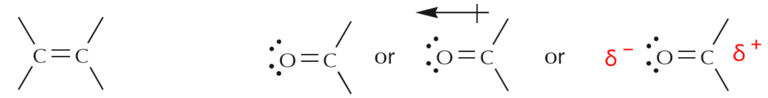
- To introduce the concept of electron delocalization from the perspective of molecular orbitals, to understand the relationship between electron delocalization and resonance, and to learn the principles of electron movement used in writing resonance structures in Lewis notation, known as the *curved arrow* formalism.

Mobility Of π Electrons and Unshared Electron Pairs

Now that we understand the difference between sigma and π electrons, we remember that the π bond is made up of loosely held electrons that form a diffuse cloud which can be easily distorted. This can be illustrated by comparing two types of double bonds, one polar and one nonpolar. The C=C double bond on the left below is nonpolar. Therefore the π electrons occupy a relatively symmetric molecular orbital that's evenly distributed (shared) over the two carbon atoms. The C=O double bond, on the other hand, is polar due to the higher electronegativity of oxygen. The π cloud is distorted in a way that results in higher electron density around oxygen compared to carbon. Both atoms still share electrons, but the electrons spend more time around oxygen. The drawing on the right tries to illustrate that concept.



Using simple Lewis formulas, or even line-angle formulas, we can also draw some representations of the two cases above, as follows.



nonpolar *pi* bond

polar *pi* bond representations

The dynamic nature of π electrons can be further illustrated with the use of arrows, as indicated below for the polar C=O bond:

CURVED ARROW FORMALISM

The CURVED ARROW FORMALISM is a convention used to represent the movement of electrons in molecules and reactions according to certain rules. We'll study those rules in some detail. For now, we keep a few things in mind:

a. Curved arrows always represent the movement of electrons, not atoms.
b. Electrons always move towards more electronegative atoms or towards positive charges.

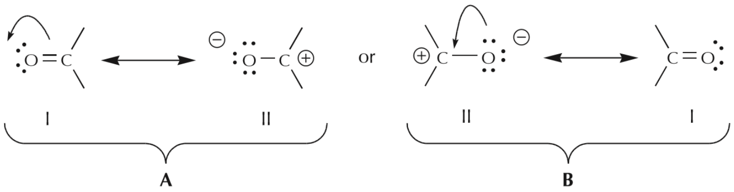
We notice that the two structures shown above as a result of *"pushing electrons"* towards the oxygen are RESONANCE STRUCTURES. That is to say, they are both valid Lewis representations of the same species. The actual species is therefore a hybrid of the two structures. We conclude that:

Curved arrows can be used to arrive from one resonance structure to another by following certain rules.

Just like π electrons have a certain degree of mobility due to the diffuse nature of π molecular orbitals, unshared electron pairs can also be moved with relative ease because they are not engaged in bonding. No bonds have to be broken to move those electrons. As a result, we keep in mind the following principle:

> **Curved arrows usually originate with π electrons or unshared electron pairs, and point towards more electronegative atoms, or towards partial or full positive charges.**

Going back to the two resonance structures shown before, we can use the curved arrow formalism either to arrive from structure I to structure II, or vice versa.



In case A, the arrow originates with π electrons, which move towards the more electronegative oxygen. In case B, the arrow originates with one of the unshared electron pairs, which moves towards the positive charge on carbon. We further notice that π electrons from one structure can become unshared electrons in another, and vice versa. We'll look at additional guidelines for how to use mobile electrons later.

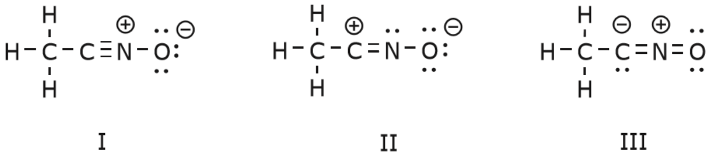
Finally, in addition to the above, we notice that the oxygen atom, for example, is sp^2 hybridized (trigonal planar) in structure I, but sp^3 hybridized (tetrahedral) in structure II. So, which one is it? Again, what we are talking about is the real species. The real species is a hybrid that contains contributions from both resonance structures. In this particular case, the best we can do for now is issue a qualitative statement: since structure I is the major contributor to the hybrid, we can say that the oxygen atom in the actual species is mostly trigonal planar because it has greater sp^2 character, but it still has some tetrahedral character due to the minor contribution from structure II. We'll explore and expand on this concept in a variety of contexts throughout the course.

What about sigma electrons, that is to say those forming part of single bonds? These bonds represent the "glue" that holds the atoms together and are a lot more difficult to disrupt. As a result, they are not as mobile as π electrons or unshared electrons, and are therefore rarely moved. There are however some exceptions, notably with highly polar bonds, such as in the case of HCl illustrated below. We will not encounter such situations very frequently.

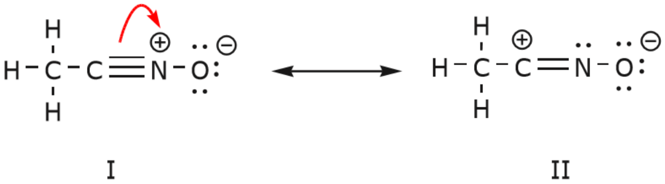
This representation better conveys the idea that the H–Cl bond is highly polar.

Using Curved Arrows

We now go back to an old friend of ours, CH_3CNO, which we introduced when we first talked about resonance structures. We use this compound to further illustrate how mobile electrons are "pushed" to arrive from one resonance structure to another.

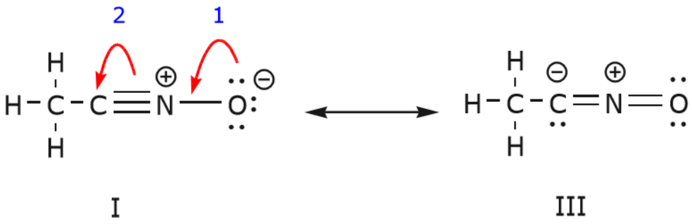


The movement of electrons that takes place to arrive at structure II from structure I starts with the triple bond between carbon and nitrogen. We'll move one of the two π bonds that form part of the triple bond towards the positive charge on nitrogen, as shown:



When we do this, we pay close attention to the new status of the affected atoms and make any necessary adjustments to the charges, bonds, and unshared electrons to preserve the validity of the resulting formulas. In this case, for example, the carbon that forms part of the triple bond in structure I has to acquire a positive charge in structure II because it's lost one electron. The nitrogen, on the other hand, is now neutral because it gained one electron and it's forming three bonds instead of four.

We can also arrive from structure I to structure III by pushing electrons in the following manner. The arrows have been numbered in this example to indicate which movement starts first, but that's not part of the conventions used in the curved arrow formalism.



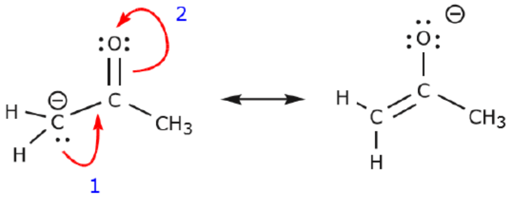
As we move a pair of unshared electrons from oxygen towards the nitrogen atom as shown in step 1, we are forced to displace electrons from nitrogen towards carbon as shown in step 2. Otherwise we would end up with a nitrogen with 5 bonds, which is impossible, even if only momentarily. Again, notice that in step 1 the arrow originates with an unshared electron pair from oxygen and moves towards the positive charge on nitrogen. A new π bond forms between nitrogen and oxygen. At the same time, the π electrons being displaced towards carbon in step 2 become a pair of unshared electrons in structure III. Finally, the hybridization state of some atoms also changes. For example the carbon atom in structure I is sp hybridized, but in structure III it is sp^3 hybridized.

You may want to play around some more and see if you can arrive from structure II to structure III, etc. However, be warned that sometimes it is trickier than it may seem at first sight.

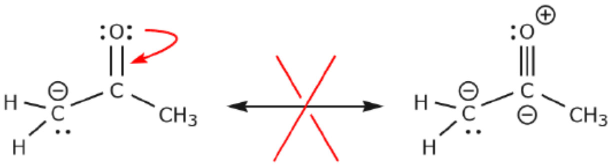
Additional rules for moving electrons to write Resonance Structures:

1. Electron pairs can only move to adjacent positions. Adjacent positions means neighboring atoms and/or bonds.
2. The Lewis structures that result from moving electrons must be valid and must contain the same net charge as all the other resonance structures.

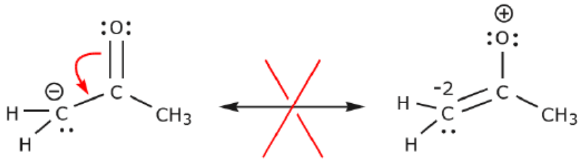
The following example illustrates how a lone pair of electrons from carbon can be moved to make a new π bond to an adjacent carbon, and how the π electrons between carbon and oxygen can be moved to become a pair of unshared electrons on oxygen. None of the previous rules has been violated in any of these examples.



Now let's look at some examples of HOW NOT TO MOVE ELECTRONS. Using the same example, but moving electrons in a different way, illustrates how such movement would result in invalid Lewis formulas, and therefore is unacceptable. Not only are we moving electrons in the wrong direction (away from a more electronegative atom), but the resulting structure violates several conventions. First, the central carbon has five bonds and therefore violates the octet rule. Second, the overall charge of the second structure is different from the first. To avoid having a carbon with five bonds we would have to destroy one of the C–C single bonds, destroying the molecular skeleton in the process.

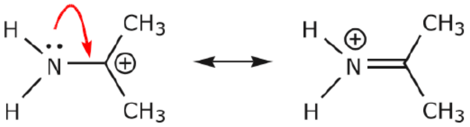


In the example below electrons are being moved towards an area of high electron density (a negative charge), rather than towards a positive charge. In addition, the octet rule is violated for carbon in the resulting structure, where it shares more than eight electrons.

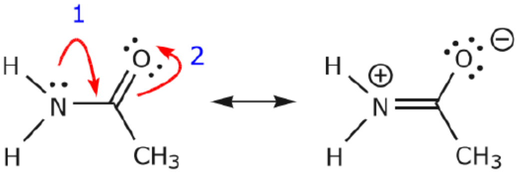


Additional examples further illustrate the rules we've been talking about.

(a) **Unshared electron pairs** (lone pairs) located on a given atom can only move to an adjacent position to make **a new π bond** to the next atom.

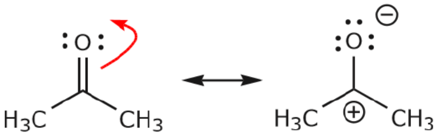


(b) Unless there is a positive charge on the next atom (carbon above), other electrons will have to be displaced to preserve the octet rule. In resonance structures these are almost always π electrons, and almost never sigma electrons.



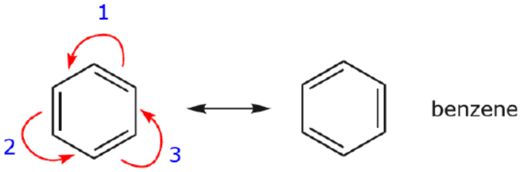
As the electrons from the nitrogen lone pair move towards the neighboring carbon to make a new π bond, the π electrons making up the C=O bond must be displaced towards the oxygen to avoid ending up with five bonds to the central carbon.

c) As can be seen above, **π electrons** can move towards one of the two atoms they share to form a new lone pair. In the example above, the π electrons from the C=O bond moved towards the oxygen to form a new lone pair. Another example is:



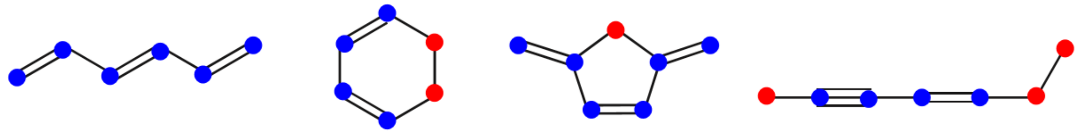
(d) π electrons can also move to an adjacent position to make new π bond. Once again, the octet rule must be observed:

One of the most common examples of this feature is observed when writing resonance forms for benzene and similar rings.



Delocalization, Conjugated Systems, and Resonance Energy

The presence of alternating π and σ bonds in a molecule such as benzene is known as a conjugated system, or conjugated π bonds. Conjugated systems can extend across the entire molecule, as in benzene, or they can comprise only part of a molecule. A conjugated system always starts and ends with a π bond (i.e. an sp^2 or an sp-hybridized atom), or sometimes with a charge. The atoms that form part of a conjugated system in the examples below are shown in blue, and the ones that do not are shown in red. Most of the times it is sp^3 hybridized atoms that break a conjugated system.

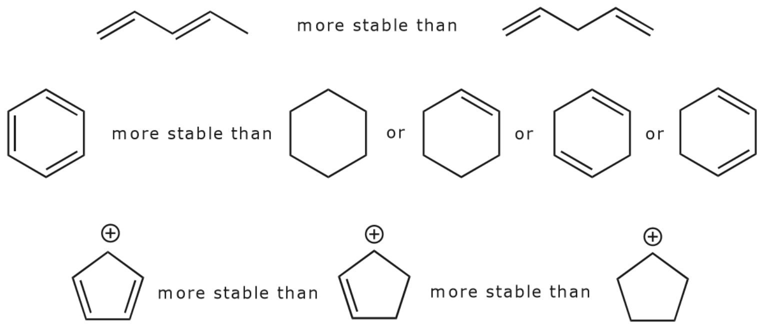


Practically every time there are π bonds in a molecule, especially if they form part of a conjugated system, there is a possibility for having resonance structures, that is, several valid Lewis formulas for the same compound. What resonance forms show is that there is **electron delocalization**, and sometimes **charge delocalization**. All the examples we have seen so far show that electrons move around and are not static, that is, they are delocalized. **Charge delocalization is a stabilizing force** because it spreads energy over a larger area rather than keeping it confined to a small area. Since electrons are charges, the presence of delocalized electrons brings extra stability to a system compared to a similar system where electrons are localized. The stabilizing effect of charge and electron delocalization is known as resonance energy.

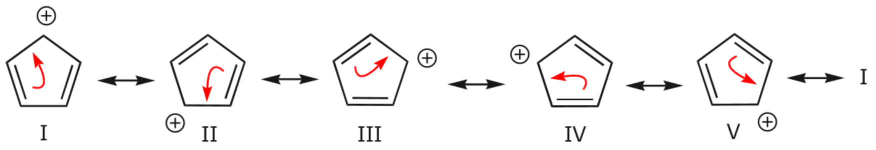
Since conjugation brings up electron delocalization, it follows that **the more extensive the conjugated system, the more stable the molecule** (i.e. the lower its potential energy). If there are positive or negative charges, they also spread out as a result of resonance.

> *The more resonance forms one can write for a given system, the more stable it is. That is, the greater its resonance energy.*

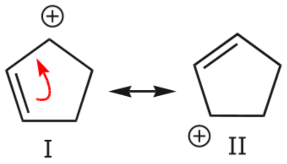
Examine the following examples and write as many resonance structures as you can for each to further explore these points:



Let’s look for a moment at the three structures in the last row above. In the first structure, delocalization of the positive charge and the π bonds occurs over the entire ring. This becomes apparent when we look at all the possible resonance structures as shown below.



In the second structure, delocalization is only possible over three carbon atoms. This is demonstrated by writing all the possible resonance forms below, which now number only two.

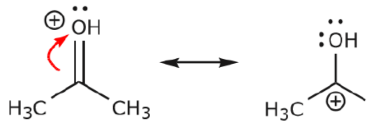


Finally, the third structure has no delocalization of charge or electrons because no resonance forms are possible. Therefore, it is the least stable of the three. This brings us to the last topic. How do we recognize when delocalization is possible? Let’s look at some delocalization setups, that is to say, structural features that result in delocalization of electrons.

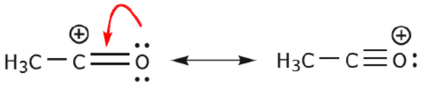
Delocalization Setups

There are specific structural features that bring up electron or charge delocalization. **The presence of a conjugated system is one of them**. Other common arrangements are:

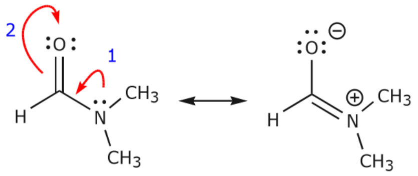
(a) **The presence of a positive charge next to a π bond.** The positive charge can be on one of the atoms that make up the π bond, or on an adjacent atom.

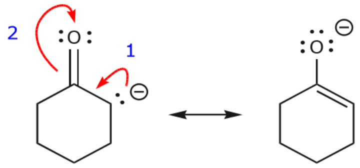


(b) The presence of a positive charge next to an atom bearing lone pairs of electrons.



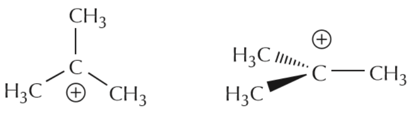
(c) The presence of a π bond next to an atom bearing lone pairs of electrons.



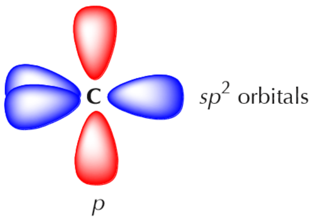


Orbital Pictures of Delocalization

The orbital view of delocalization can get somewhat complicated. For now we’re going to keep it at a basic level. We start by noting that sp^2 carbons actually come in several varieties. Two of the most important and common are neutral sp^2 carbons and positively charged sp^2 carbons. Substances containing neutral sp^2 carbons are regular alkenes. Species containing positively charged sp^2 carbons are called carbocations. The central carbon in a carbocation has trigonal planar geometry, and the unhybridized p orbital is empty. The following representations convey these concepts.

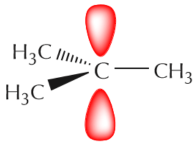


Top and side view of a carbocation in Lewis and 3-D notation



Orbital view of a carbocation. The unhybridized p orbital is empty

A combination of orbital and Lewis or 3-D formulas is a popular means of representing certain features that we may want to highlight. For example, if we're not interested in the sp2 orbitals and we just want to focus on what the p orbitals are doing we can use the following notation.

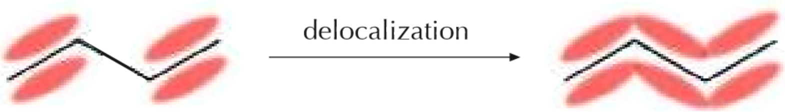


Let's now focus on two simple systems where we know delocalization of π electrons exists. One is a system containing two pi bonds in conjugation, and the other has a pi bond next to a positively charged carbon. We can represent these systems as follows.

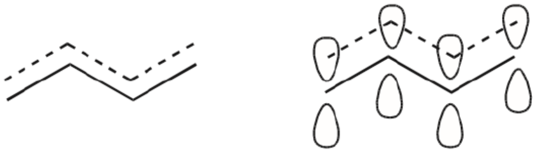
Line angle and orbital picture of a simple conjugated system

Line angle and orbital picture of a system containing a carbocation next to a *pi* bond

If we focus on the orbital pictures, we can immediately see the potential for electron delocalization. The two π molecular orbitals shown in red on the left below are close enough to overlap. Overlapping is a good thing because it delocalizes the electrons and spreads them over a larger area, bringing added stability to the system.

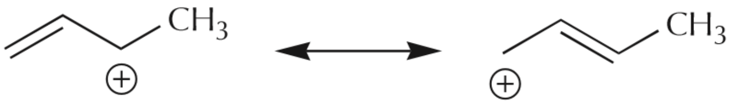


It is however time-consuming to draw orbitals all the time. The following representations are used to represent the delocalized system.

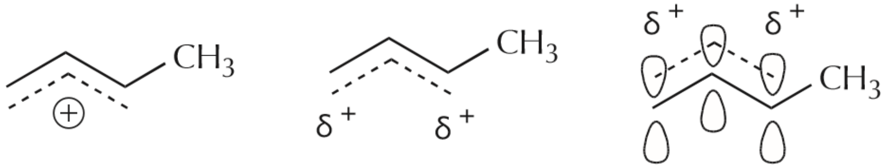


A similar process applied to the carbocation leads to a similar picture.

The resonance representation conveys the idea of delocalization of charge and electrons rather well.



Finally, the following representations are sometimes used, but again, the simpler they are, the less accurately they represent the delocalization picture.



There will be plenty of opportunity to observe more complex situations as the course progresses.

Contributors and Attributions

- Template:ContribCortez

1.3.5: Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other’s space, they repel each other; the force of repulsion is far greater than the force of attraction.

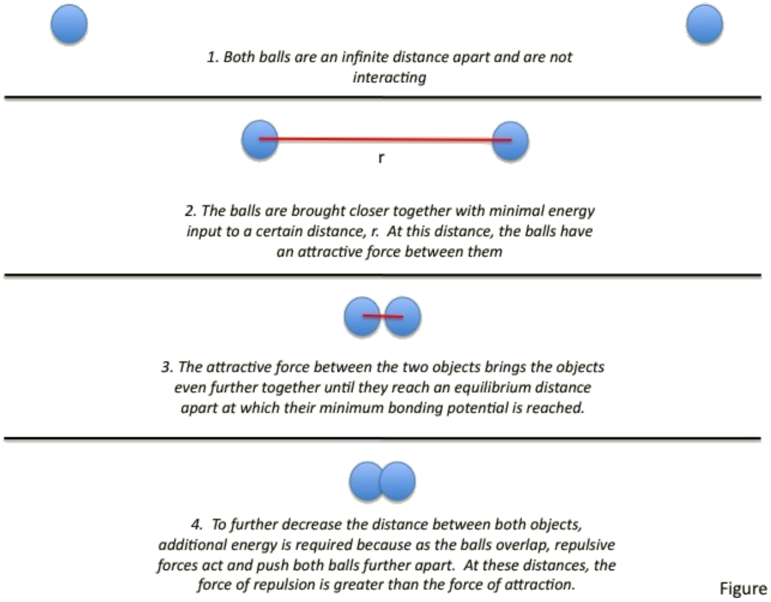


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1.3.5.1}$$

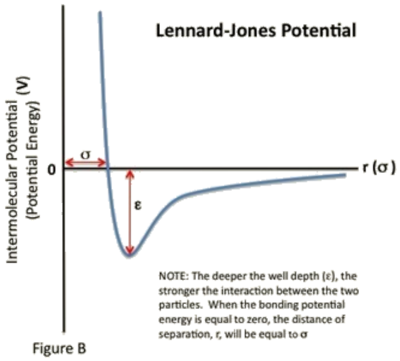
or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{1.3.5.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.
- σ is the distance at which the intermolecular potential between the two particles is zero (Figure $1.3.5.1$). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the

internuclear distance between nonbonding particles.
- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.



NOTE: The deeper the well depth (ε), the stronger the interaction between the two particles. When the bonding potential energy is equal to zero, the distance of separation, r, will be equal to σ

Figure B

Figure 1.3.5.1: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

✓ Example 1.3.5.1: The van der Waals Radius

The ϵ and σ values for Xenon (Xe) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

$$r = \sigma/2 = 4.10 \text{ Angstroms}/2 = 2.05 \text{ Angstroms}$$

Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other’s orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

✓ Example 1.3.5.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997 \text{ kJ/mol}$,
- $\sigma = 3.40 \text{ Angstroms}$, and
- the distance of separation, $r = 4.0 \text{ Angstroms}$.

We plug these values into Equation 1.3.5.1and solve as follows:

$$\begin{aligned} V &= 4(0.997 \text{ kJ/mol}) \left[\left(\frac{3.40 \text{ Angstroms}}{4.0 \text{ Angstroms}} \right)^{12} - \left(\frac{3.40 \text{ Angstroms}}{4.0 \text{ Angstroms}} \right)^{6} \right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

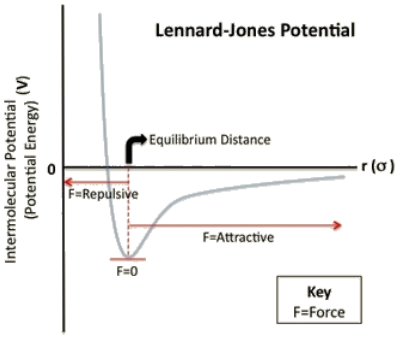


Figure C

Example 1.3.5.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ (4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

? Exercise 1.3.5.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

? Exercise 1.3.5.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

References

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2. Royer, Donald J. *Bonding Theory*. New York, NY.:McGraw-Hill, Inc., 1968.
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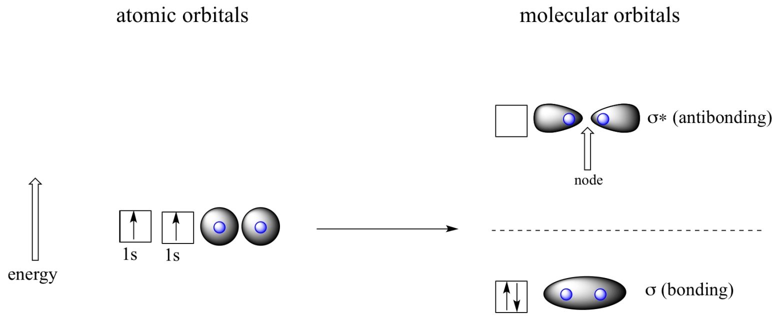
1.4: Molecular orbital theory- conjugation and aromaticity

Valence bond theory does a remarkably good job at explaining the bonding geometry of many of the functional groups in organic compounds. There are some areas, however, where the valence bond theory falls short. It fails to adequately account, for example, for some interesting properties of compounds that contain alternating double and single bonds. In order to understand these properties, we need to think about chemical bonding in a new way, using the ideas of molecular orbital (MO) theory.

Let's go back and consider again the simplest possible covalent bond: the one in molecular hydrogen (H_2). When we described the hydrogen molecule using valence bond theory, we said that the two 1*s* orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic 1*s* orbitals mathematically combine to form two new orbitals. Recall that an atomic orbital (such as the 1s orbital of a hydrogen atom) describes a region of space around a single atom inside which electrons are likely to be found. *A molecular orbital describes a region of space around two or more atoms inside which electrons are likely to be found.*

Mathematical principles tell us that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result from the combination – orbitals don't just disappear! We saw this previously when we discussed hybrid orbitals: one *s* and three *p* orbitals make four sp^3 hybrids. When two atomic 1*s* orbitals combine in the formation of H_2, the result is *two* **sigma (σ) orbitals**.



Molecular orbitals for H_2

According to MO theory, one sigma orbital is lower in energy than either of the two isolated atomic 1*s* orbitals –this lower sigma orbital is referred to as a **bonding molecular orbital**. The second, **'sigma star' (sigma*, σ*) orbital** is higher in energy than the two atomic 1*s* orbitals, and is referred to as an **antibonding molecular orbital**.

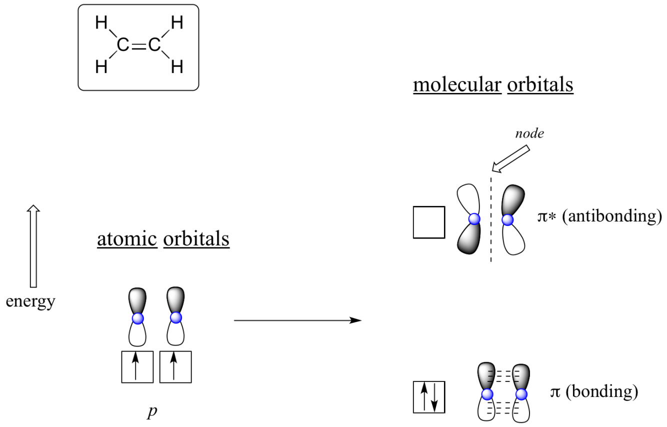
The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, antibonding sigma* orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

Remember that we are thinking here about electron behavior as *wave behavior*. When two separate waves combine, they can do so with **constructive interference**, where the two amplitudes build up and reinforce one another, or **destructive interference**, where the two amplitudes cancel one another out. Bonding MOs are the consequence of constructive interference between two atomic orbitals, which results in an attractive interaction and an increase in electron density between the nuclei. Antibonding MO's are the consequence of destructive interference which results in a repulsive interaction and a region of zero electron density between the nuclei (in other words, a node).

Following the same *aufbau* ('building up') principle you learned in General Chemistry for writing out electron configurations, we place the two electrons in the H_2 molecule in the lowest energy molecular orbital, which is the (bonding) sigma orbital. The bonding (attracting) MO is full, and the antibonding (repulsing) MO is empty.

MO theory and conjugated pi bonds

The advantage of using MO theory to understand bonding in organic molecules becomes more apparent when we think about pi bonds. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the sigma bonds in the molecule, and thinking *only* about the pi bond). We start with two atomic orbitals: one unhybridized 2p orbital from each carbon. Each contains a single electron. In MO theory, the two atomic combine mathematically to form two **pi (π) molecular orbitals**, one a low-energy pi bonding orbital and one a high-energy pi* (π*) antibonding orbital.



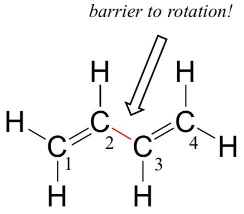
Molecular orbitals for ethene (ethylene)

In the bonding pi orbital, the two shaded lobes of the *p* orbitals interact *constructively* with each other, as do the two unshaded lobes (remember, the arbitrary shading choice represents mathematical (+) and (-) signs for the mathematical wavefunction describing the orbital). There is increased electron density between the two carbon nuclei in the molecular orbital - it is a bonding interaction.

In the higher-energy antibonding pi* orbital, the shaded lobe of one *p* orbital interacts *destructively* with the unshaded lobe of the second *p* orbital, leading to a node between the two nuclei and overall repulsion between the carbon nuclei.

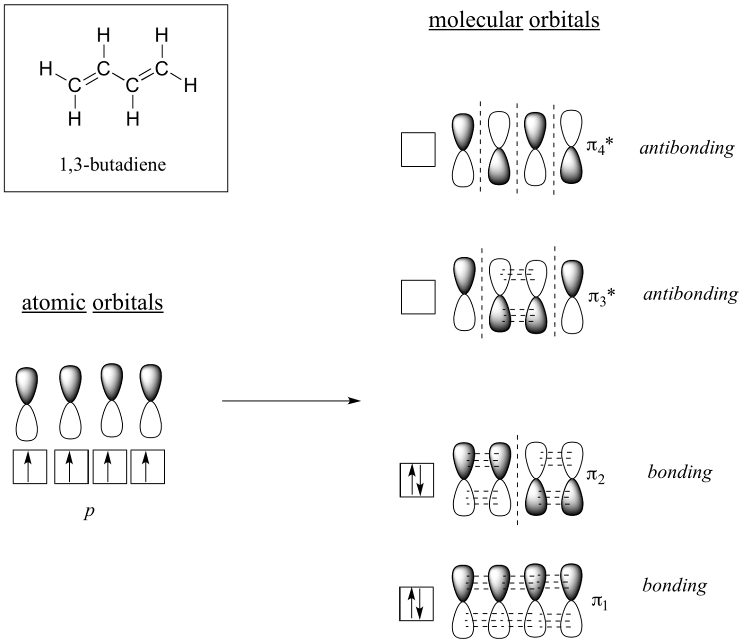
Again using the 'building up' principle, we place the two electrons in the lower-energy, bonding pi molecular orbital. The antibonding pi* orbital remains empty.

Next, we'll consider the 1,3-butadiene molecule. From valence orbital theory alone we might expect that the C_2-C_3 bond in this molecule, because it is a sigma bond, would be able to rotate freely.



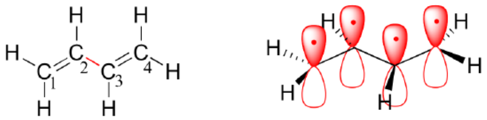
Experimentally, however, it is observed that there is a significant barrier to rotation about the C_2-C_3 bond, and that the entire molecule is planar. In addition, the C_2-C_3 bond is 148 pm long, shorter than a typical carbon-carbon single bond (about 154 pm), though longer than a typical double bond (about 134 pm).

Molecular orbital theory accounts for these observations with the concept of **delocalized pi bonds**. In this picture, the four *2p* atomic orbitals combine mathematically to form four pi molecular orbitals of increasing energy. Two of these - the bonding pi orbitals - are lower in energy than the *p* atomic orbitals from which they are formed, while two - the antibonding pi* orbitals - are higher in energy.



The lowest energy molecular orbital, pi$_1$, has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated *p* orbitals, the pi$_2$ orbital has one node but two constructive interactions - thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, pi$_3$* has two nodes and one constructive interaction, while pi$_4$* has three nodes and zero constructive interactions.

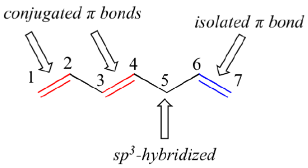
By the *aufbau* principle, the four electrons from the isolated 2p_z atomic orbitals are placed in the bonding pi$_1$ and pi$_2$ MO's. Because pi$_1$ includes constructive interaction between C_2 and C_3, there is a degree, in the 1,3-butadiene molecule, of pi-bonding interaction between these two carbons, which accounts for its shorter length and the barrier to rotation. The valence bond picture of 1,3-butadiene shows the two pi bonds as being isolated from one another, with each pair of pi electrons 'stuck' in its own pi bond. However, molecular orbital theory predicts (accurately) that the four pi electrons are to some extent delocalized, or 'spread out', over the whole pi system.



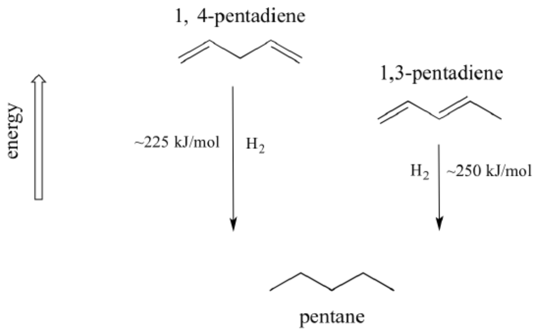
1,3-butadiene

space-filling view

1,3-butadiene is the simplest example of a system of **conjugated pi bonds**. To be considered conjugated, two or more pi bonds must be separated by only one single bond – in other words, there cannot be an intervening sp^3-hybridized carbon, because this would break up the overlapping system of parallel *p* orbitals. In the compound below, for example, the C_1-C_2 and C_3-C_4 double bonds are conjugated, while the C_6-C_7 double bond is **isolated** from the other two pi bonds by sp^3-hybridized C_5.

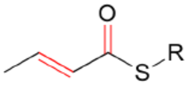


A very important concept to keep in mind is that *there is an inherent thermodynamic stability associated with conjugation.* This stability can be measured experimentally by comparing the **heat of hydrogenation** of two different dienes. (Hydrogenation is a reaction type that we will learn much more about in chapter 15: essentially, it is the process of adding a hydrogen molecule - two protons and two electrons - to a pi bond). When the two *conjugated* double bonds of 1,3-pentadiene are 'hydrogenated' to produce pentane, about 225 kJ is released per mole of pentane formed. Compare that to the approximately 250 kJ/mol released when the two *isolated* double bonds in 1,4-pentadiene are hydrogenated, also forming pentane.

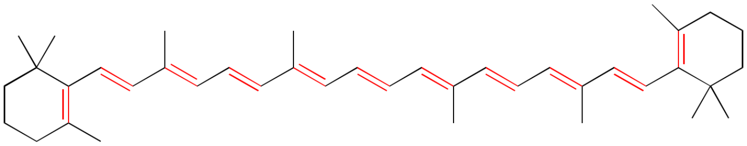


The conjugated diene is lower in energy: in other words, it is more stable. In general, conjugated pi bonds are more stable than isolated pi bonds.

Conjugated pi systems can involve oxygen and nitrogen atoms as well as carbon. In the metabolism of fat molecules, some of the key reactions involve alkenes that are conjugated to carbonyl groups.



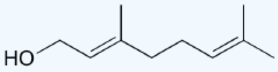
In chapter 4, we will see that MO theory is very useful in explaining why organic molecules that contain extended systems of conjugated pi bonds often have distinctive colors. beta-carotene, the compound responsible for the orange color of carrots, has an extended system of 11 conjugated pi bonds.

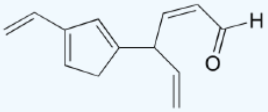


beta-carotene

Exercise 2.9

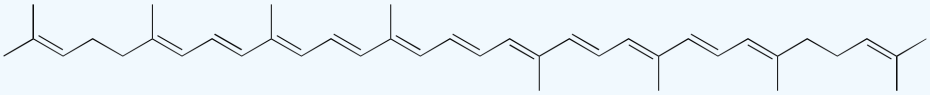
Identify all conjugated and isolated double bonds in the structures below. For each conjugated pi system, specify the number of overlapping *p* orbitals, and how many pi electrons are shared among them.





Exercise 2.10

Identify all isolated and conjugated double bonds in lycopene, the red-colored compound in tomatoes. How many pi electrons are contained in the conjugated pi system?

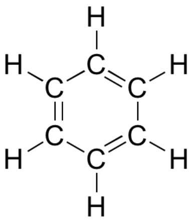


lycopene

Solutions to exercises

Aromaticity

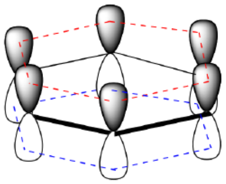
Molecular orbital theory is especially helpful in explaining the unique properties of **aromatic** compounds such as benzene:



3D interactive model of benzene

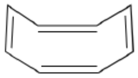
Although benzene is most often drawn with three double bonds and three single bonds, in fact all of the carbon-carbon bonds are exactly the same length (138 pm). In addition, the pi bonds in benzene are significantly less reactive than 'normal' pi bonds, either isolated or conjugated. Something about the structure of benzene makes its pi bonding arrangement especially stable. This ‘something’ has a name: it is called ‘aromaticity’.

What exactly is this ‘aromatic’ property that makes the pi bonds in benzene so stable? In large part, the answer to this question lies in the fact that benzene is a *cyclic* molecule in which all of the ring atoms are sp^2-hybridized. This allows the pi electrons to be delocalized in molecular orbitals that extend all the way around the ring, above and below the plane. For this to happen, of course, the ring must be planar – otherwise the *p* orbitals couldn’t overlap properly. Benzene is indeed known to be a flat molecule.



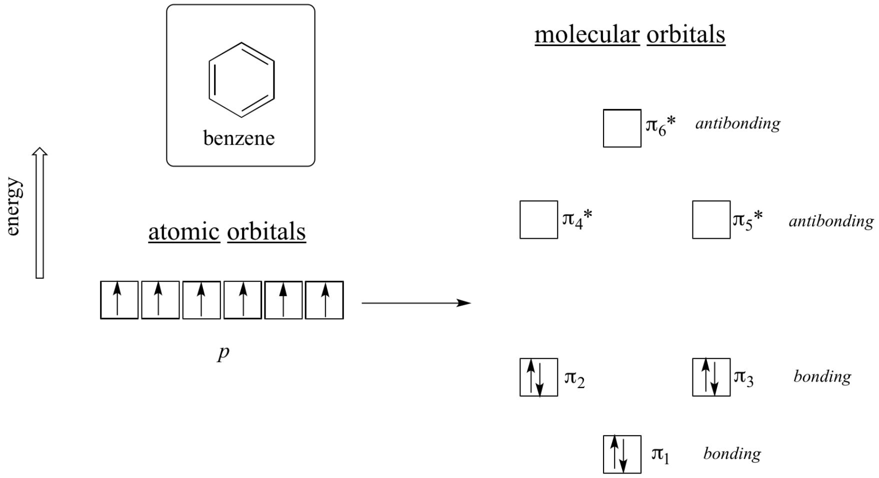
π electrons delocalized around the ring, above and below the plane

Do all cyclic molecules with alternating single and double bonds have this same aromatic stability? The answer, in fact, is ‘no’. The eight-membered cyclooctatetraene ring shown below is *not* flat, and its pi bonds react like 'normal' alkenes. π



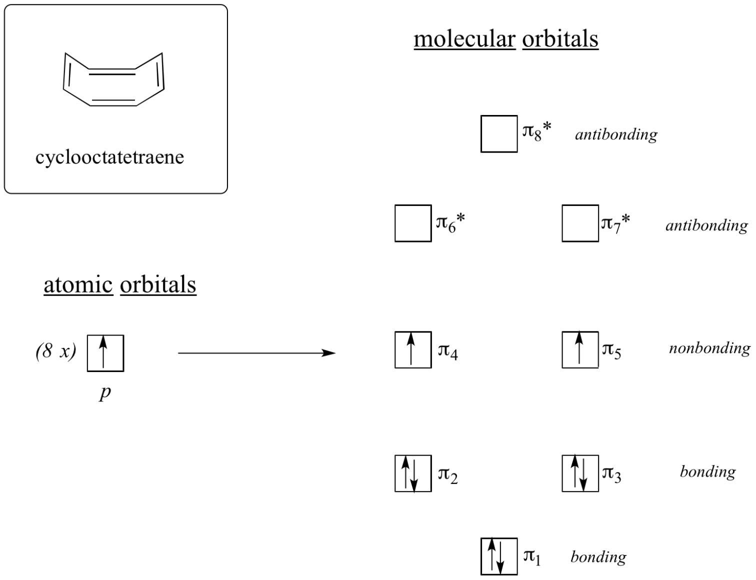
cyclooctatetraene
(not aromatic)

Clearly it takes something more to be aromatic, and this can best be explained with molecular orbital theory. Let’s look at an energy diagram of the pi molecular orbitals in benzene.



Quantum mechanical calculations tell us that the six pi molecular orbitals in benzene, formed from six atomic *p* orbitals, occupy four separate energy levels. pi$_1$ and pi$_6$* have unique energy levels, while the pi$_2$ - pi$_3$ and pi$_4$*- pi$_5$* pairs are **degenerate**, meaning they are at the same energy level. When we use the *aufbau* principle to fill up these orbitals with the six pi electrons in benzene, we see that the bonding orbitals are completely filled, and the antibonding orbitals are empty. This gives us a good clue to the source of the special stability of benzene: a full set of bonding MO's is similar in many ways to the 'full shell' of electrons in the atomic orbitals of the stable noble gases helium, neon, and argon.

Now, let's do the same thing for cyclooctatetraene, which we have already learned is *not* aromatic.



The result of molecular orbital calculations tells us that the lowest and highest energy MOs (pi$_1$ and pi$_8$*) have unique energy levels, while the other six form degenerate pairs. Notice that pi$_4$ and pi$_5$ are at the same energy level as the isolated $2p_z$ atomic orbitals: these are therefore neither bonding nor antibonding, rather they are referred to as **nonbonding MOs**. Filling up the MOs with the eight pi electrons in the molecule, we find that the last two electrons are unpaired and fall into the two degenerate nonbonding orbitals. Because we don't have a perfect filled shell of bonding MOs, our molecule is not aromatic. As a consequence, each of the double bonds in cyclooctatetraene acts more like an *isolated* double bond.

Here, then, are the conditions that must be satisfied for a molecule or group to be considered aromatic:

✓ Criteria for aromaticity:

The molecule or group must be cyclic.

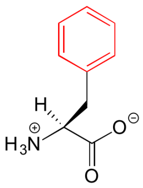
The ring must be planar.

Each atom in the ring must be sp^2-hybridized.

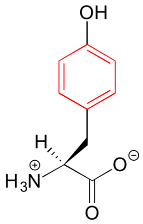
The number of pi electrons in the ring must equal $4n+2$, where n is any positive integer including zero.

Rule #4 is known as the **Hückel rule**, named after Erich Hückel, a German scientist who studied aromatic compounds in the 1930's. If $n = 0$, the Hückel number is **2**. If $n = 1$, the Hückel number is **6** (the Hückel number for benzene). The series continues with **10, 14, 18, 22,** and so on. Cyclooctatetraene has eight pi electrons, which is *not* a Hückel number. Because six is such a common Hückel number, chemists often use the term **'aromatic sextet'**.

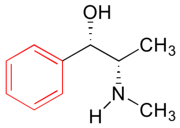
Benzene rings are ubiquitous in biomolecules and drugs - below are just a few examples.



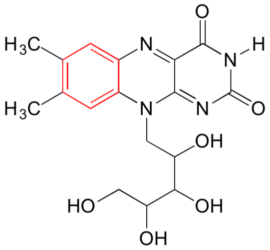
phenylalanine
(an amino acid)



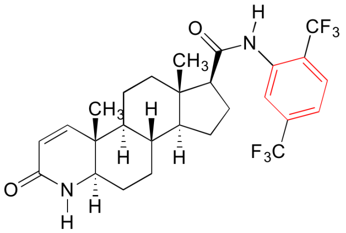
tyrosine
(an amino acid)



pseudoephidrine
(decongestant)



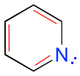
riboflavin
(a vitamin)



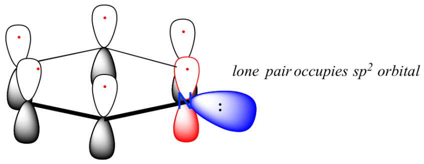
dutasteride
(GlaxoSmithKline drug for urinary condition in men)

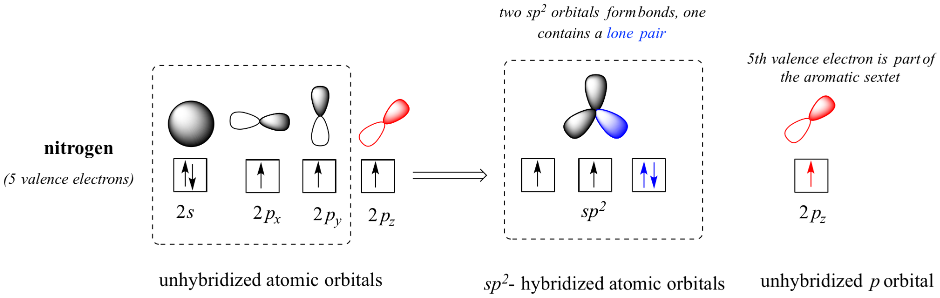
Recall that a benzene ring with a hydoxyl substituent -such as seen in the tyrosine structure above - is called a **phenol**.

Heterocycles - cyclic structures in which the ring atoms may include oxygen or nitrogen - can also be aromatic. Pyridine, for example, is an aromatic heterocycle. In the bonding picture for pyridine, the nitrogen is *sp*^{2}-hybridized, with two of the three *sp*^{2} orbitals forming sigma overlaps with the *sp*^{2} orbitals of neighboring carbon atoms, and the third nitrogen *sp*^{2} orbital containing the lone pair. The unhybridized *p* orbital contains a single electron, which is part of the 6 pi-electron system delocalized around the ring.



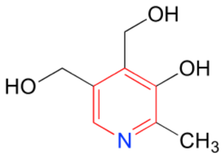
pyridine
(aromatic)



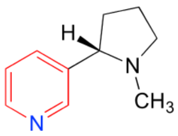


another image of orbitals in pyridine

Pyridoxine, commonly known as vitamin B$_6$, and nicotine are both substituted pyridines.

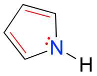


pyridoxine
(vitamin B_6)

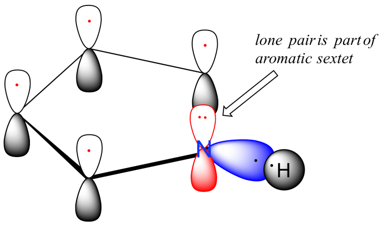


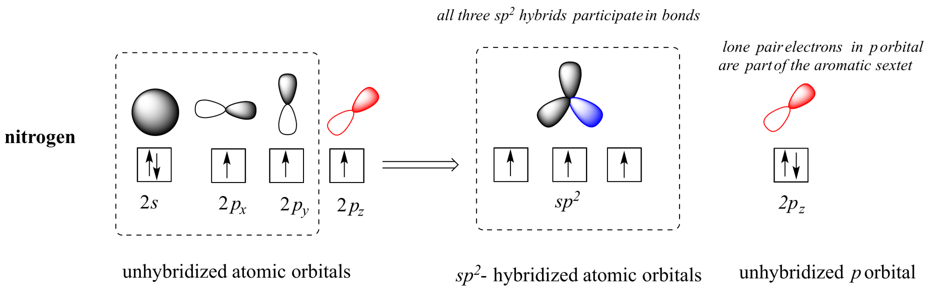
nicotine

Pyrrole is a five-membered aromatic heterocycle. In pyrrole, the lone pair electrons on the sp^2-hybridized nitrogen are part of the aromatic sextet (contrast this to pyridine, where the lone pair occupies one of the sp^2 hybrid orbitals).



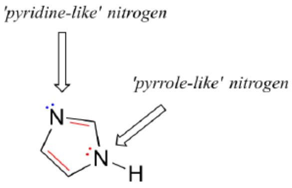
pyrrole



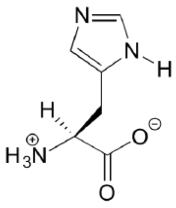


Why don't we assume that the nitrogen in pyrrole is sp^3-hybridized, like a normal secondary amine? The answer is simple: if it were, then pyrrole could not be aromatic, and thus it would not have the stability associated with aromaticity. In general, *if a molecule or group can be aromatic, it will be*, just as water will always flow downhill if there is a downhill pathway available.

Imidazole is another important example of an aromatic heterocycle found in biomolecules - the side chain of the amino acid histidine contains an imidazole ring.



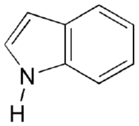
imidazole



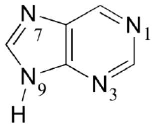
histidine

In imidazole, one nitrogen is 'pyrrole-like' (the lone pair contributes to the aromatic sextet) and one is 'pyridine-like' (the lone pair is located in an sp^2 orbital, and is *not* part of the aromatic sextet).

Fused-ring structures can also fulfill the Hückel criteria, and often have many of the same properties as monocyclic aromatic compounds, including a planar structure. Indole (a functional group on the side chain of the amino acid tryptophan) and purine (found in guanine and adenine nucleotide bases) both have a total of ten pi electrons delocalized around two rings.



indole

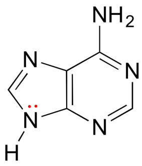


purine

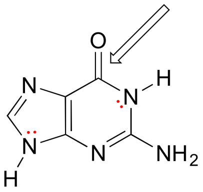
The nucleic acid bases of DNA and RNA - guanine, adenine, cytosine, thymine, and uracil - are all aromatic systems, with the characteristic aromatic properties of planarity and delocalized pi electron density. When you study the structure and function of DNA and RNA in a biochemistry or molecular biology course, you will see that the planar shape of the bases plays a critically important role.

red lone pairs are part of aromatic system

electrons in carbonyl π bonds are ***not*** *part of aromatic system*

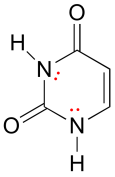


adenine

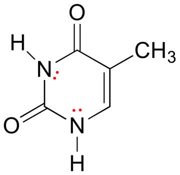


guanine

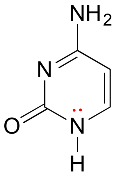
10 aromatic π electrons



uracil



thymine



cytosine

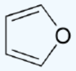
6 aromatic π electrons

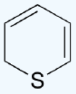
Exercise 2.11

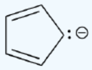
Classify the nitrogen atoms of indole and purine as either 'pyrrole-like' or 'pyridine-like', in terms of where the lone pair electrons are located.

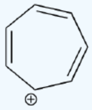
Exercise 2.12

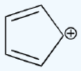
Are the following molecules/ions aromatic? Explain, using criteria you learned in this section.

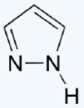
a) 

b) 

c) 

d) 

e) 

f) 

Solutions to exercises

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

1.4.1: The H₂⁺ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

1.4.1.1: The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry and it also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation (i.e., fixed nuclei). This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

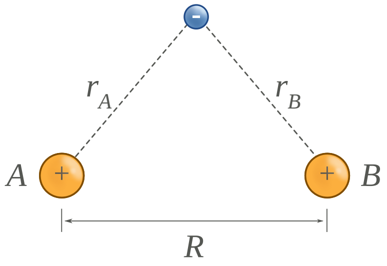


Figure 9.2.1 : Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{1.4.1.1}$$

where r_A and r_B are the distances electron from the A and B hydrogen nuclei, respectively and R is the distance between the two protons.

Although the Schrödinger equation for H_2^+ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

1.4.1.2: Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position r of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{1.4.1.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 1.4.1.2with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.

For H_2^+, the simplest molecule, the starting function is given by Equation 1.4.1.2 We must determine the values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{1.4.1.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{1.4.1.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

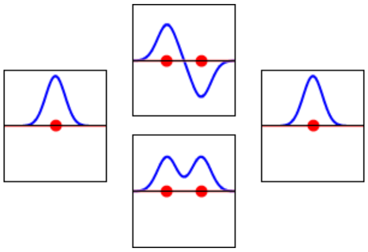


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Rudolf Winter (Aberystwyth University)

1.4.2: Bonding and Antibonding Orbitals

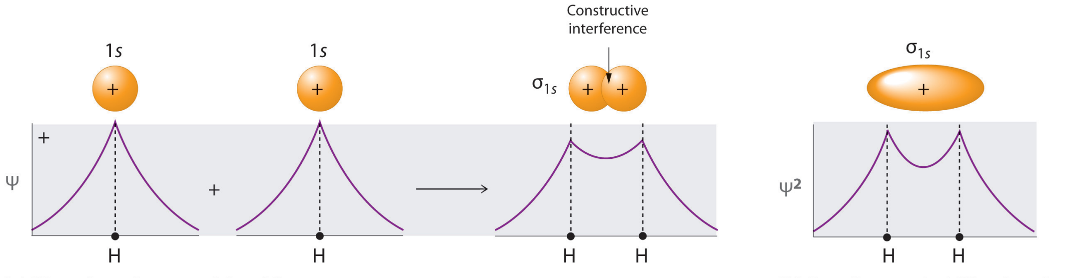
Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in H^+

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j$^{\text{th}}$ molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

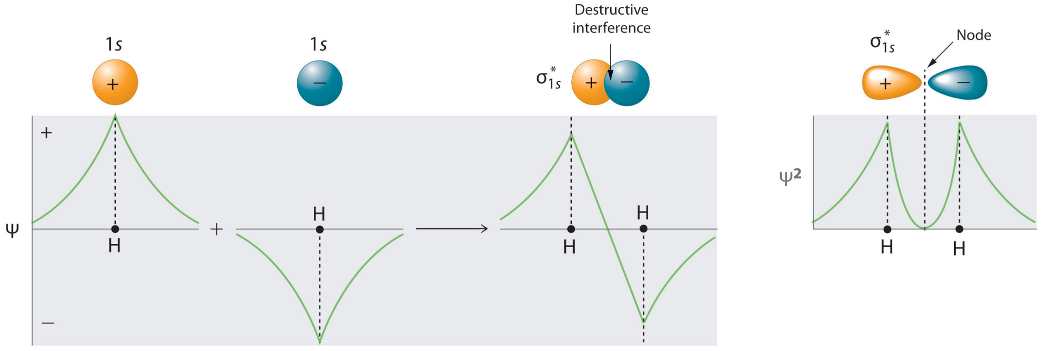
$$|\psi_J\rangle = \sum_i^N c_{J,i}|\phi_i\rangle \tag{1.4.2.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 1.4.2.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wavefunction.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wavefunction (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. (CC BY-SA-NC; anonymous).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}(|1s_A\rangle + |1s_B\rangle) \tag{1.4.2.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma^*_{1s}\rangle = \frac{1}{\sqrt{2(1-S)}}(|1s_A\rangle - |1s_B\rangle) \tag{1.4.2.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wavefunctions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^\star_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^\star_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^\star_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 9.5.2

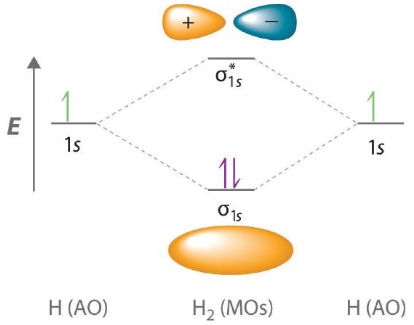


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

1.4.2.1: Expanding Beyond the 1s Orbital Basis Set

This picture of bonding in H_2^+ in the previous section is very simple, but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact). To better describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide additional parameters, which can be optimized by the linear variational method, to give a better function with a lower energy and more accurate description of the charge density.

The energy of the non-normalized molecular orbital can be calculated from the expectation value integral of the Hamiltonian,

$$E_J = \frac{\left\langle \psi_J | \hat{H}_{elec} | \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{1.4.2.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 1.4.2.1) into the energy expression of Equation 1.4.2.4results in:

$$E_J = \frac{\left\langle \sum_i c^*_{J,i} \phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c^*_{J,i} \phi_j | \sum_j c_{J,j} \phi_j \right\rangle} \tag{1.4.2.5}$$

$$= \frac{\sum_{i,j} c^*_{J,i} c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c^*_{J,i} c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{1.4.2.6}$$

$$= \frac{\sum_{i,j} c^*_{J,i} c_{J,j} H_{ij}}{\sum_{i,j} c^*_{J,i} c_{J,j} S_{ij}} \tag{1.4.2.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{1.4.2.8}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - ES_{ki}) = 0 \tag{1.4.2.9}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1 , these are

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{1.4.2.10}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{1.4.2.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 1.4.2.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \tag{1.4.2.12}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 1.4.2.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all N(N –1)/2 values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_J solve the set of linear equations to determine the basis set coefficients \(c_{ij\}) for the j-th molecular orbital

For more information on solving the Secular equations check here.

The greater the number of atomic orbitals N that combine to genera the molecular orbitals (Equation 1.4.2.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{1.4.2.13}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

1.4.3: A Simple Molecular-Orbital Treatment of H₂ Places Both Electrons in a Bonding Orbital

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{1.4.3.1}$$

where

- j is the index for the j^{th} basis function (e.g., atomic orbital)
- i is the i^{th} molecular orbitals and
- c_{ij} is the expansion coefficient of the j^{th} basis function for the i^{th} molecular orbital.

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. Just as for atoms, each electron in a molecule can be described by a product of spin-orbitals. Since electrons are fermions, the electronic wavefunction must be **antisymmetric** with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1) \\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2) \end{vmatrix} \tag{1.4.3.2}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ. Following the Aufbau Principle, two electrons with different spins (α and β, consistent with the Pauli Exclusion Principle discussed for muliti-electron atoms) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\psi_2^2\psi_3^2\ldots\psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure 9.6.1 . Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure 9.6.1 .

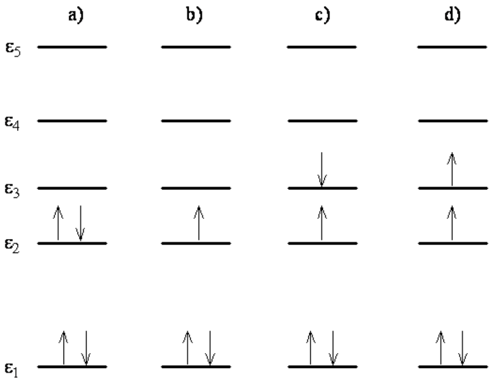


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

1.4.3.1: Symmetry

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a g or a u is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x,-y,-z)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to $(-x,-y,-z)$. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{1.4.3.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei $(charge = +2e)$ separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

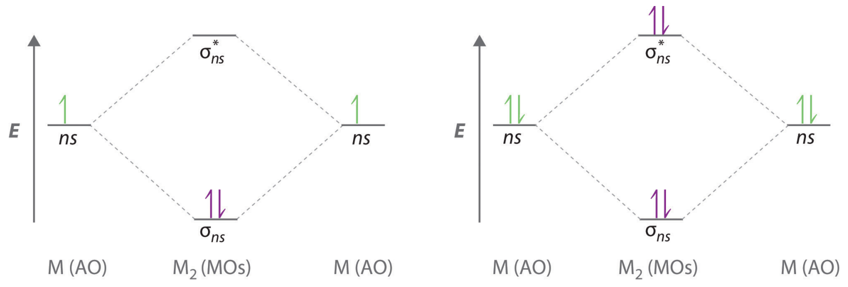
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)

1.4.4: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

1.4.4.1: Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.1 , where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.



(a) Alkali metals **(b) Alkaline earth metals**

Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure 1.4.4.1b, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

✓ Example 9.7.1 : Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

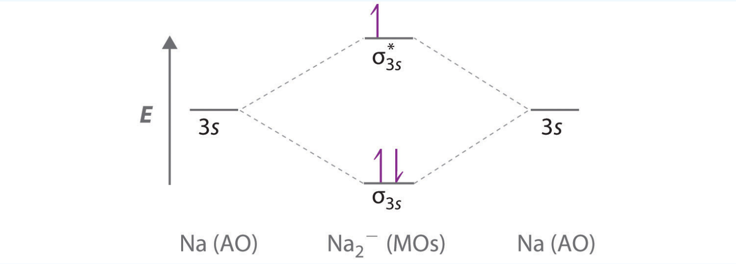
Strategy

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma_{3s}^\star)^1$ electron configuration.



(CC BY-SA-NC; anonymous).

C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 9.7.1 : Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma_{4s}^\star)^1$ electron configurations and a bond order of 1/2 and should exist.

1.4.4.2: Molecular Orbitals Formed from *np* Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.4.4.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.2 , it is the mathematical *difference* of their wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.4.4.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{1.4.4.3}$$

In this combination, shown in part (b) in Figure 9.7.2 , the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

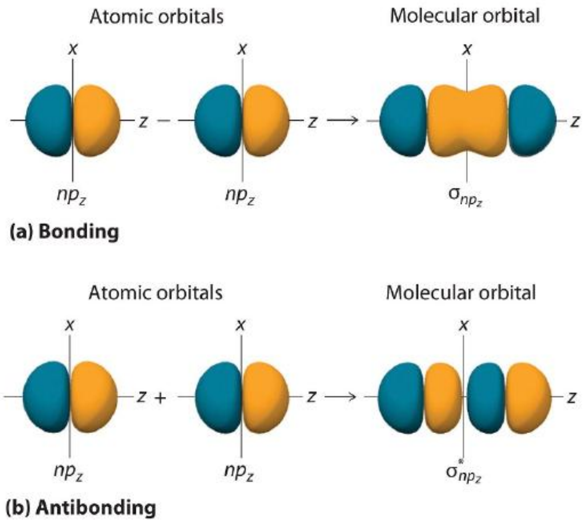


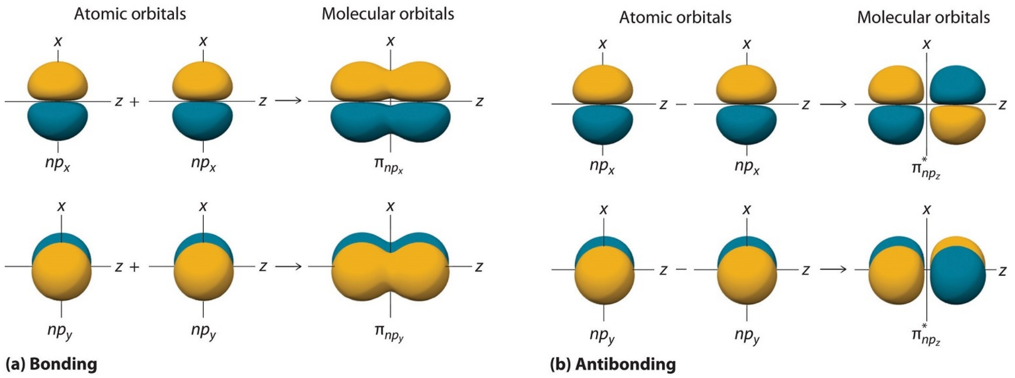
Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3 , we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\left(A\right) + np_x\left(B\right) \tag{1.4.4.4}$$

$$\pi^\star_{np_x} = np_x\left(A\right) - np_x\left(B\right) \tag{1.4.4.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^\star_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^\star_{np_x}$ and $\pi^\star_{np_y}$ molecular orbitals.



(a) Bonding

(b) Antibonding

Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

1.4.4.3: Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 9.7.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

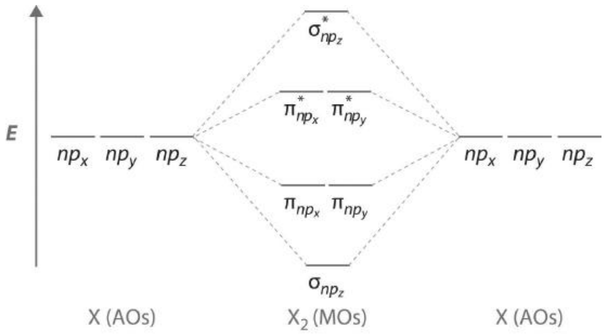


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous).

> *The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.*

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure $1.4.4.5a$; the *n* = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the *n* = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

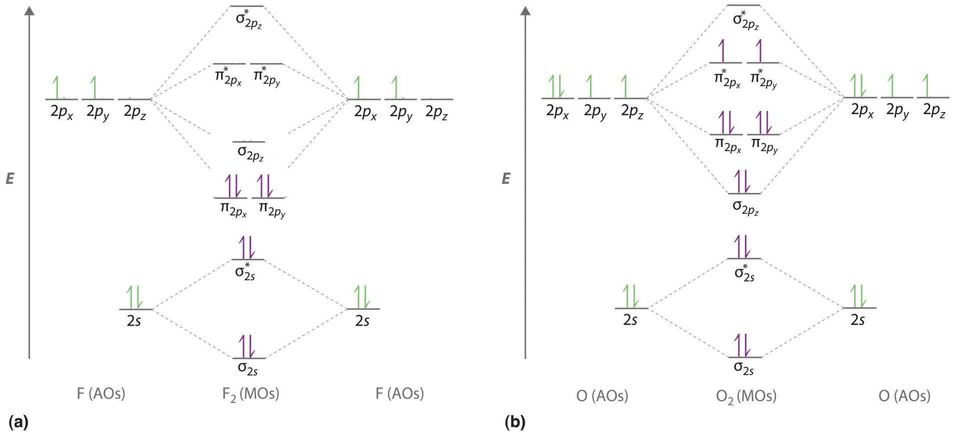


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 9.7.6 . Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 9.7.6). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

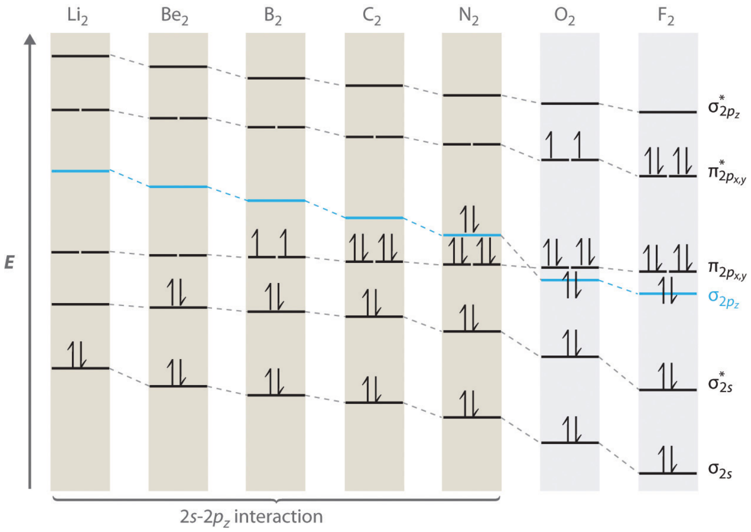


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous).

✓ Example 9.7.2 : Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

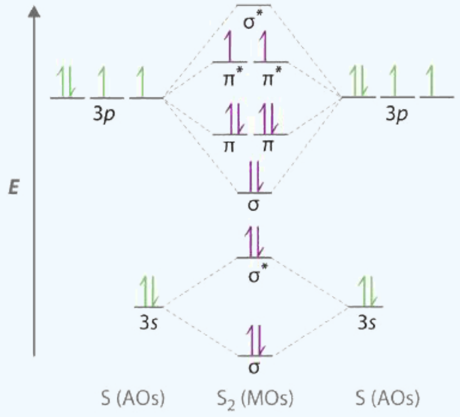
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund’s rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figures 9.7.6 and 9.7.7 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



(CC BY-SA-NC; anonymous).

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^\star_{3p_x}$ and $\pi^\star_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^\star_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^\star_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.7.2

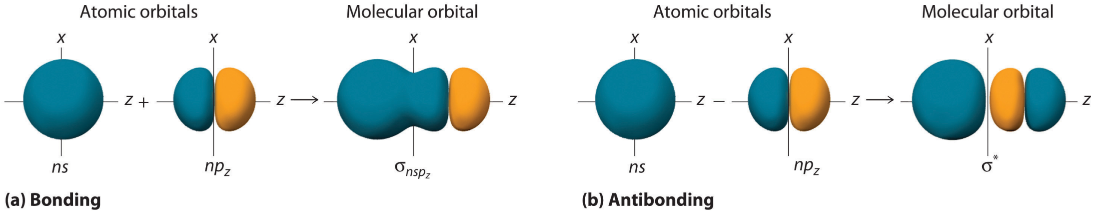
Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^\star_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^\star_{x,y}})^4$ bond order of 1; no unpaired electrons

1.4.4.4: Molecular Orbitals Formed from *ns* with *np* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.7 , the sum of the two atomic wavefunctions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.



(a) Bonding

(b) Antibonding

Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

1.4.5: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 1.4.5.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

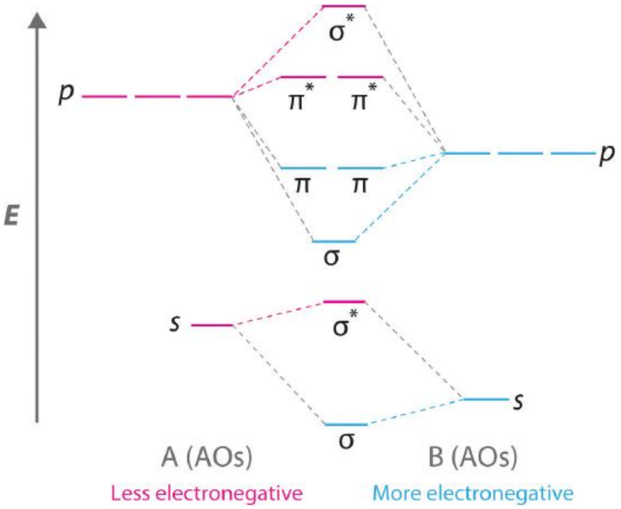


Figure 1.4.5.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 1.4.5.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 1.4.5.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

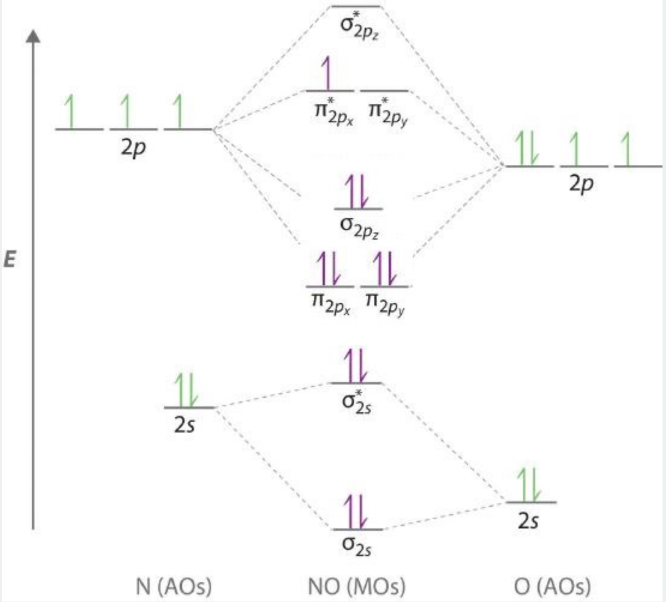


Figure 1.4.5.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x}, \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 1.4.5.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 1.4.5.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

1.4.5.1: Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 1.4.5.6 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - -Cl^{\delta-}$.

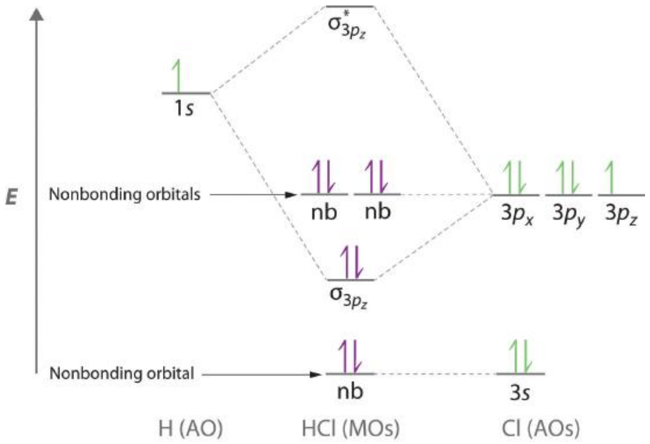


Figure 1.4.5.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

✓ Example 1.4.5.4: The Cyanide Ion

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 1.4.5.4to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

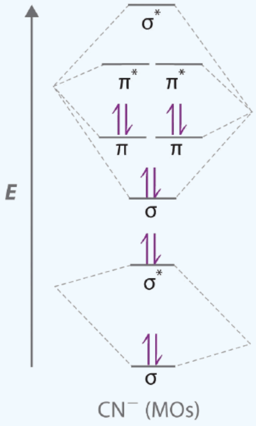
Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 1.4.5.4in order of increasing energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 1.4.5.4fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 1.4.5.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

1.4.5.2: Summary

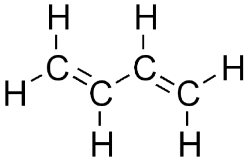
Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

1.4.6: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula C_4H_6 and can be viewed structurally as two vinyl groups ($CH_2{=}CH_2$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{1.4.6.1}$$

for the ith molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{1.4.6.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 1.4.6.2become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{1.4.6.3}$$

Solving Equation 1.4.6.3for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{1.4.6.4}$$

If both sides of Equation 1.4.6.4were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha-E}{\beta} \tag{1.4.6.5}$$

then Equation 1.4.6.4simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{1.4.6.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 1.4.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{1.4.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 1.4.6.7can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm 0.618$ and $x = \pm 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{1.4.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{1.4.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{1.4.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{1.4.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

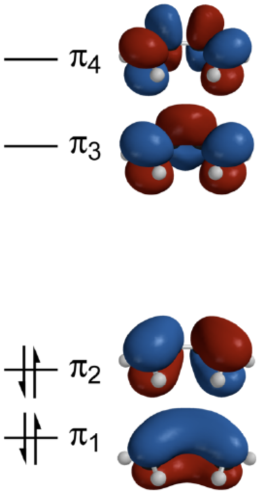


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 1.4.6.8-1.4.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha+1.618\beta) + 2(\alpha+0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{1.4.6.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

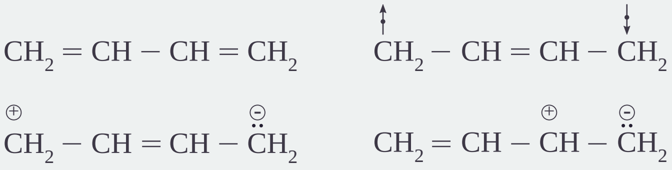
$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{1.4.6.13}$$

Comparing Equation 1.4.6.12 with Equation 1.4.6.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β (the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

> *The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.*

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure $2a$ dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.



$$\mathrm{CH_2=CH-CH=CH_2} \qquad \mathrm{\overset{\uparrow}{C}H_2-CH=CH-\overset{\downarrow}{C}H_2}$$

$$\mathrm{\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{\ddot{C}}H_2} \qquad \mathrm{CH_2=CH-\overset{\oplus}{C}H-\overset{\ominus}{\ddot{C}}H_2}$$

Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 1.4.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 1.4.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{1.4.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{1.4.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{1.4.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{1.4.6.17}$$

These are depicted in Figure 10.6.3 .

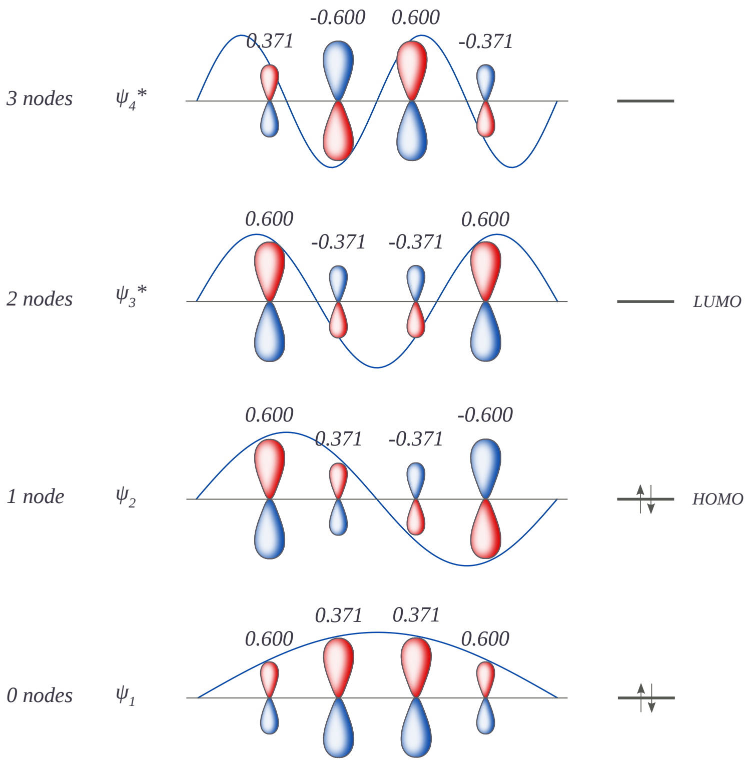


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

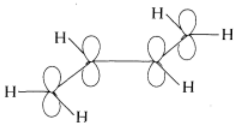
Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

1.4.6.1: Application of the MO Method to 1,3-Butadiene

To treat the π-electron system of 1,3-butadiene by simple MO theory, we combine the four p carbon orbitals of an atomic-orbital model, such as 17, to obtain four molecular orbitals:



17

Figure 21-8). Therefore the delocalization energy is $(4\alpha+4.48\beta)-(4\alpha+4\beta)=0.48\beta$ or $9\,\text{kcal}$, assuming that $\beta=19\,\text{kcal}$. (The corresponding VB calculation gives the delocalization in good agreement as $0.23J$ or $8\,\text{kcal}$; Section 21-3D.)

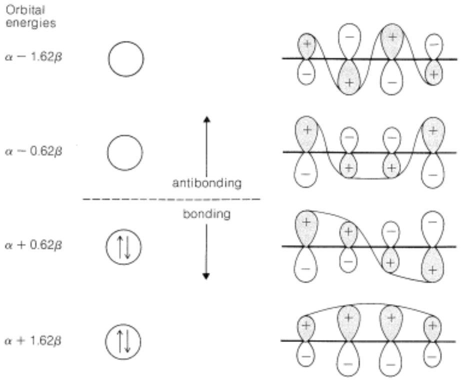


Figure 21-7: Energies and schematic representations of the π molecular orbitals of 1,3-butadiene. If four electrons are placed in the two lowest orbitals, the π-electron energy is $2(\alpha+1.62\beta)+2(\alpha+0.62\beta)=4\alpha+4.48\beta$. The schematic representations show the number of phase changes (nodes) in each molecular orbital, and the sizes of the atomic orbitals are drawn to represent crudely the extent to which each contributes to each molecular orbital. Again, the energy of the orbitals increases with increasing number of nodes.

We can estimate a stabilization energy for butadiene from heats of hydrogenation, and it is useful to compare the values obtained with the calculated delocalization energy. Thus the heat of hydrogenation of 1,3-butadiene is $57.1\,\text{kcal}$, whereas that of ethene is $32.8\,\text{kcal}$ and of propene $30.1\,\text{kcal}$. If ethene is used as the model alkene, the stabilization energy of 1,3-butadiene is $(2\times32.8-57.1)=8.5\,\text{kcal}$, whereas with propene as the model, it would be $(2\times30.1-57.1)=3.1\,\text{kcal}$. The bond energies (Table 4-3) in combination with the heat of formation at 25^{o} $(26.33\,\text{kcal})$ give a stabilization energy of $5.0\,\text{kcal}$.

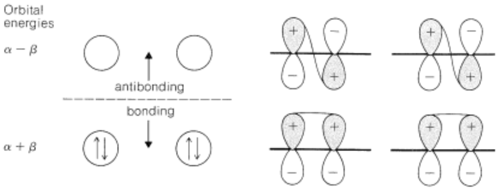


Figure 21-8: Energies and schematic representations of the π molecular orbitals of localized 1,3-butadiene. The orbitals are the π orbitals of two isolated ethene bonds and the total π-electron energy is $4(\alpha+\beta)=4\alpha+4\beta$.

1.4.6.1.1: Contributors and Attributions

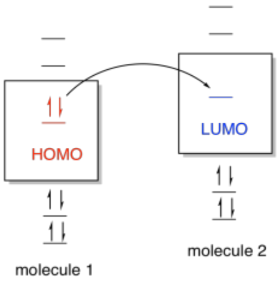
John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

1.4.7: Molecular Orbitals of Conjugated Pi Systems

Frontier Molecular Orbital Theory

Prior to 1965, pericyclic reactions were known as "no mechanism reactions" since no one could adequately explain why reaction outcomes changed depending on whether reactants were exposed to heat or light. In 1965 Robert Burns Woodward and Roald Hoffmann used **Frontier Molecular Orbital Theory**, initially proposed by Kenichi Fukui, to develop their **Theory of Conservation of Orbital Symmetry** where outcomes of pericyclic reactions are explained by examining the **Highest Occupied Molecular Orbital (HOMO)** or **Lowest Unoccupied Molecular Orbital (LUMO)** of the reacting system. Their analysis of cycloadditions, electrocyclic reactions, and sigmatropic rearrangements is commonly referred to as the Woodward-Hoffmann Rules. A detailed analysis of three reaction types is provided in the subsequent sections of this chapter.

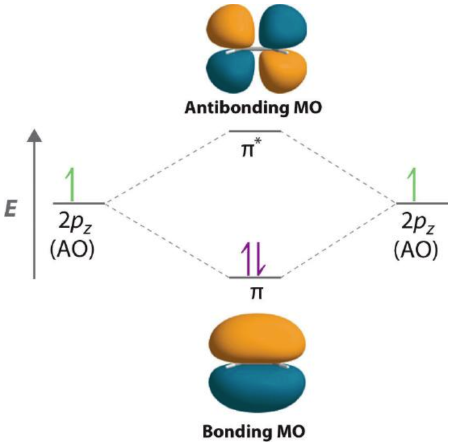
HOMO and LUMO are often referred to as **frontier orbitals** and their energy difference is termed the **HOMO–LUMO gap**. One common way of thinking about reactions in this way is through the concept of frontier orbitals. This idea says that if one species is going to donate electrons to another in order to form a new bond, then the donated electrons are most likely going to come from the highest occupied energy level. In this level, called the highest occupied molecular orbital (HOMO), the electrons are further from the nucleus and therefore less tightly held by the protons in the nucleus. The electrons would be donated, in turn, to the lowest empty energy level on the other species, called the lowest unoccupied molecular orbital (LUMO).



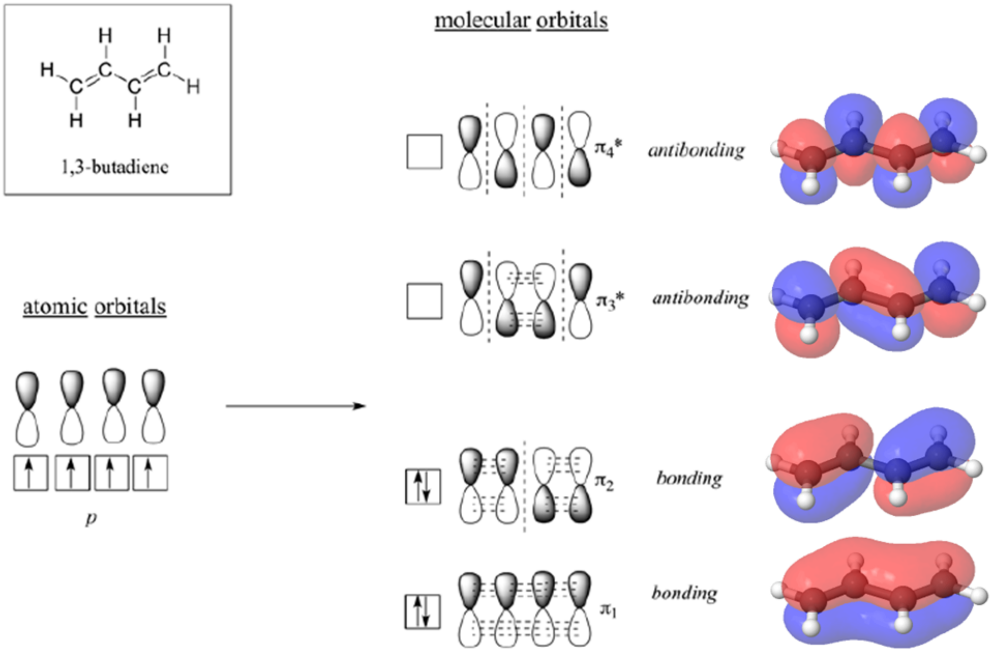
Molecular orbital interaction between frontier orbitals.

Molecular Orbitals

According to MO theory discussed in **Section 1-11**, when a double bond is non-conjugated, the two atomic 2p_z orbitals combine to form two **pi (π) molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **π-star (π*) anti-bonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π. In the bonding Ψ_1 orbital, the two (+) lobes of the $2p_z$ orbitals interact constructively with each other, as do the two (-) lobes. Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital. In the higher-energy anti-bonding Ψ_2* orbital, the (+) lobes of one 2p_z orbital interacts destructively with the (-) lobe of the second 2p_z orbital, leading to a node between the two nuclei and overall repulsion. By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy $\Psi_1$orbital when the molecule is in the ground state.

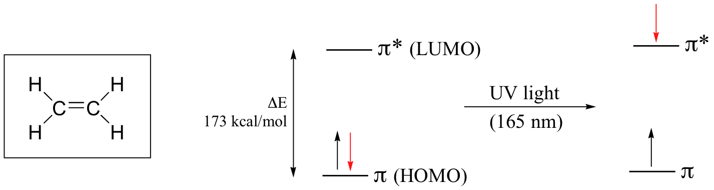


With a conjugated diene, such as 1,3-butadiene, the four *2p* atomic orbitals combine to form four pi molecular orbitals of increasing energy. Two bonding pi orbitals and two antibonding pi* orbitals. The combination of four pi molecular orbitals allow for the formation of a bonding molecular orbital that is lower in energy than those created by an unconjugated alkene. The 4 pi electrons of 1,3-butadiene completely fill the bonding molecular orbitals giving is the additional stability associated with conjugated double bonds.

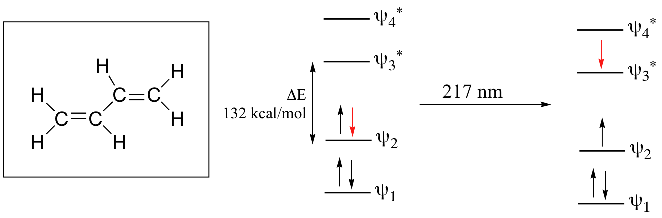


Electronic Transitions

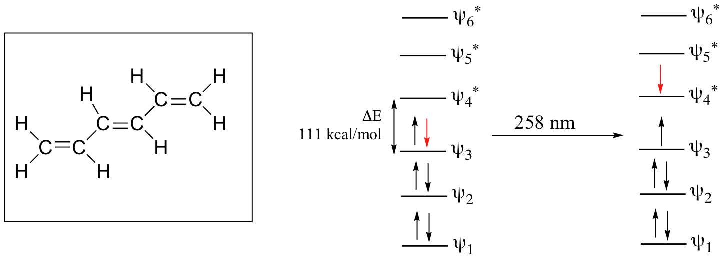
When a double-bonded molecule such as ethene (common name ethylene) absorbs 165 nm light, it undergoes a **π - π* transition**. An electron is moved from the HOMO of ethene to the LUMO placing the molecule in an **excited state**.



Where electronic transition becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems. In these groups, the HOMO–LUMO gap energy gap for π -π* transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. The MO diagram for 1,3-butadiene, the simplest conjugated system. Recall that we can draw a diagram showing the four pi MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are pi bonding, while the upper two are pi antibonding. Comparing this MO picture to that of ethene, our isolated pi-bond example the HOMO would be psi 2 and the LUMO would be psi 3. The HOMO-LUMO energy gap is smaller for the conjugated 1,3-butadiene system which absorbs UV light with a wavelength of 217 nm.



As conjugated pi systems become larger, the HOMO–LUMO gap energy gap for a π - π* transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the π - π* transition in 1,3,5-hexatriene, for example, occurs at 258 nm.



Woodward-Hoffmann Rules

Much of what we have said about the electronic factors controlling pericyclic reaction was formulated in the mid 1960's by the American chemists R. B. Woodward and R. Hoffmann, in terms of what came to be called the **orbital symmetry** principles, or the **Woodward-Hoffmann rules**. This is a particularly simple approach says that many details of pericyclic reactions can explained by "conservation of orbital symmetry." This requires the symmetries of the molecular orbitals of reactants to be the same as the molecular orbitals of the products for a reaction to proceed.

The original approach of Woodward and Hoffmann involved construction of an "orbital correlation diagram" to see if the lobes of the reactant molecular orbitals match phases and allow for overlap required for bonding to occur. The symmetries of the appropriate reactant and product orbitals were matched to determine whether the transformation could proceed without a symmetry imposed conversion of bonding reactant orbitals to antibonding product orbitals. If the correlation diagram indicated that the reaction could occur without encountering such a **symmetry-imposed barrier**, it was termed **symmetry allowed**. If a symmetry barrier was present, the reaction was designated **symmetry-forbidden**.

? Exercise 1.4.7.1

Using the molecular orbital diagram for 1,3,5-hexatriene determine the HOMO and LUMO for both the ground and excited state.

Answer

For the ground state the HOMO is psi 3 and LUMO is psi 4.

For the excited state the HOMO is psi 4 and LUMO is psi 5.

1.4.8: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of CnHn where n is the number of carbon atoms in the ring. The molecule from this important class of organic molecule that you are most familiar with is benzene (C_6H_6) with $n = 6$, although many other molecules exist like cyclobutadiene (C_4H_4) with $n = 4$ (Figure 10.7.1).

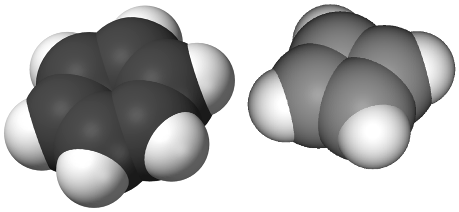


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

Structure of Benzene

The structure of benzene is an interesting historical topic. In 1865, the German chemist Friedrich August Kekulé published a paper suggesting that the structure of benzene contained a ring of six carbon atoms with alternating single and double bonds. Within this argument, two resonance structures can be formulated.

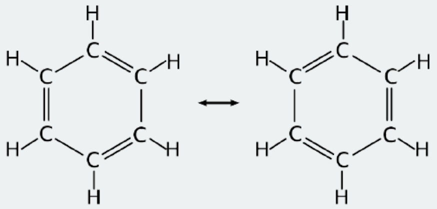


Figure 10.7.2 : Resonance structures of benzene.

However, X-ray diffraction shows that all six carbon-carbon bonds in benzene are of the same length, at 140 pm. The C–C bond lengths are greater than a double bond (135 pm), but shorter than a typical single bond (147 pm). This means that neither of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{1.4.8.1}$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$
- $E_3 = \alpha + \beta$

- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

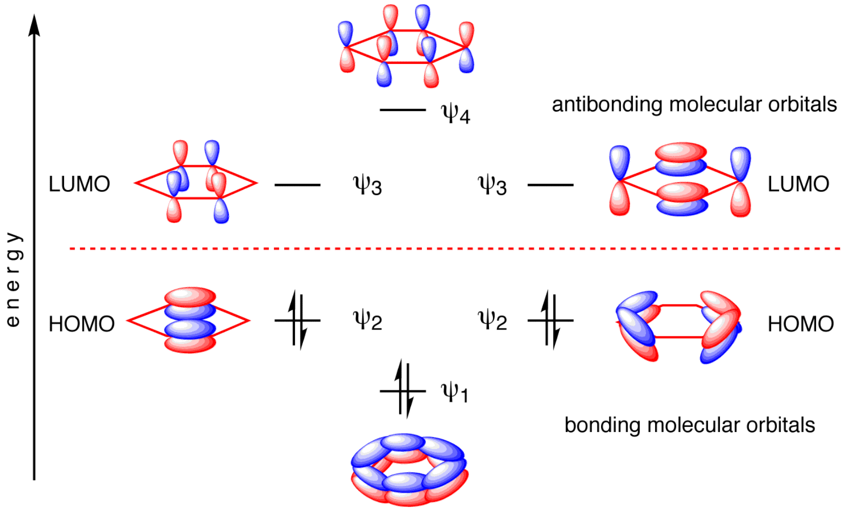


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$\begin{aligned}
|\psi_1\rangle &= \frac{1}{\sqrt{6}}[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle] \\
|\psi_2\rangle &= \frac{1}{\sqrt{4}}[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle] \\
|\psi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_4\rangle &= \frac{1}{\sqrt{4}}[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle] \\
|\psi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_6\rangle &= \frac{1}{\sqrt{6}}[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle]
\end{aligned}$$

Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π-bonding energy is

$$\begin{aligned}
E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\
&= 6\alpha + 8\beta
\end{aligned} \tag{1.4.8.2}$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$\begin{aligned}
\Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\
&= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\
&= 2\beta
\end{aligned}$$

The experimental thermochemical value is -152 kJ mol^{-1}.

1.4.8.1: Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n+2)\pi$ electrons (n=0,1,2…). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is 2β (Equation 1.4.8.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n+2)\pi$ electrons with n=2, 6, 10, ... electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.

$$\mathrm{C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}}$$

In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1}. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1}. These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

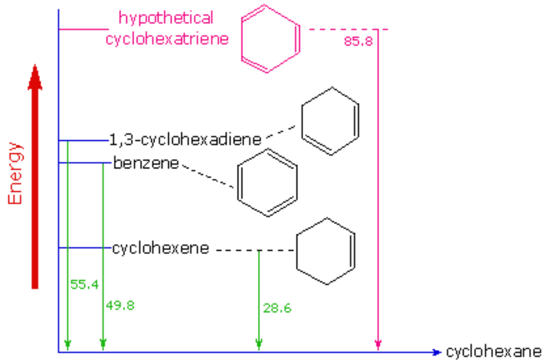


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resuch);

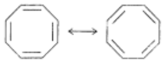
In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1}, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol-1 more stable than expected. This additional stability is a characteristic of all aromatic compounds.

1.4.8.1: Hückel's 4n + 2 Rule

1.4.8.1.1: Cyclobutadiene and Cyclooctatetraene

More than 100 years ago, Kekule recognized the possible existence of other conjugated cyclic polyalkenes, which at least superficially would be expected to have properties like benzene. The most interesting of these are cyclobutadiene, 23, and cyclooctatetraene, 24:

23



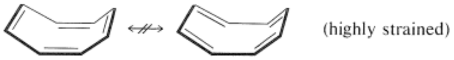
24

For each we can write two equivalent planar VB structures, and the qualitative VB method would suggest that both compounds, like benzene, have substantial electron-delocalization energies. However, the planar structures would have abnormal $\mathrm{C-C=C}$ angles, and consequently at least some degree of *destabilization* associated with these bond angles (Section 12-7). Nonetheless, estimation of the strain energies show that while they are substantial, they are not prohibitive. Should then these molecules be stabilized by resonance in the same sense as benzene is postulated to be?

In 1911 a German chemist, R. Willstatter (Nobel Prize 1915), reported an extraordinary thirteen-step synthesis of cyclooctatetraene from a rare alkaloid called pseudopelletierine isolated from the bark of pomegranate trees. The product was reported to be a light-yellow, highly unsaturated compound that absorbed four moles of hydrogen to form cyclooctane. Numerous tries to repeat the Willstatter synthesis were unsuccessful, and in the 1930s the prevailing opinion was that the product had been misidentified. However, during the Second World War, the German chemist W. Reppe found that cyclooctatetraene can be made in reasonable yields by the tetramerization of ethyne under the influence of a nickel cyanide catalyst:

The properties of the product substantiated Willstatter's reports and it became clear that cyclooctatetraene is *not* like benzene.

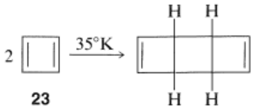
Subsequent studies of the geometry of the molecule revealed further that it is *nonplanar*, with alternating single and double bonds, $25a$:



25a **25b**

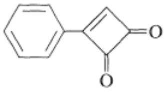
This geometry precludes the possibility of two equivalent VB structures, as for benzene, because, as you will see if you try to make a ball-and-stick model, $25b$ is highly strained and not energetically equivalent to $25a$ at all. Thus we can conclude that the delocalization energy of cyclooctatetraene is not large enough to overcome the angle strain that would develop if the molecule were to become planar and allow the π electrons to form equivalent π bonds between all of the pairs of adjacent carbons.

Cyclobutadiene, 23, eluded Kekule, Willstatter, and a host of other investigators for almost 100 years. As more work was done, it became increasingly clear that the molecule, when formed in reactions, was immediately converted to something else. Finally, the will-o'-the-wisp was captured in an essentially rigid matrix of argon at 8 K. It was characterized by its spectral properties (not by combustion analysis). On warming to even 35 K, it dimerizes to yield 26:

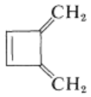


23 **26**

One possibility for the lack of stability[4] of cyclobutadiene is that the angle strain associated with having four sp^2 carbons in a four-membered ring is much greater than estimated. However, the stable existence of many compounds with four such sp^2 carbons, for example 27 and 28, make this argument weak, if not invalid:



27



28

Why, then, is cyclobutadiene so unstable and reactive? On this point, and also with respect to the nonaromatic character of cyclooctatetraene, the simple qualitative VB method that we have outlined is no help whatsoever. There is no way simply to look at the electron-pairing schemes 23 and 24 and see any difference between them and the corresponding schemes for benzene.[5]

It is in this area that qualitative MO procedures have great success because there are general characteristics of the π molecular orbitals of monocyclic, conjugated polyene systems that predict differences in the properties of cyclobutadiene, benzene, cyclooctatetraene, and other similar compounds that are not obvious from the simple VB method.

As a rule, for N parallel atomic p orbitals overlapping in the π manner in a monocyclic array, there will be just one lowest molecular orbital, with all the atomic orbitals having the same phase. This will be seen for benzene in Figure 21-5. What is harder to understand without going through the calculations is that the higher-energy molecular orbitals for cyclic conjugated polyenes are predicted to come in successive degenerate[6] pairs, as shown in Figure 21-13 for $N = 3$ to 9.

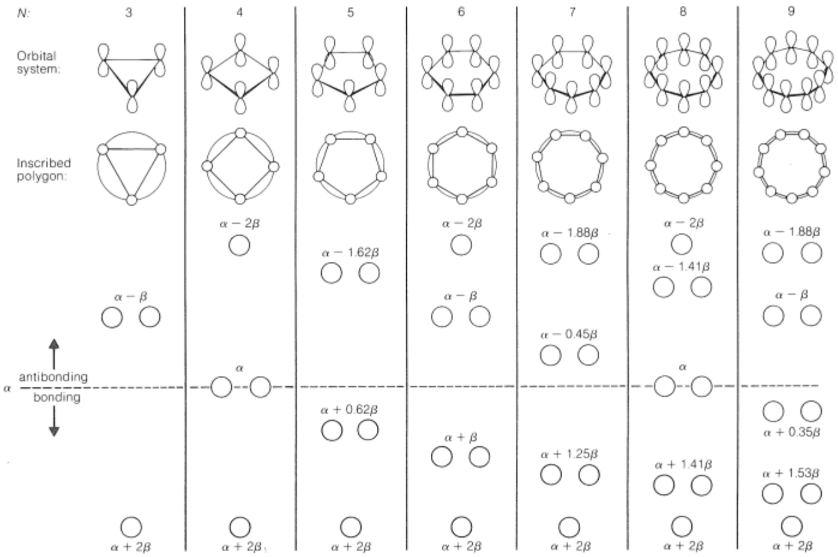
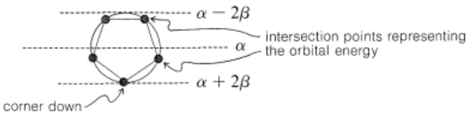


Figure 21-13: Calculated molecular-orbital energies of planar cyclic π-orbital systems made up of N $2p$ carbon atomic orbitals, in units of α and β.

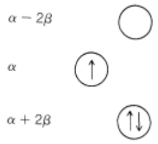
The qualitative ordering and, indeed, the numerical values of the energies of the π molecular orbitals for a cyclic system of N p orbitals can be derived in a very simple way. It is necessary only to inscribe a regular polygon with N sides inside a circle of radius 2β with *a corner down*. For example, for $N = 5$ we get the following:



The molecular orbital energies are in units of β at *the corners of the polygon*. The nonbonding level corresponds to the horizontal dashed line drawn through the *center* of the circle.

The data of Figure 21-13 provide a rationale for the instability of cyclobutadiene and cyclooctatetraene. For cyclobutadiene, we can calculate that four π electrons in the lowest orbitals will lead to a predicted π-electron energy of $2(\alpha + 2\beta) + 2(\alpha) = 4\alpha + 4\beta$, which is just the π-electron energy calculated for *two ethene bonds* (see Figure 21-3). The delocalization energy of the π electrons of cyclobutadiene therefore is predicted to be zero!

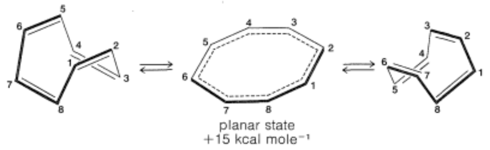
Another feature of the π system of cyclobutadiene is that the four π electrons do not suffice to fill the three lowest orbitals and, if we apply Hund's rule (Section 6-1), the best way to arrange the electrons is as in 29, with two *unpaired* electrons, which is known as a **triplet state**:[7]



29

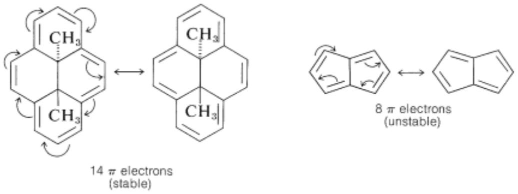
With the MO predictions of zero delocalization energy and an electronic configuration with unpaired electrons, we should not be surprised that cyclobutadiene readily dimerizes to give 26 even at very low temperatures.

The energies of the molecular orbitals calculated for *planar* cyclooctatetraene (Figure 21-13) lead to a predicted delocalization energy of $(8\alpha + 9.64\beta) - (8\alpha + 8\beta) = 1.64\beta$ $(\sim 31\text{ kcal})$, which is smaller than that of benzene, even though there are eight atomic orbitals instead of six through which the electrons are delocalized. Furthermore, the lowest electronic configuration for the planar molecule is, like cyclobutadiene, predicted to be a triplet. Experimental evidence indicates that the positions of the double bonds of cyclooctatetraene shift slowly as the result of formation of the molecule in the unstable planar state. The energy input required to flatten the molecule is about 15 kcal mol^{-1}:

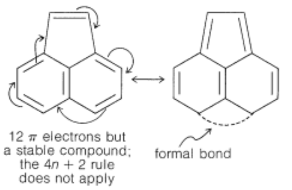


> Figure 21-13 will be just filled with 2, 6, or 10 electrons to give singlet states, and 4 or 8 electrons would give triplet states, a $(4n+2)$ π-electron rule was formulated for stable configurations and a $4n$ π-electron rule for unstable configurations, where n is an integer. Thus 2, 6, 10, 14, $\cdots$ π electrons will be favorable and 4, 8, 12 $\cdots$ π electrons will be unfavorable. This rule is the work of the German theoretician, E. Huckel, who devised the simple form of molecular orbital theory we have described in this chapter. The theory is appropriately called Huckel MO theory, and the rule is Huckel's $4n+2$ rule.

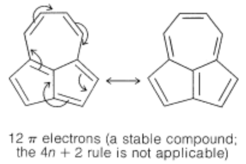
As Huckel formulated, the $4n+2$ rule applies only to monocyclic systems. However, as a practical matter it can be used to predict the properties of polycyclic conjugated polyenes, provided the important VB structures involve only the perimeter double bonds, as in the following examples:



Application of the $4n+2$ rule to other π systems, such as 30 and 31, is not valid because good VB structures cannot be written that involve changes in the pairing schemes of the perimeter electrons all at once.



30



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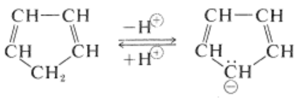
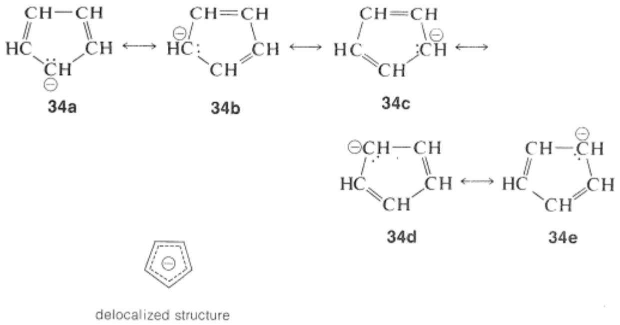
1.4.8.1.2: Application of Resonance and of the $4n+2$ Rule to Cyclic Ions

The hydrogens of the $-CH_2-$ group of 1,3-cyclopentadiene are acidic. In fact, they are considerably more acidic than the ethyne hydrogens of the 1-alkynes (Section 11-8). This means that 1,3-cyclopentadiene is at least 10^{30} times more acidic than the ordinary alkanes. The reason is that loss of one of the CH_2 protons of cyclopentadiene results in formation of an especially stabilized anion:



The structure of the anion may be described as a hybrid of *five* energetically equivalent structures, $34a$ through (34e). The unshared electron pair therefore is delocalized over five carbon atoms, and the resulting delocalized anion is much more stable than expected for any *one* of the equivalent localized structures:



This looks very reasonable, although the simple beauty is seemingly destroyed by the fact that the cyclopentadienyl *cation* is not very stable, despite the five structures, $35a$ through $35e$, that may be written for it:

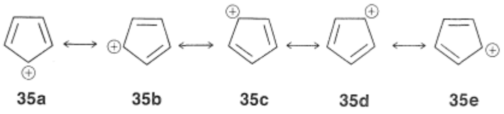
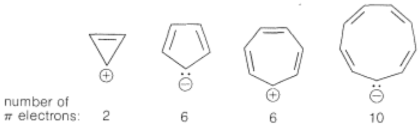
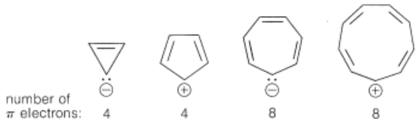


Figure 21-13 for a cyclic system with five p orbitals, and also with the $4n+2$ rule, because 34 has six π electrons, whereas 35 has only four.

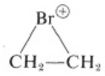
Extension of these ideas to the other ring sizes of Figure 21-13 suggests that all of the following ions, which have $(4n+2)$ π electrons, should be unusually stable:



In contrast, the following should be unstable with $4n$ π electrons and triplet electronic configurations:



These predictions indeed are borne out by many experiments, some of which we will discuss later.

[4] It should be recognized that the term "stability" is subject to many interpretations. One criterion of stability would be whether an isolated molecule would fragment spontaneously in interstellar space, such as one would expect for a "molecule" consisting of two neon atoms 1.5 Å apart (see Figure 4-6). A different criterion would be whether a molecule could be preserved in the presence of the same or other kinds of molecules at some specified temperature. The classical criterion would be whether the substance could be isolated, put into a bottle and preserved for at least a short time. All of the existing evidence indicates that cyclobutadiene molecules would not spontaneously decompose in interstellar space, but they do react with each other extremely readily, even at low temperatures, and can be preserved only by being held isolated from one another in a rigid matrix of a very inert material, such as solid argon. "Stability" in the sense of "lack of reactivity" has to be carefully defined in terms of experimental conditions. For example,  is very *unstable* in the presence of nucleophiles such as water or methanol, whereas it is quite *stable* in "super-acid solutions" where no good nucleophiles are present (Section 10-3B).

[5] A rather simple extension of the VB method by what is called the "orbital-phase continuity principle" does permit the qualitative judgment that cyclobutadiene should be less stable than benzene [see W. A. Goddard III, *J. Amer. Chem. Soc.* **94**, 743 (1972), for applications to many processes for which VB theory generally has been regarded as incapable of giving much insight].

[6] Degenerate orbitals have the same energy; see Section 6-1.

[7] The name "triplet state" is used because a system with two unpaired electrons has *three* different energy states in a magnetic field.

1.4.8.1.3: Contributors and Attributions

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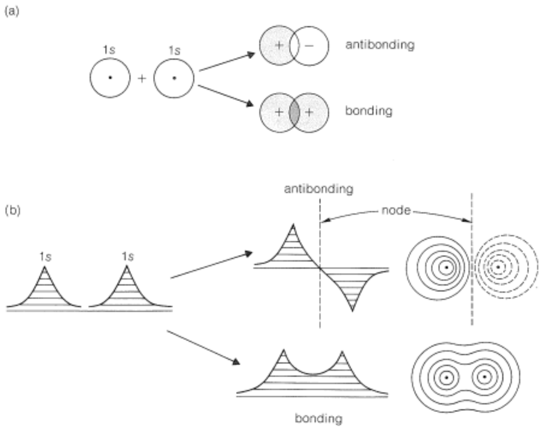
1.5: Comparison of the Resonance and Molecular-Orbital Methods

1.5.1: The Electron-Pair Bond

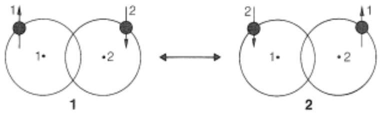
In this section, we will sketch the similarities and differences in the resonance (or valence-bond, VB) and molecular-orbital (MO) approaches for electron-pair bonds. Both methods normally start with atomic orbitals $1s$, $2s$, $2p$, and so on, of the types discussed in Section 6-1. Where the methods differ is in how these orbitals are used. For a bond between two atoms, the **MO procedure** combines (or mixes) *two atomic orbitals*, one from each atom, with proper account of orbital phase (Section 6-2) to obtain *two molecular orbitals*, one of low energy and one of higher energy. The atomic orbitals can be pure or hybrid orbitals (Sections 6-1 and 6-4). In Figure 21-2, we show the results of combining the $1s$ orbitals of hydrogen. The calculation for the most stable state proceeds by determining the energy of the system when two *paired* electrons are in the low-energy molecular orbital. The binding energy is the difference between the energy so calculated and the energies of the separated atoms. Because the molecular orbital extends over *both* atoms, the bonding electrons must be associated with both atoms.



node. (Do not confuse + and − amplitudes with + and − electronic charges.)

Remember, the MO method first combines the atomic orbitals to give molecular orbitals, then populates the molecular orbitals with electrons (no more than two *paired* electrons per orbital). This part of the procedure is similar to the way electrons are allocated to atomic orbitals (Section 6-1).

The **VB treatment** starts with the same atomic orbitals but assigns one electron to each orbital. For an electron-pair bond between two hydrogen atoms, the VB treatment in its simplest form considers two *electronic configurations*. One of these has electron 1 in the orbital of hydrogen 1 and electron 2 in the orbital of hydrogen 2, (1). The other configuration, 2, has electron 2 in the orbital of hydrogen 1 and electron 1 in the orbital of hydrogen 2:



The calculation then proceeds to predict a low-energy state and a high-energy state. These states can be regarded as *hybrids* of 1 and 2. The low-energy state, which is the one of more interest to us, usually is called a *resonance hybrid*.

In the VB method, *each* of the electrons becomes associated with *both* atoms through the mixing of the two configurations. A very important point here is that the calculation that mixes 1 and 2 leads to a six times greater binding energy than calculated for 1 and 2 alone. Thus in the VB treatment we combine *electronic configurations* (here 1 and 2, ↔ symbolizing mixing), whereas in the MO treatment we combine *atomic orbitals* to get low- and high-energy molecular orbitals.

1.5.2: What is the Glue in These Bonds?

The forces that hold atoms together through chemical bonds are electrostatic, that is, the attraction of positively charged nuclei for negatively charged electrons. But the energy calculated for a single configuration, such as 1, only accounts for about one sixth of the total binding. In either the VB or the MO method the electrons in an electron pair between two nuclei brought to within bonding distances are equivalent and indistinguishable. That is, we are unable to identify one electron any more than the other with a given atom. The significance of the pairing of the electrons is that is permits each electron to have maximum possible freedom to move through the orbitals of the two-atom system rather than being "localized" on particular atoms. Quantum-mechanical calculations tell us that freedom of motion of the electrons is very important. Thus, using the VB method, we calculate that fully five sixths of the binding of the hydrogen molecule is associated with the "delocalization" of the electrons between the two nuclei.

There are many compounds with structures in which electrons are delocalized over *more than two atoms*. Such molecules should be more stable than would be expected for molecules with the same geometry but with electron pairs constrained to be associated with just one or two atoms. We will shortly discuss some specific examples, but because most of these examples involve the delocalization of π electrons, it is expedient to first discuss ethene as a prototype, using both the MO and VB methods.

1.5.3: The π Bond in Ethene

The atomic-orbital picture of ethene (Figure 6-14) formulates the π bond as resulting from overlap of two adjacent p atomic orbitals, one from each of two sp^2 hybridized carbons. The p orbitals are directed perpendicularly to the plane defined by the hybrid orbitals of the σ bonds, and to a first approximation, we assume that exchange of the π and σ electrons between their respective orbitals does not affect the energy of the molecule. If this assumption is valid, π bonding can be treated independently of σ bonding. Although undoubtedly oversimplified, the VB and MO methods have been remarkably successful using this assumption. In our subsequent discussions, we shall treat the π electrons separately from localized σ electrons.

The π bond of the ethene molecule can be formulated very much like the bond in the hydrogen molecule (Section 21-2A), with the difference that the bonding is achieved by the overlap of two $2p$ atomic orbitals of carbon rather than two $1s$ atomic orbitals of hydrogen.

In the MO method the mixing of the two $2p$ atomic orbitals gives two molecular orbitals. The details of the mathematics of the mixing process to give an optimum set of molecular orbitals are well beyond the scope of this book,[1] but the results are shown in Figure 21-3. The two π electrons of ethene are taken as occupying the low-energy bonding orbital, while the high-energy antibonding orbital normally is empty.

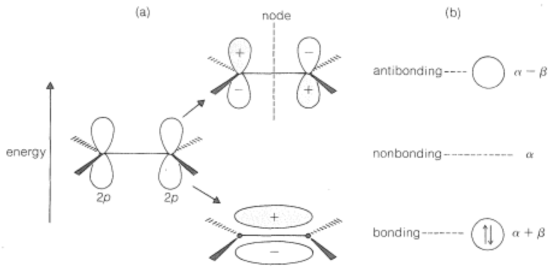


Figure 21-3: *(a) Representation of the bonding and antibonding molecular orbitals formed by the combination of two p atomic orbitals on adjacent sp^2-hybridized carbons, as in ethene. (b) Relative energies of the bonding and antibonding orbitals. The bonding orbital is populated with two paired electrons in the normal (or ground) state of the ethene π bond. The π-electron energy for each electron is $\alpha+\beta$. Therefore the π-electron energy of ethene is $2(\alpha+\beta)=2\alpha+2\beta$. The energy terms, α and β, are* negative quantities.

How much more stable is the bonding molecular orbital relative to a pair of noninteracting p atomic orbitals? It is difficult to provide a numerical answer in kcal mol^{-1} that is meaningful, but we can describe the energy in symbolic terms. First, the energy of one electron in the p atomic orbital of an sp^2-hybridized carbon, as in $\mathbf{3}$, is taken as a standard quantity, α, often called the **Coulomb energy**:

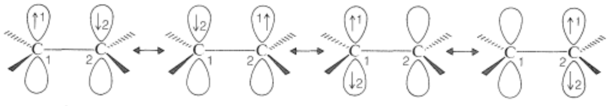
3

Thus, if there were no π bonding in ethene and no repulsion between the electrons, the energy of the two electrons (one in each of the two adjacent p orbitals of the carbons) would be twice the Coulomb energy, or 2α. This would be the situation for two carbons such as $\mathbf{3}$ that are widely separated.

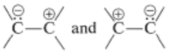
The MO calculation shows that the bonding molecular orbital of ethene is more stable (of lower energy) than the nonbonding level, α, by a quantity, β, where β is a *negative* energy term (Figure 21-3). Likewise, the antibonding level is destabilized by an amount

$-\beta$. For *two* paired electrons in the bonding molecular orbital, the π-electron energy of ethene is calculated to be $2(\alpha + \beta) = 2\alpha + 2\beta$.

In the valence-bond approach, the π bond of ethene is considered to be a hybrid of all reasonable electronic configurations of two indistinguishable paired electrons distributed between two p orbitals. Each of the configurations that can be written, $4a$, $4b$, $4c$, and $4d$, have identical locations of the atomic nuclei in space:



The four valence-bond structures or configurations, $4a$-d, are combined mathematically to give four hybrid states, and of these, the lowest-energy one corresponds approximately to the normal state of the molecule. The calculation shows that the structures $4a$ and $4b$, which have one electron in each p orbital, are the major contributors to the "hybrid" of ethene. The valence-bond structures, $4c$ and $4d$, are *ionic structures*, which correspond to the conventional formulas, $4e$ and $4f$:



4e 4f

These valence-bond structures are not important to the π bond of the ground state of ethene, although they are important for carbonyl bonds (Section 16-1B).

[1] There are many excellent books that cover this subject in great detail; however, the simplest introductory work is J. D. Roberts; *Molecular Orbital Calculations*, W. A. Benjamin, Inc., Menlo Park, Calif., 1961.

1.5.4: Contributors and Attributions

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1.5.1: Which Is Better- MO or VB?

The calculated energy of the electron-pair bond of the hydrogen molecule as a function of $\mathrm{H{-}H}$ intermolecular distance r by the *ab initio* (exact), MO, and VB procedures is shown in Figure 21-11. The results show that neither the MO nor the VB calculations come close to the *ab initio* calculation in reproducing the experimental dissociation energy, D_e, or the variation of the energy with the intermolecular distance. The VB method gives a little better energy value at the minimum and the MO method gives poor results at larger values of r. We can say that, as calculated by the MO method, the molecule does not "dissociate properly".

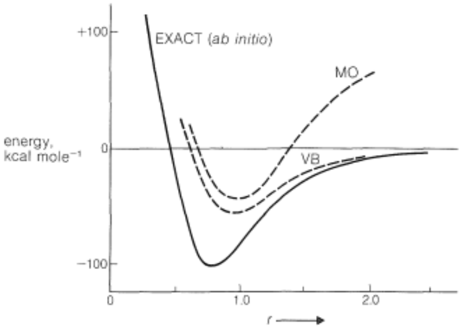

Figure 21-11: Comparison of calculated "exact" ab initio energies of $\mathrm{H_2}$ as a function of internuclear distance, r, with the energies calculated for simple MO and simple VB methods. The dissociation energy calculated by the ab initio procedure is in close agreement with the experimental value of $102\,\mathrm{kcal}$. The zero of the energy scale in this figure is the energy of widely separated hydrogen atoms.

> *Within the calculations of the MO method, the molecule does not "dissociate properly".*

Why do these calculations yield results so far from the *ab initio* curve? There are two reasons. First, atomic orbitals are used that are appropriate for *isolated* atoms, but are hardly expected to be the best orbitals for the electrons when two or more atoms are in close proximity. It is convenient to use atomic orbitals in simple calculations because they are mathematically simple, but more complicated orbitals are known to give better results. Second, neither treatment properly takes into account electron-electron repulsions. For two electrons, a term of the form $\frac{e^2}{r_{12}^2}$ (in which e is the electronic charge and r_{12} is the distance between the electrons) is required to describe the repulsion between electrons. The exact calculations avoid both difficulties but are so complex mathematically as to be devoid of any capability for providing qualitative understanding.

The VB method gives a slightly lower energy than the MO method at the minimum, because in the simple MO method, when we calculate the energy resulting from two electrons going into the lowest molecular orbital, we put no restraints on their being close together. As a result there is a 50% probability for *both* electrons being simultaneously in either half of the molecular orbital. In contrast, the simple VB method combines configurations 1 and 2, each having just *one* electron per atomic orbital, and no account is taken of the possibility of either atomic orbital containing more than one electron. This is equivalent to neglecting the pairing schemes $\mathrm{H^{\ominus}H^{\oplus} \leftrightarrow H^{\oplus}H^{\ominus}}$. Neither the VB nor the MO approximation is the best possible; the simple MO method tends to take too little account of interelectronic repulsion, whereas the VB method tends to take too much account of it. However, as can be seen in Figure 21-11, taking too much account of electron repulsion is the better approximation.

Why does an electron-pair bond calculated by the MO method not dissociate properly? We have seen that half of the time both electrons in the low-energy molecular orbital are in the vicinity of just *one* of the nuclei. But as the nuclei move *far apart*, this corresponds to a far greater energy than having only one electron in the vicinity of each nucleus, as the VB method suggests.

There is no unequivocal answer to the question as to which is the better method. Calculations by the VB method are likely to be more reliable than those by the MO method, but in practice are much more difficult to carry out. For many-electron molecules the MO procedure is simpler to visualize because we combine atomic orbitals into molecular orbitals and then populate the lower-energy orbitals with electrons. In the VB method, atomic orbitals are occupied, but the electrons of different atoms are paired to form bonds, a process that requires explicit consideration of many-electron wave functions. To put it another way, it is easier to visualize a system of molecular orbitals containing N electrons than it is to visualize a hybrid wave function of N electrons.

How can the MO and VB methods be improved? The answer depends on what one wants - more accurate calculations or better qualitative understanding. To improve VB calculations we need orbitals that allow the electrons to spread out over more than one atom. The GVB orbitals discussed in Section 6-6 suit this purpose and give an energy curve only slightly above the exact curve of Figure 21-11. In the GVB treatment the orbitals delocalize less as r increases.

When atomic orbitals are derived for each carbon of the π-electron system of benzene by the GVB method, they are somewhat more spread out than simple carbon p orbitals (Figure 21-12). Use of these orbitals in VB calculations gives excellent results with just the two pairing schemes of benzene, 9 and 10.

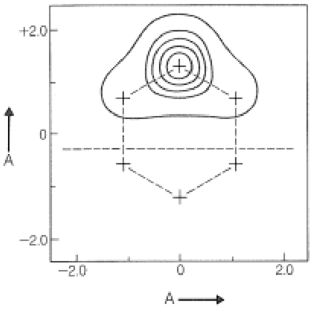

Figure 21-12: Top view of a GVB atomic orbital for the π-electron system of benzene. The contour lines show electron amplitudes, and there is a phase change represented by the dashed line. The crosses show the positions of the carbon nuclei. Six such orbitals are used to make up the electron-pairing schemes, 9 and 10, used in the GVB calculation of the electronic energy of benzene.

Improvement of the MO method involves better orbitals, better account of interelectronic repulsion, and introduction of mixing of different electron configurations in the molecular orbitals ("configuration interaction"). Improved MO calculations give much more accurate energies at the minimum of a plot such as Figure 21-11, but the bonds still do not dissociate properly, for the same reason as with the simple MO method.

We cannot say that either the VB or the MO method is more *correct*; only that one approximation may be more useful than the other in attempting to solve a particular problem. The fact is, the more each is refined, the more they appear to merge into a common procedure; but, unfortunately, in the refinement process the mathematics become so complex that qualitative understanding of what is being done tends to disappear altogether.

> *We cannot say that either the VB or the MO method is more correct; only that one approximation may be more useful than the other in attempting to solve a particular problem.*

1.5.1.1: Contributors and Attributions

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CHAPTER OVERVIEW

2: Reaction Kinetics

2.1: Introduction to Reaction Kinetics

How can an experiment confirm that a reaction is happening in a particular way? What is the mechanism of the reaction? What intermediates are occurring, and in what order do the bond-making and bond-breaking steps take place?

There are many experiments designed to illustrate how reactions happen. One of the methods used is chemical kinetics, in which the rate of a reaction is measured. By making changes in the reaction conditions and measuring the effect of the changes on the rate of reaction, we can infer what is going on at the molecular level.

- Chemical kinetics is the measurement of how quickly reactions occur.
- If changes in conditions affect the speed of reaction, we can learn something about how the reaction happens.

Kinetic studies are important in understanding reactions, and they also have practical implications. For example, in industry, reactions are conducted in reactors in which compounds are mixed together, possibly heated and stirred for a while, and then moved to the next phase of the process. It is important to know how long to hold the reaction at one stage before moving on, to make sure that reaction has finished before starting the next one.

By understanding how a reaction takes place, many processes can be improved. For example, if it is known that a particular intermediate is involved in a reaction, the use of conditions (such as certain solvents) that are incompatible with that intermediate might be avoided. In addition, reagents might be added that would make certain steps in the reaction happen more easily.

Not only are kinetic studies important in industry, but they are also used to understand biological processes, especially enzyme-catalyzed reactions. They also play a role in environmental and atmospheric chemistry, as part of an effort to understand a variety of issues ranging from the fate of prescription pharmaceuticals in wastewater to the cascade of reactions involved in the ozone cycle.

Contributors and Attributions

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2.1.1: First-Order Reactions

A **first-order reaction** is a reaction that proceeds at a rate that depends *linearly* on only one reactant concentration.

The Differential Representation

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The differential equation describing first-order kinetics is given below:

$$Rate = -\frac{d[A]}{dt} = k[A]^1 = k[A] \tag{2.1.1.1}$$

The "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time). However, the units of k vary for non-first-order reactions. These differential equations are separable, which simplifies the solutions as demonstrated below.

The Integral Representation

First, write the differential form of the rate law.

$$Rate = -\frac{d[A]}{dt} = k[A]$$

Rearrange to give:

$$\frac{d[A]}{[A]} = -k\,dt$$

Second, integrate both sides of the equation.

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -\int_{t_o}^{t} k\,dt$$

$$\int_{[A]_o}^{[A]} \frac{1}{[A]} d[A] = -\int_{t_o}^{t} k\,dt$$

Recall from calculus that:

$$\int \frac{1}{x} = \ln(x)$$

Upon integration,

$$\ln[A] - \ln[A]_o = -kt$$

Rearrange to solve for [A] to obtain one form of the rate law:

$$\ln[A] = \ln[A]_o - kt$$

This can be rearranged to:

$$\ln[A] = -kt + \ln[A]_o$$

This can further be arranged into y=mx +b form:

$$\ln[A] = -kt + \ln[A]_o$$

The equation is a straight line with slope m:

$$mx = -kt$$

and y-intercept b:

$$b = \ln[A]_o$$

Now, recall from the laws of logarithms that

$$\ln\left(\frac{[A]_t}{[A]_o}\right) = -kt$$

where [A] is the concentration at time t and $[A]_o$ is the concentration at time 0, and k is the first-order rate constant.

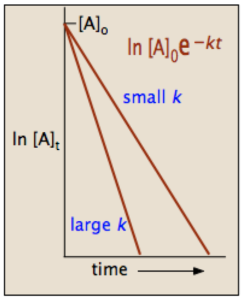


Figure 2.1.1.1: Decay profiles for first-order reactions with large and small rate constants. (CC BY; Stephen Lower)

Because the logarithms of numbers do not have any units, the product $-kt$ also lacks units. This concludes that unit of k in a first order of reaction must be time^{-1}. Examples of time^{-1} include s^{-1} or min^{-1}. Thus, the equation of a straight line is applicable:

$$\ln[A] = -kt + \ln[A]_o. \tag{2.1.1.2}$$

To test if it the reaction is a first-order reaction, plot the natural logarithm of a reactant concentration versus time and see whether the graph is linear. If the graph is linear and has a negative slope, the reaction must be a first-order reaction.

To create another form of the rate law, raise each side of the previous equation to the exponent, e:

$$e^{\ln[A]} = e^{\ln[A]_o - kt} \tag{2.1.1.3}$$

Simplifying gives the second form of the rate law:

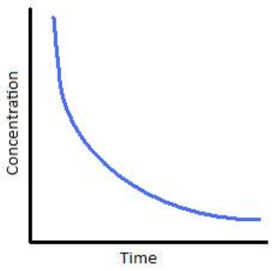
$$[A] = [A]_o e^{-kt} \tag{2.1.1.4}$$

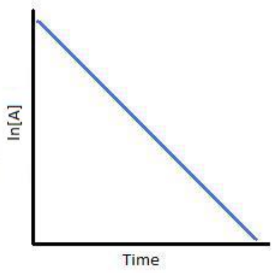
The integrated forms of the rate law can be used to find the population of reactant at any time after the start of the reaction. Plotting $\ln[A]$ with respect to time for a first-order reaction gives a straight line with the slope of the line equal to $-k$. More information can be found in the article on rate laws.

This general relationship, in which a quantity changes at a rate that depends on its instantaneous value, is said to follow an exponential law. Exponential relations are widespread in science and in many other fields. Consumption of a chemical reactant or the decay of a radioactive isotope follow the exponential decay law. Its inverse, the law of exponential growth, describes the manner in which the money in a continuously-compounding bank account grows with time, or the population growth of a colony of reproducing organisms. The reason that the exponential function $y = e^x$ so efficiently describes such changes is that dy/dx = e^x; that is, e^x is its own derivative, making the rate of change of y identical to its value at any point.

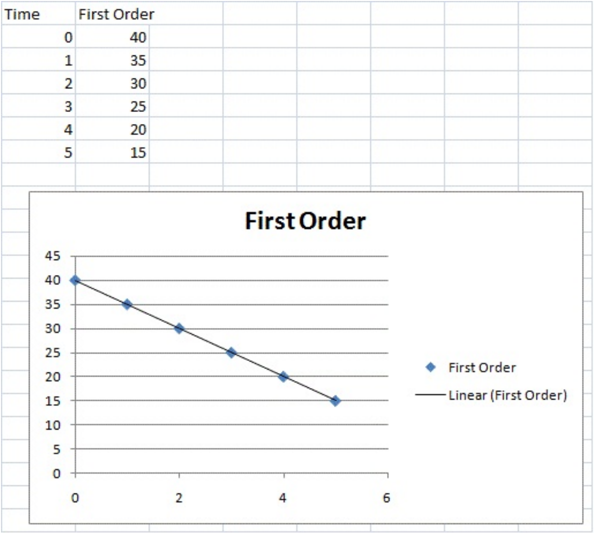
Graphing First-order Reactions

The following graphs represents concentration of reactants versus time for a first-order reaction.





Plotting $\ln[A]$ with respect to time for a first-order reaction gives a straight line with the slope of the line equal to $-k$.



Time	First Order
0	40
1	35
2	30
3	25
4	20
5	15

Half-lives of first order reactions

The half-life ($t_{1/2}$) is a timescale on which the initial population is decreased by half of its original value, represented by the following equation.

$$[A] = \frac{1}{2}[A]_o$$

After a period of one half-life, $t = t_{1/2}$ and we can write

$$\frac{[A]_{1/2}}{[A]_o} = \frac{1}{2} = e^{-k\,t_{1/2}} \tag{2.1.1.5}$$

Taking logarithms of both sides (remember that $\ln e^x = x$) yields

$$\ln 0.5 = -kt \tag{2.1.1.6}$$

Solving for the half-life, we obtain the simple relation

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k} \tag{2.1.1.7}$$

This indicates that the half-life of a first-order reaction is a constant.

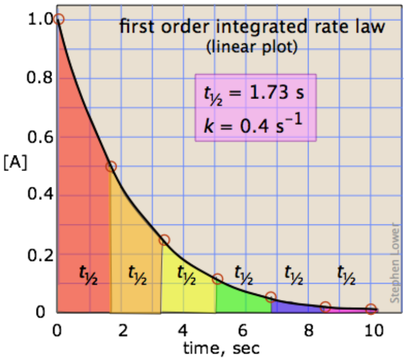


Figure 2.1.1.2: Half lives graphically demonstrated for first-order reaction. Notice the the half-life is independent of initial concentration. This is not the case with other reaction orders. (CC BY; Stephen Lower)

Example 1: Estimated Rate Constants

The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?

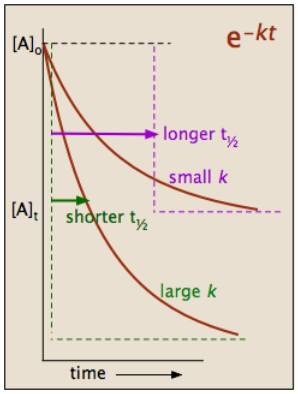
Solution

Use Equation 20 that relates half life to rate constant for first order reactions:

$$k = \frac{0.693}{600\ s} = 0.00115\ s^{-1}$$

As a check, dimensional analysis can be used to confirm that this calculation generates the correct units of inverse time.

Notice that, for first-order reactions, the half-life is *independent* of the initial concentration of reactant, which is a unique aspect to first-order reactions. The practical implication of this is that it takes as much time for [A] to decrease from 1 M to 0.5 M as it takes for [A] to decrease from 0.1 M to 0.05 M. In addition, the rate constant and the half life of a first-order process are inversely related.



Example 2.1.1.1: Determining Half life

If 3.0 g of substance A decomposes for 36 minutes the mass of unreacted A remaining is found to be 0.375 g. What is the half life of this reaction if it follows first-order kinetics?

Solution

There are two ways to approach this problem: The "simple inspection approach" and the "brute force approach"

Approach #1: "The simple Inspection Approach"

This approach is used when one can recognize that the final concentration of A is $\frac{1}{8}$ of the initial concentration and hence three half lives $\left(\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}\right)$ have elapsed during this reaction.

$$t_{1/2} = \frac{36 \text{ min}}{3} = 12 \text{ min}$$

This approach works only when the final concentration is $\left(\frac{1}{2}\right)^n$ that of the initial concentration, then n is the number of half lives that have elapsed. If this is not the case, then approach #2 can be used.

Approach #2: "The brute force approach"

This approach involves solving for k from the integral rate law (Equation 2.1.1.4) and then relating k to the $t_{1/2}$ via Equation 2.1.1.7.

$$\frac{[A]_t}{[A]_o} = e^{-k\,t}$$

$$\begin{aligned} k &= -\frac{\ln \dfrac{[A]_t}{[A]_o}}{t} \\ &= -\frac{\ln \dfrac{0.375\,g}{3\,g}}{36\,\text{min}} \\ &= 0.0578\,\text{min}^{-1} \end{aligned}$$

Therefore, via Equation 2.1.1.7

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{0.0578\,\text{min}^{-1}} \approx 12\,\text{min}$$

The first approach is considerably faster (if the number of half lives evolved is apparent).

? Exercise $2.1.1.2a$

Calculate the half-life of the reactions below:

a. If 4.00 g A are allowed to decompose for 40 min, the mass of A remaining undecomposed is found to be 0.80 g.
b. If 8.00 g A are allowed to decompose for 34 min, the mass of A remaining undecomposed is found to be 0.70 g.
c. If 9.00 g A are allowed to decompose for 24 min, the mass of A remaining undecomposed is found to be 0.50 g.

Answer

Use the half life reaction that contains initial concentration and final concentration. Plug in the appropriate variables and solve to obtain:

a. 17.2 min
b. 9.67 min
c. 5.75 min

? Exercise $2.1.1.2b$

Determine the percent H_2O_2 that decomposes in the time using $k = 6.40 \times 10^{-5}\,s^{-1}$

a. The time for the concentration to decompose is 600.0 s after the reaction begins.
b. The time for the concentration to decompose is 450 s after the reaction begins.

Answer

a. Rearranging Eq. 17 to solve for the $[H_2O_2]_t/[H_2O_2]_0$ ratio

$$\frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-kt}$$

This is a simple plug and play application once you have identified this equation.

$$\frac{[H_2O_2]_{t=600\ s}}{[H_2O_2]_0} = e^{-(6.40 \times 10^{-5} s^{-1})(600\ s)}$$

$$\frac{[H_2O_2]_{t=600\ s}}{[H_2O_2]_0} = 0.9629$$

So 100-96.3=3.71% of the hydrogen peroxide has decayed by 600 s.

b. Rearranging Eq. 17 to solve for the $[H_2O_2]_t/[H_2O_2]_0$ ratio

$$\frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-kt}$$

This is a simple plug and play application once you have identified this equation.

$$\frac{[H_2O_2]_{t=450\ s}}{[H_2O_2]_0} = e^{-(6.40 \times 10^{-5} s^{-1})(450\ s)}$$

$$\frac{[H_2O_2]_{t=450\ s}}{[H_2O_2]_0} = 0.9720$$

So 100-97.2=2.8% of the hydrogen peroxide has decayed by 450 s.

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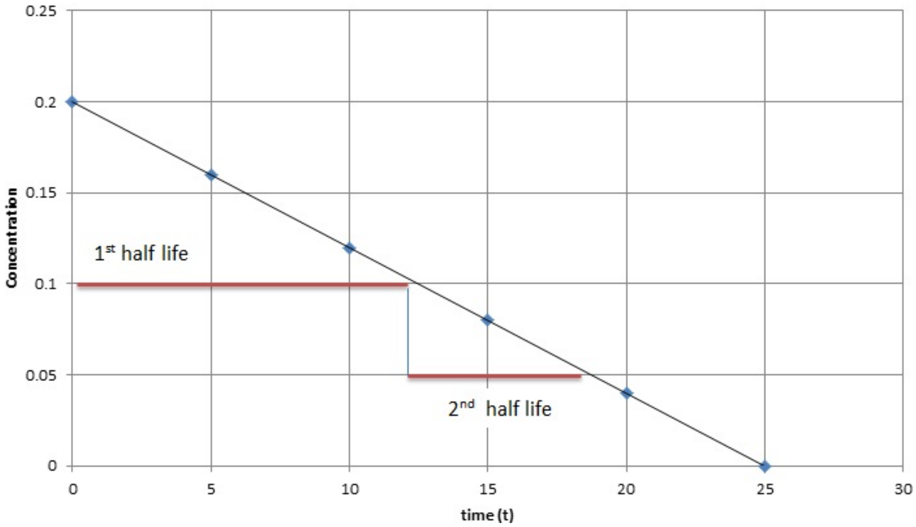
2.1.2: Half-lives

The **half-life** of a reaction ($t_{1/2}$), is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration. Its application is used in chemistry and medicine to predict the concentration of a substance over time. The concepts of half life plays a key role in the administration of drugs into the target, especially in the elimination phase, where half life is used to determine how quickly a drug decrease in the target after it has been absorbed in units of time (e.g., s, min., day, etc.) or elimination rate constant k in units of 1/time (e.g., min^{-1}, hr^{-1}, day^{-1}, etc.). It is important to note that the half-life is varied between different type of reactions. The following section will go over different type of reaction, as well as how its half-life reaction are derived. The last section will talk about the application of half-life in the elimination phase of pharmacokinetics.

Zero-Order Kinetics

In zero-order kinetics, the rate of a reaction does not depend on the substrate concentration. In other words, saturating the amount of substrate does not speed up the rate of the reaction. Below is a graph of time (t) vs. concentration ($[A]$) in a zero order reaction, several observation can be made: the slope of this plot is a straight line with negative slope equal negative k, the half-life of zero order reaction decreases as the concentration decreases.



We learn that the zero-order kinetic rate law is as followed, where $[A]$ is the current concentration, $[A]_o$ is the initial concentration, and k is the reaction constant and t is time:

$$[A] = [A]_o - kt \tag{2.1.2.1}$$

We need to isolate $t_{1/2}$ when

$$[A] = \frac{[A]_o}{2}$$

Substituting into Equation 2.1.2.1

$$\frac{[A]_o}{2} = [A]_o - kt_{1/2}$$

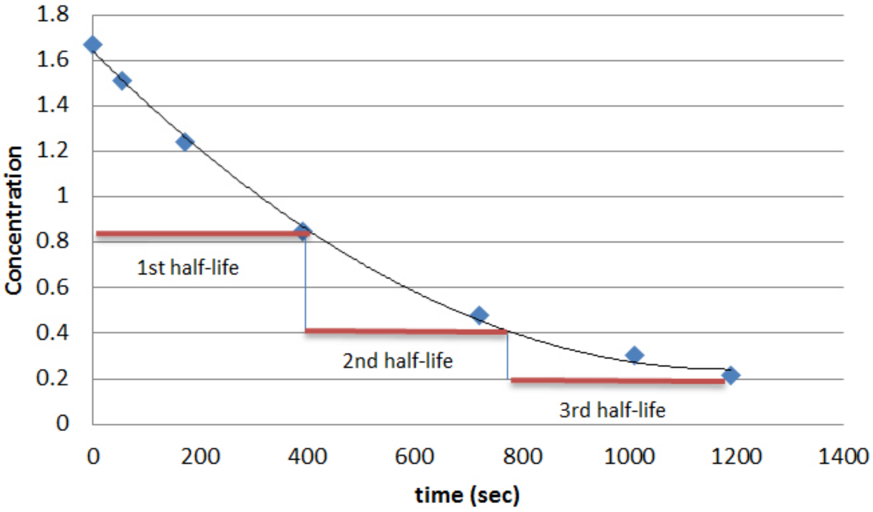
$$kt_{1/2} = [A]_o - \frac{[A]_o}{2}$$

$$t_{1/2} = \frac{[A]_o}{2k} \tag{2.1.2.2}$$

Equation 2.1.2.2show the half-life for a zero-order reaction depends on both the initial concentration and rate constant.

First-Order Kinetics

In First order reactions, the graph represents the half-life is different from zero order reaction in a way that the slope continually decreases as time progresses until it reaches zero. We can also easily see that the length of half-life will be constant, independent of concentration. For example, it takes the same amount of time for the concentration to decrease from one point to another point.



In order to solve the half life of first order reactions, we recall that the rate law of a first order reaction was:

$$[A] = [A]_o e^{-kt} \tag{2.1.2.3}$$

We need to isolate $t_{1/2}$ when

$$[A] = \frac{[A]_o}{2}$$

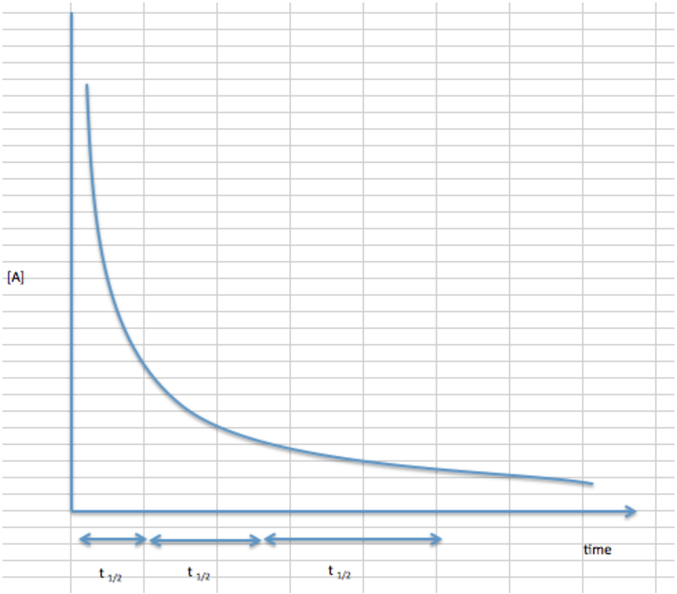
Substituting into Equation 2.1.2.3

$$\begin{aligned} \frac{[A]_0}{2} &= [A]_o e^{-kt_{1/2}} \\ \frac{1}{2} &= e^{-kt_{1/2}} \\ \ln \frac{1}{2} &= -kt_{1/2} \\ t_{1/2} &= \frac{\ln 2}{k} \\ &\approx \frac{0.693}{k} \end{aligned} \tag{2.1.2.4}$$

Equation 2.1.2.4 shows that for first-order reactions, the half-life depends solely on the reaction rate constant, k. We can visually see this on the graph for first order reactions when we note that the amount of time between one half life and the next are the same. Another way to see it is that the half life of a first order reaction is independent of its initial concentration.

Second-Order Kinetics

Half-life of second order reactions shows concentration $[A]$ vs. time (t), which is similar to first order plots in that their slopes decrease to zero with time. However, second order reactions decrease at a much faster rate as the graph shows. We can also note that the length of half-life increase while the concentration of substrate constantly decreases, unlike zero and first order reaction.



In order to solve for half life of second order reactions we need to remember that the rate law of a second order reaction is:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{2.1.2.5}$$

As in zero-order and first-order reactions, we need to isolate $t_{1/2}$ when

$$[A] = \frac{[A]_o}{2}$$

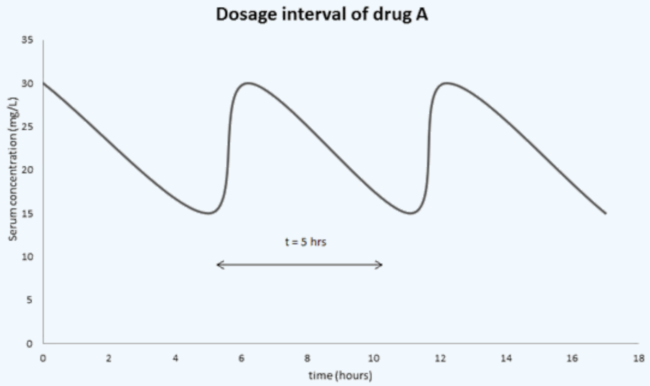
Substituting into Equation 2.1.2.5

$$\begin{aligned} \frac{2}{[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ -kt_{1/2} &= \frac{1}{[A]_0} - \frac{2}{[A]_0} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned} \tag{2.1.2.6}$$

Equation 2.1.2.6shows that for second-order reactions, the half-life depends on both the initial concentration and the rate constant.

✓ Example 2.1.2.1: Pharmacokinetics

A following example is given below to illustrate the role of half life in pharmacokinetics to determine the drugs dosage interval.



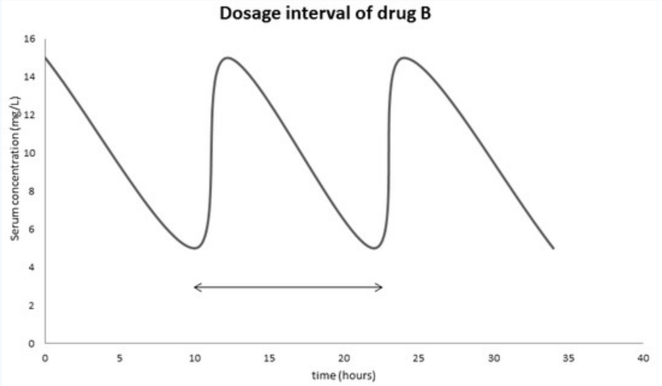
Doage interval

The therapeutic range of drug A is 15-30 mg/L. Its half life in the target in 5 hours. Once the drug is metabolized in the target, its concentration will decrease over time. To ensure its maximal effect of the drug in the target, the administration will be monitored so that the minimum serum concentration will never go lower than 15 mg/L and the maximum serum concentration will never exceed 30 mg/L. As a result, it is important to administer drug A to the target every 5 hours to ensure its effective therapeutic range.

Another important application of half life in pharmacokinetics is that half-life tells how tightly drugs bind to each ligands before it is undergoing decay (k_s). The smaller the value of k_s, the higher the affinity binding of drug to its target ligand, which is an important aspect of drug design

Exercise 2.1.2.1

Examine the following graph and answer



a. What is the therapeutic range of drug B?
b. From the graph, estimate the dosage interval of drug B to ensure its maximum effect?
c. The patient forgot to take the drug at the end of the dosage interval, he decided to take double the amount of drug B at the end of the next dosage interval. Will the drug still be in its therapeutic range?

Answer

Looking at the graph, we can see the therapeutic range is the amplitude of the graph, which is 5-15 mg/L

The dosage interval is the half-life of the drug, looking at the graph, the half-life is 10 hours.

Even though it will get in the therapeutic range, such practice is not recommended.

? Exercise 2.1.2.2

A patient is treating with ^{32}P. How long does it takes for the radioactivity to decay by 90%? The half-life of the material is 15 days.

Answer

If we want the product to decay by 90%, that means 10% is left non-decayed, so

$$\frac{[A]_t}{[A]_o} = 0.1$$

From ln($[A]_t/[A]_o$) = -kt, plug in value of k and $[A]_t/[A]_o$ we then have t = 50 days

? Exercise 2.1.2.3

In first order half life, what is the best way to determine the rate constant k? Why?

Answer

The best way to determine rate constant k in half-life of first order is to determine half-life by experimental data. The reason is half-life in first order order doesn't depend on initial concentration.

? Exercise 2.1.2.4

In a first order reaction, $\mathrm{A} \longrightarrow \mathrm{B}$. The half-life is 10 days.

a. Determine its rate constant k?
b. How much time required for this reaction to be at least 50% and 60% complete?

Answer

a. This is a direct application of Equation 2.1.2.6 The rate constant, k, will be equal to

$$k = \frac{\ln 2}{t_{1/2}}$$

so $k = 0.0693\, day^{-1}$.

b. For the reaction to be 50% complete, that will be exactly the half-life of the reaction at 10 days. For the reaction to be 60% complete, using the similar equation derived from question 4, we have

$$\frac{[A]_t}{[A]_o} = 0.4$$

$$t = 13.2\, days$$

References

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2. Bauer, Larry. Applied Clinical Pharmacokinetics. New York City, New York: McGraw-Hill. 2008
3. Mozayani, Ashraf and Raymond, Lionel. Handbook of Drug Interactions: A Clinical and Forensic Guide. Totowa, New Jersy: Humana Press. 2003

2.1.3: Reaction Rate

During the course of the reaction shown below, reactants A and B are consumed while the concentration of product AB increases. The reaction rate can be determined by measuring how fast the concentration of A or B decreases, or by how fast the concentration of AB increases.

$$A + B \longrightarrow AB$$

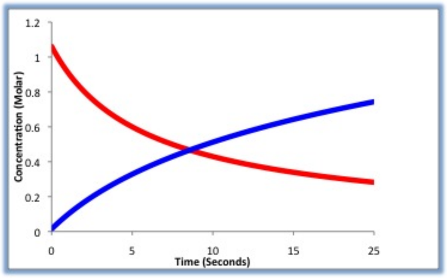

Figure $2.1.3.1$: The above picture shows a hypthetical reaction profile in which the reactants (red) decrease in concentration as the products increase in concetration (blue).

For the stochiometrically complicated Reaction:

$$aA + bB \longrightarrow cC + dD \tag{2.1.3.1}$$

$$\text{Rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Looking at Figure $2.1.3.1$above, we can see that the rate can be measured in terms of either reactant (A or B) or either product (C or D). Not all variables are needed to solve for the rate. Therefore, if you have the value for "A" as well as the value for "a" you can solve for the reaction rate.

You can also notice from Equation 2.1.3.1that the change in reactants over the change in time must have a negative sign in front of them. The reason for this is because the reactants are decreasing as a function of time, the rate would come out to be negative (because it is the reverse rate). Therefore, putting a negative sign in front of the variable will allow for the solution to be a positive rate.

Chemical reactions vary greatly in the speed at which they occur. Some are ultrafast, while others may take millions of years to reach equilibrium.

Definition of Reaction Rate

The **Reaction Rate** for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time. The speed of a chemical reaction may be defined as the change in concentration of a substance divided by the time interval during which this change is observed:

$$\text{rate} = \frac{\Delta\text{concentration}}{\Delta\text{time}} \tag{2.1.3.2}$$

For a reaction of the form $A + B \rightarrow C$, the rate can be expressed in terms of the change in concentration of any of its components

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = -\frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[C]}{\Delta t}$$

in which $\Delta[A]$ is the difference between the concentration of A over the time interval $t_2 - t_1$:

$$\Delta[A] = [A]_2 - [A]_1 \tag{2.1.3.3}$$

Notice the minus signs in the first two examples above. The concentration of a reactant always decreases with time, so $\Delta[A]$ and $\Delta[A]$ are both negative. Since negative rates do not make much sense, rates expressed in terms of a reactant concentration are **always** preceded by a minus sign to make the rate come out positive.

Consider now a reaction in which the coefficients are different:

$$A + 3B \rightarrow 2D$$

It is clear that $[B]$ decreases three times as rapidly as $[A]$, so in order to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{3\Delta t} = \frac{\Delta[D]}{2\Delta t} \tag{2.1.3.4}$$

✓ Example 2.1.3.1: Oxidation of Ammonia

For the oxidation of ammonia

$$4\,\mathrm{NH_3} + 3\,\mathrm{O_2} \longrightarrow 2\,\mathrm{N_2} + 6\,\mathrm{H_2O}$$

it was found that the rate of formation of N_2 was 0.27 mol L^{-1} s^{-1}.

a. At what rate was water being formed?
b. At what rate was ammonia being consumed?

Solution

a) From the equation stoichiometry, $\Delta[H_2O] = 6/2\ \Delta[N_2]$, so the rate of formation of H_2O is

$$3 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.81 \text{ mol L}^{-1} \text{ s}^{-1}.$$

b) 4 moles of NH_3 are consumed for every 2 moles of N_2 formed, so the rate of disappearance of ammonia is

$$2 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.54 \text{ mol L}^{-1} \text{ s}^{-1}.$$

Comment: Because of the way this question is formulated, it would be acceptable to express this last value as a negative number.

Instantaneous rates

Most reactions slow down as the reactants are consumed. Consequently, the rates given by the expressions shown above tend to lose their meaning when measured over longer time intervals Δt. Note: Instantaneous rates are also known as differential rates.

Thus for the reaction whose progress is plotted here, the actual rate (as measured by the increasing concentration of product) varies continuously, being greatest at time zero. The *instantaneous rate* of a reaction is given by the slope of a tangent to the concentration-vs.-time curve.

An instantaneous rate taken near the beginning of the reaction (t = 0) is known as an *initial rate* (label **(1)** here). As we shall soon see, initial rates play an important role in the study of reaction kinetics. If you have studied differential calculus, you will know that these tangent slopes are *derivatives* whose values can very at each point on the curve, so that these instantaneous rates are really *limiting rates* defined as

$$\text{rate} = \lim_{\Delta t \rightarrow 0} \frac{-[A]}{\Delta T}$$

If you do not know calculus, bear in mind that the larger the time interval Δt, the smaller will be the precision of the instantaneous rate.

Rate Laws and Rate Constants

A rate law is an expression which relates that rate of a reaction to the rate constant and the concentrations of the reactants. A rate constant, k, is a proportionality constant for a given reaction. The general rate law is usually expressed as:

$$\text{Rate} = k[A]^s[B]^t \tag{2.1.3.5}$$

As you can see from Equation 2.1.3.5above, the reaction rate is **dependent** on the concentration of the reactants as well as the rate constant. However, there are also other factors that can influence the rate of reaction. These factors include temperature and catalysts. When you are able to write a rate law equation for a certain reaction, you can determine the Reaction Order based on the values of s and t.

Reaction Order

The reaction rate for a given reaction is a crucial tool that enables us to calculate the specific order of a reaction. The order of a reaction is important in that it enables us to classify specific chemical reactions easily and efficiently. Knowledge of the reaction order quickly allows us to understand numerous factors within the reaction including the rate law, units of the rate constant, half life, and much more. Reaction order can be calculated from the rate law by adding the exponential values of the reactants in the rate law.

$$\text{Rate} = k[A]^s[B]^t \tag{2.1.3.6}$$

$$\text{Reaction Order} = s + t \tag{2.1.3.7}$$

It is important to note that although the reaction order can be determined from the rate law, there is in general, **no relationship** between the reaction order and the stoichiometric coefficients in the chemical equation.

> *NOTE: The rate of reaction must be a non-negative value. It can be zero and does not need to be an integer.*

As shown in Equation 2.1.3.7, the complete reaction order is equal to the sum of "s" and "t." But what does each of these variables mean? Each variable represents the order of the reaction with respect to the reactant it is placed on. In this certain situation, s is the order of the reaction with respect to [A] and t is the order of the reaction with respect to [B].

Here is an example of how you can look at this: If a reaction order with respect to [A] was 2 (s = 2) and [B] was 1 (t = 1), then that basically means that the concentration of reactant A is decreasing by a factor of 2 and the concentration of [B] is decrease by a factor of 1.

So if you have a reaction order of Zero (i.e., $s + t = 0$), this basically means that the concentration of the reactants does not affect the rate of reaction. You could remove or add reactants to the mixture but the rate will not change.

A list of the different reaction rate equations for zero-, first-, and second-order reactions can be seen in Table 2.1.3.1. This table also includes further equations that can be determine by this equation once the order of the reaction is known (Half life, integrated rate law, etc.)

Table 2.1.3.1: The table below displays numerous values and equations utilized when observing chemical kinetics for numerous reactions types

	Zero-Order	First-Order	Second-Order
Rate Law	$Rate = k$	$Rate = k[A]$	$\text{Rate} = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$ln[A]_t = -kt + ln[A]_0$	$\frac{1}{[A]_t} = +kt + \frac{1}{[A]_0}$
Units of Rate Constant (k):	$molL^{-1}s^{-1}$	s^{-1}	$Lmol^{-1}s^{-1}$
Linear Plot to Determine (k):	$[A]$ versus time	$\ln[A]$ versus time	$\frac{1}{[A]}$ versus time
Relationship of Rate Constant to the Slope of Straight Line:	$slope = -k$	$slope = -k$	$slope = k$
Half-life:	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$

Sample Problems

1. Define Reaction Rate

2. TRUE or FALSE: Changes in the temperature or the introduction of a catalyst will affect the rate constant of a reaction

For sample problems 3-6, use **Formula 6** to answer the questions

$$H_2O \longrightarrow 2H_2 + O_2 \tag{2.1.3.8}$$

*Assume the reaction occurs at constant temperature

3. For the given reaction above, state the rate law.

4. State the overall order of the reaction.

5. Find the rate, given k = 1.14 x 10^{-2} and [H_2O] = 2.04M

6. Find the half-life of the reaction.

Answers

1. Reaction Rate is the measure of the change in concentration of the disappearance of reactants or the change in concentration of the appearance of products per unit time.

2. FALSE. The rate constant is not dependant on the presence of a catalyst. Catalysts, however, can effect the total rate of a reaction.

3. $Rate = k[H_2O]$

4. First - Order

5. 2.33 x 10^{-2} s^{-1}

6. 60.8 s (($t_{1/2}$ = ln 2 / k = ln 2 / 1.14 x 10^{-2} = 60.8 s).

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2.1.3.1: The "Speed" of a Chemical Reaction

How long does it take for a chemical reaction to occur under a given set of conditions? As with many "simple" questions, no meaningful answer can be given without being more precise. In this case,

How do we define the point at which the reaction is "completed"?

A reaction is "completed" when it has reached equilibrium — that is, when concentrations of the reactants and products are no longer changing.

If the equilibrium constant is quite large, then the answer reduces to a simpler form: the reaction is completed when the concentration of a reactant falls to zero. In the interest of simplicity, we will assume that this is the case in the remainder of this discussion.

"How long?" may be too long

If the reaction takes place very slowly, the time it takes for every last reactant molecule to disappear may be too long for the answer to be practical. In this case, it might make more sense to define "completed" when a reactant concentration has fallen to some arbitrary fraction of its initial value — 90%, 70%, or even only 20%.

The particular fraction one selects depends on the cost of the reactants in relation to the value of the products, balanced against the cost of operating the process for a longer time or the inconvenience of waiting for more product. This kind of consideration is especially important in industrial processes in which the balances of these costs affect the profitability of the operation.

The half-life of a reaction

Instead of trying to identify the time required for the reaction to become completed, it is far more practical to specify the the time required for the concentration of a reactant to fall to half of its initial value. This is known as the *half-life* (or half-time) of the reaction.

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2.1.3.2: The Rate of a Chemical Reaction

The rate of a chemical reaction is the *change* in concentration over the *change* in time.

Introduction

The rate of a chemical reaction is the *change* in concentration over the *change* in time and is a metric of the "speed" at which a chemical reactions occurs and can be defined in terms of two observables:

1. The Rate of Disappearance of Reactants

$$-\frac{\Delta[Reactants]}{\Delta t}$$

   Note this is negative because it measures the rate of disappearance of the reactants.
2. The Rate of Formation of Products

$$\frac{\Delta[Products]}{\Delta t}$$

   This is the rate at which the products are formed.

They both are linked via the balanced chemical reactions and can both be used to measure the reaction rate.

Outside links

- http://en.Wikipedia.org/wiki/Reaction_rate
- www.chm.davidson.edu/vce/kinetics/ReactionRates.html(this website lets you play around with reaction rates and will help your understanding)
- goldbook.iupac.org/R05156.html
- www.youtube.com/watch?v=FfoQsZa8F1c YouTube video of a very fast exothermic reaction.

References

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2. Connors, Kenneth. Chemical Kinetics: The Study of Reaction Rates in Solution. New York City: VCH Publishers, Inc., 1990.

Problems

1. Consider the reaction $2A + B \longrightarrow C$. The concentration of [A] is 0.54321M and the rate of reaction is $3.45 \times 10^{-6} M/s$. What Concentration will [A] be 3 minutes later?
2. Consider the reaction $A + B \longrightarrow C$. The rate of reaction is 1.23*10-4. [A] will go from a 0.4321 M to a 0.4444 M concentration in what length of time?
3. Write the rate of the chemical reaction with respect to the variables for the given equation.

$$2A + 3B \rightarrow C + 2D$$

4. True or False: The Average Rate and Instantaneous Rate are equal to each other.
5. How is the rate of formation of a product related to the rates of the disappearance of reactants.

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2.1.4: Reaction Rates- A Microscopic View

The Learning Objective of this Module is to determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2C_8H_{18\ (l)} + 25O_2(g) \rightarrow 16CO_{2\ (g)} + 18H_2O_{(g)} \tag{14.34}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_{2\ (g)} + CO(g) \rightarrow NO_{(g)} + CO_{2\ (g)} \tag{14.35}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[NO_2]^2 \tag{14.36}$$

The fact that the reaction is second order in $[NO_2]$ and independent of [CO] tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be $rate = k[NO_2][CO]$.

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

step 1	$\mathrm{NO_2 + NO_2 \xrightarrow{slow} NO_3 + NO}$	elementary reaction
step 2	$\underline{\mathrm{NO_3 + CO \rightarrow NO_2 + CO_2}}$	elementary reaction
sum	$\mathrm{NO_2 + CO \rightarrow NO + CO_2}$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

Note

The sum of the elementary reactions in a reaction mechanism must give the overall balanced chemical equation of the reaction.

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as unimolecular; if there are two reactant molecules, it is bimolecular; and if there are three reactant molecules (a relatively rare situation), it is termolecular. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 14.7). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is rate = $k[A]$. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 14.19. For a bimolecular elementary reaction of the form A + B → products, the general rate law is rate = $k[A][B]$.

Table 14.7 *Common Types of Elementary Reactions and Their Rate Laws*

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = $k[A]$	first
2A → products	bimolecular	rate = $k[A]^2$	second
A + B → products	bimolecular	rate = $k[A][B]$	second
2A + B → products	termolecular	rate = $k[A]^2[B]$	third
A + B + C → products	termolecular	rate = $k[A][B][C]$	third

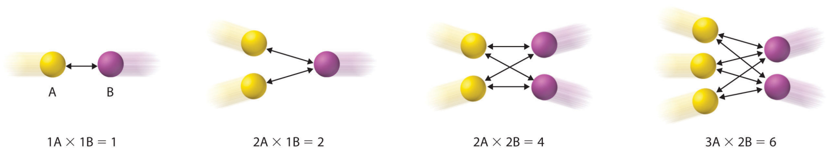


Figure 14.19 The Basis for Writing Rate Laws of Elementary Reactions. *This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.

Rate-determining step. *The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.*

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO}$	$\text{rate} = k_1[\mathrm{NO_2}]^2$ (predicted)
step 2	$\underline{\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}}$	$\text{rate} = k_2[\mathrm{NO_3}][\mathrm{CO}]$ (predicted)
sum	$\mathrm{NO_2 + CO \xrightarrow{k} NO + CO_2}$	$\text{rate} = k[\mathrm{NO_2}]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, $\mathrm{NO_3}$ is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 12

In an alternative mechanism for the reaction of NO_2 with CO, N_2O_4 appears as an intermediate.

step 1	$\mathbf{NO_2 + NO_2 \xrightarrow{k_1} N_2O_4}$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.

B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise 12

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2ICl(l) + H_2(g) \rightarrow 2HCl(g) + I_2(s)$$

The experimentally determined rate law is rate = $k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	$\text{rate} = k_1[ICl][H_2]\ (\text{slow})$
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	$\text{rate} = k_2[HI][ICl]\ (\text{fast})$
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 12b: NO with H_2

Is the the reaction between NO and H_2 occurs via a three-step process:

step 1	$\mathrm{NO + NO \xrightarrow{k_1} N_2O_2}$	(fast)
step 2	$\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O}$	(slow)
step 3	$\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O}$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = $k[NO]^2[H^2]$?

Answer:

- Step 1: $rate = k_1[NO]^2$;
- Step 2: $rate = k_2[N2O2][H_2]$;
- Step 3: $rate = k_3[N_2O][H_2]$;
- OVer all reaction:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting $k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Chain Reactions

Many reaction mechanisms, like those discussed so far, consist of only two or three elementary reactions. Many others consist of long series of elementary reactions. The most common mechanisms are **chain reactions**, in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process. Chain reactions occur in fuel combustion, explosions, the formation of many polymers, and the tissue changes associated with aging. They are also important in the chemistry of the atmosphere.

Chain reactions are described as having three stages. The first is initiation, a step that produces one or more reactive intermediates. Often these intermediates are **radicals**, species that have an unpaired valence electron. In the second stage, propagation, reactive intermediates are continuously consumed and regenerated while products are formed. Intermediates are also consumed but not regenerated in the final stage of a chain reaction, termination, usually by forming stable products.

Let us look at the reaction of methane with chlorine at elevated temperatures (400°C–450°C), a chain reaction used in industry to manufacture methyl chloride (CH_3Cl), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4):

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

Direct chlorination generally produces a mixture of all four carbon-containing products, which must then be separated by distillation. In our discussion, we will examine only the chain reactions that lead to the preparation of CH_3Cl.

In the initiation stage of this reaction, the relatively weak Cl–Cl bond cleaves at temperatures of about 400°C to produce chlorine atoms (Cl·):

$$Cl_2 \rightarrow 2Cl\cdot$$

During propagation, a chlorine atom removes a hydrogen atom from a methane molecule to give HCl and $CH_3\cdot$, the methyl radical:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The methyl radical then reacts with a chlorine molecule to form methyl chloride and another chlorine atom, Cl·:

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

The sum of the propagation reactions is the same as the overall balanced chemical equation for the reaction:

$$\begin{array}{c} \mathrm{Cl}\cdot + \mathrm{CH_4} \rightarrow \mathrm{CH_3}\cdot + \mathrm{HCl} \\ \mathrm{CH_3}\cdot + \mathrm{Cl_2} \rightarrow \mathrm{CH_3Cl} + \mathrm{Cl}\cdot \\ \hline \mathrm{Cl_2} + \mathrm{CH_4} \rightarrow \mathrm{CH_3Cl} + \mathrm{HCl} \end{array}$$

Without a chain-terminating reaction, propagation reactions would continue until either the methane or the chlorine was consumed. Because radical species react rapidly with almost anything, however, including each other, they eventually form neutral compounds, thus terminating the chain reaction in any of three ways:

$$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$$

$$CH_3\cdot + CH_3\cdot \rightarrow H_3CCH_3$$

$$Cl\cdot + Cl\cdot \rightarrow Cl_2$$

Here is the overall chain reaction, with the desired product (CH_3Cl) in bold:

Initiation:	$Cl_2 \rightarrow 2Cl\cdot$
Propagation:	$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$
	$CH_3\cdot + Cl_2 \rightarrow \mathbf{CH_3Cl} + Cl\cdot$
Termination:	$CH_3\cdot + Cl\cdot \rightarrow \mathbf{CH_3Cl}$
	$CH_3\cdot + CH_3\cdot \rightarrow H_3CCH_3$
	$Cl\cdot + Cl\cdot \rightarrow Cl_2$

The chain reactions responsible for explosions generally have an additional feature: the existence of one or more chain branching steps, in which one radical reacts to produce two or more radicals, each of which can then go on to start a new chain reaction. Repetition of the branching step has a cascade effect such that a single initiation step generates large numbers of chain reactions. The result is a very rapid reaction or an explosion.

The reaction of H_2 and O_2, used to propel rockets, is an example of a chain branching reaction:

Initiation:	$H_2 + O_2 \rightarrow HO_2\cdot + H\cdot$
Propagation:	$HO_2\cdot + H_2 \rightarrow H_2O + OH\cdot$
	$OH\cdot + H_2 \rightarrow H_2O + H\cdot$
Termination:	$H\cdot + O_2 \rightarrow OH\cdot + \cdot O\cdot$
	$\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot$

Termination reactions occur when the extraordinarily reactive H· or OH· radicals react with a third species. The complexity of a chain reaction makes it unfeasible to write a rate law for the overall reaction.

Summary

A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its molecularity, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step. Chain reactions consist of three kinds of reactions: initiation, propagation, and termination. Intermediates in chain reactions are often radicals, species that have an unpaired valence electron.

Key Takeaway

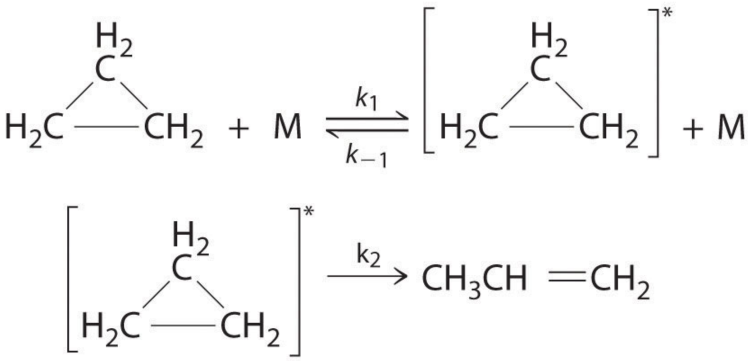
- A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law.

Conceptual Problems

1. How does the term molecularity relate to elementary reactions? How does it relate to the overall balanced chemical equation?
2. What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?
3. When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?
4. If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?
5. Give the rate-determining step for each case.
    a. Traffic is backed up on a highway because two lanes merge into one.
    b. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
    c. A document containing text and graphics is downloaded from the Internet.
6. Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

Numerical Problems

1. Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

2. Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

3. Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$	(fast)
$O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$	(slow)
$H^+ + OH^- \xrightarrow{k_3} H_2O$	(fast)

Assume that the rates of the forward and reverse reactions in the first equation are equal.

4. The following reactions are given:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$\mathrm{D+E\xrightarrow{k_2}F}$$

What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the rate law Δ[F]/Δt = k[A][B][E]/[C]? How does the magnitude of k_1 compare to that of k_2? Under what conditions would you expect the rate law to be Δ[F]/Δt =k'[A][B]? Assume that the rates of the forward and reverse reactions in the first equation are equal.

Numerical Answers

1. The k_2 step is likely to be rate limiting; the rate cannot proceed any faster than the second step.
3.

$$\text{rate}=k_2\frac{k_1[\mathrm{O_2NNH_2}]}{k_{-1}[\mathrm{H^+}]}=k\frac{[\mathrm{O_2NNH_2}]}{[\mathrm{H^+}]}$$

2.1.5: Second-Order Reactions

Many important biological reactions, such as the formation of double-stranded DNA from two complementary strands, can be described using second order kinetics. In a second-order reaction, the sum of the exponents in the rate law is equal to two. The two most common forms of second-order reactions will be discussed in detail in this section.

To describe how the rate of a second-order reaction changes with concentration of reactants or products, the differential (derivative) rate equation is used as well as the integrated rate equation. The differential rate law can show us how the rate of the reaction changes in time, while the integrated rate equation shows how the concentration of species changes over time. The latter form, when graphed, yields a linear function and is, therefore, more convenient to look at. Nonetheless, both of these equations can be derived from the above expression for the reaction rate. Plotting these equations can also help us determine whether or not a certain reaction is second-order.

Case 1: Identical Reactants

Two of the same reactant (A) combine in a single elementary step.

$$\mathrm{A}+\mathrm{A} \longrightarrow \mathrm{P} \tag{2.1.5.1}$$

$$2\,\mathrm{A} \longrightarrow \mathrm{P} \tag{2.1.5.2}$$

The reaction rate for this step can be written as

$$\text{Rate} = -\frac{1}{2}\frac{d[A]}{dt} = +\frac{d[P]}{dt}$$

and the rate of loss of reactant A

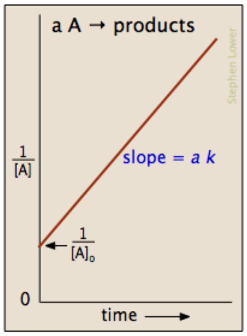
$$\frac{dA}{dt} = -k[A][A] = -k[A]^2 \tag{2.1.5.3}$$

where k is a second order rate constant with units of $\mathrm{M}^{-1}\mathrm{min}^{-1}$ or $\mathrm{M}^{-1}\mathrm{s}^{-1}$. Therefore, doubling the concentration of reactant A will quadruple the rate of the reaction. In this particular case, another reactant (B) could be present with A; however, its concentration does not affect the rate of the reaction, i.e., the reaction order with respect to B is zero, and we can express the rate law as $v = k[A]^2[B]^0$.

Integration of Equation 2.1.5.3yields

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

which is easily rearranged into a form of the equation for a straight line and yields plots similar to the one shown below.



The half-life is given by

$$t_{1/2} = \frac{1}{k[A_o]}$$

Notice that the half-life of a second-order reaction depends on the initial concentration, in contrast to first-order reactions. For this reason, the concept of half-life for a second-order reaction is far less useful. Reaction rates are discussed in more detail here. Reaction orders are defined here. Here are explanations of zero and first order reactions.

For reactions that follow Equation 2.1.5.1 or 2.1.5.2, the rate at which A decreases can be expressed using the **differential rate equation**.

$$-\frac{d[A]}{dt} = k[A]^2$$

The equation can then be rearranged:

$$\frac{d[A]}{[A]^2} = -k\,dt$$

Since we are interested in the change in concentration of A over a period of time, we integrate between $t = 0$ and t, the time of interest.

$$\int_{[A]_o}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

To solve this, we use the following rule of integration (power rule):

$$\int \frac{dx}{x^2} = -\frac{1}{x} + constant$$

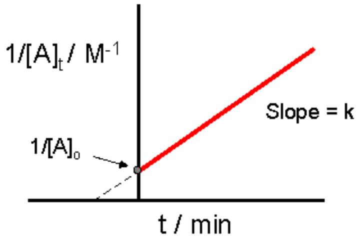
We then obtain the **integrated rate equation**.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

Upon rearrangement of the integrated rate equation, we obtain an equation of the line:

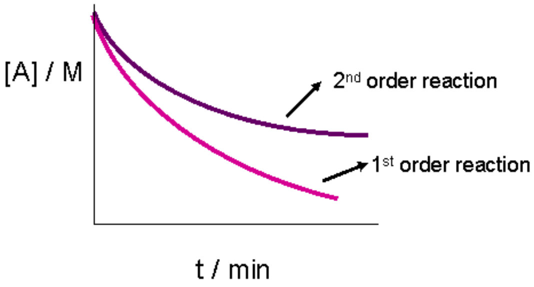
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

The crucial part of this process is not understanding precisely how to derive the integrated rate law equation, rather it is important to understand how the equation directly relates to the graph which provides a linear relationship. In this case, and for all second order reactions, the linear plot of $\frac{1}{[A]_t}$ versus time will yield the graph below.



This graph is useful in a variety of ways. If we only know the concentrations at specific times for a reaction, we can attempt to create a graph similar to the one above. If the graph yields a straight line, then the reaction in question must be second order. In addition, with this graph we can find the slope of the line and this slope is k, the reaction constant. The slope can be found be finding the "rise" and then dividing it by the "run" of the line. For an example of how to find the slope, please see the example section below. There are alternative graphs that could be drawn.

The plot of $[A]_t$ versus time would result in a straight line if the reaction were zeroth order. It does, however, yield less information for a second order graph. This is because both the graphs of a first or second order reaction would look like exponential decays. The only obvious difference, as seen in the graph below, is that the concentration of reactants approaches zero more slowly in a second-order, compared to that in a first order reaction.



Case 2: Second Order Reaction with Multiple Reactants

Two different reactants (A and B) combine in a single elementary step:

$$A + B \longrightarrow P \tag{2.1.5.4}$$

The reaction rate for this step can be written as

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[P]}{dt}$$

and the rate of loss of reactant A

$$\frac{d[A]}{dt} = -k[A][B]$$

where the reaction order with respect to each reactant is 1. This means that when the concentration of reactant A is doubled, the rate of the reaction will double, and quadrupling the concentration of reactant in a separate experiment will quadruple the rate. If we double the concentration of A and quadruple the concentration of B at the same time, then the reaction rate is increased by a factor of 8. This relationship holds true for any varying concentrations of A or B.

As before, the rate at which A decreases can be expressed using the differential rate equation:

$$\frac{d[A]}{dt} = -k[A][B]$$

Two situations can be identified.

Situation 2a: $[A]_0 \neq [B]_0$

Situation 2a is the situation that the initial concentration of the two reactants are not equal. Let x be the concentration of each species reacted at time t.

Let $[A]_0 = a$ and $[B]_0 = b$, then $[A] = a - x$;$[B] = b - x$. The expression of rate law becomes:

$$-\frac{dx}{dt} = -k([A]_o - x)([B]_o - x)$$

which can be rearranged to:

$$\frac{dx}{([A]_o - x)([B]_o - x)} = kdt$$

We integrate between $t = 0$ (when $x = 0$) and t, the time of interest.

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = k\int_0^t dt$$

To solve this integral, we use the method of partial fractions.

$$\int_0^x \frac{1}{(a-x)(b-x)}dx = \frac{1}{b-a}\left(\ln\frac{1}{a-x} - \ln\frac{1}{b-x}\right)$$

Evaluating the integral gives us:

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = \frac{1}{[B]_o - [A]_o}\left(\ln\frac{[A]_o}{[A]_o - x} - \ln\frac{[B]_o}{[B]_o - x}\right)$$

Applying the rule of logarithm, the equation simplifies to:

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = \frac{1}{[B]_o - [A]_o}\ln\frac{[B][A]_o}{[A][B]_o}$$

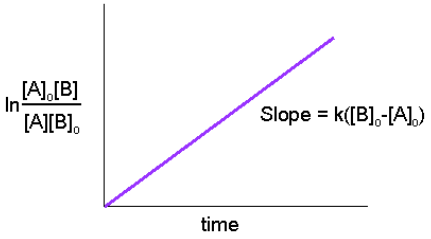
We then obtain the **integrated rate equation** (under the condition that [A] and [B] are not equal).

$$\frac{1}{[B]_o - [A]_o}\ln\frac{[B][A]_o}{[A][B]_o} = kt$$

Upon rearrangement of the integrated rate equation, we obtain:

$$\ln\frac{[B][A]_o}{[A][B]_o} = k([B]_o - [A]_o)t$$

Hence, from the last equation, we can see that a linear plot of $\ln\frac{[A]_o[B]}{[A][B]_o}$ versus time is characteristic of second-order reactions.



This graph can be used in the same manner as the graph in the section above or written in the other way:

$$\ln\frac{[A]}{[B]} = k([A]_o - [B]_o)t + \ln\frac{[A]_o}{[B]_o}$$

in form $y = ax + b$ with a slope of $a = k([B]_0 - [A]_0)$ and a y-intercept of $b = \ln\frac{[A]_0}{[B]_0}$

Situation 2b: $[A]_0 = [B]_0$

Because $A + B \rightarrow P$

Since A and B react with a 1 to 1 stoichiometry, $[A] = [A]_0 - x$ and $[B] = [B]_0 - x$

at any time t, $[A] = [B]$ and the rate law will be,

$$\text{rate} = k[A][B] = k[A][A] = k[A]^2.$$

Thus, it is assumed as the **first case**!!!

✓ Example 2.1.5.1

The following chemical equation reaction represents the thermal decomposition of gas E into K and G at 200° C

$$5\,\text{E(g)} \longrightarrow 4\,\text{K(g)} + \text{G(g)}$$

This reaction follows a second order rate law with regards to E. For this reaction suppose that the rate constant at 200° C is equivalent to $4.0 \times 10^{-2} M^{-1} s^{-1}$ and the initial concentration is $0.050\ M$. What is the initial rate of decomposition of E.

Solution

Start by defining the reaction rate in terms of the loss of reactants

$$\text{Rate (initial)} = -\frac{1}{5}\frac{d[E]}{dt}$$

and then use the rate law to define the rate of loss of E

$$\frac{d[E]}{dt} = -k[A]_i^2$$

We already know k and $[A]_i$ but we need to figure out x. To do this look at the units of k and one sees it is $M^{-1}s^{-1}$ which means the overall reaction is a second order reaction with $x = 2$.

$$\begin{aligned}\text{Initial rate } &= (4.0 \times 10^{-2} M^{-1} s^{-1})(0.050\, M)^2 \\ &= 1 \times 10^{-4}\, Ms^{-1}\end{aligned}$$

Half-Life

Another characteristic used to determine the order of a reaction from experimental data is the half-life ($t_{1/2}$). By definition, the half life of any reaction is the amount of time it takes to consume half of the starting material. For a second-order reaction, the half-life is inversely related to the initial concentration of the reactant (A). For a second-order reaction each half-life is twice as long as the life span of the one before.

Consider the reaction $2A \rightarrow P$:

We can find an expression for the half-life of a second order reaction by using the previously derived integrated rate equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

Since,

$$[A]_{t_{1/2}} = \frac{1}{2}[A]_o$$

when $t = t_{1/2}$.

Our integrated rate equation becomes:

$$\frac{1}{\frac{1}{2}[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$$

After a series of algebraic steps,

$$\begin{aligned}\frac{2}{[A]_o} - \frac{1}{[A]_o} &= kt_{1/2} \\ \frac{1}{[A]_o} &= kt_{1/2}\end{aligned}$$

We obtain the equation for the half-life of a second order reaction:

$$t_{1/2} = \frac{1}{k[A]_o} \tag{2.1.5.5}$$

This inverse relationship suggests that as the initial concentration of reactant is increased, there is a higher probability of the two reactant molecules interacting to form product. Consequently, the reactant will be consumed in a shorter amount of time, i.e. the reaction will have a shorter half-life. This equation also implies that since the half-life is longer when the concentrations are low, species decaying according to second-order kinetics may exist for a longer amount of time if their initial concentrations are small.

Note that for the second scenario in which $A + B \rightarrow P$, the half-life of the reaction cannot be determined. As stated earlier, $[A]_o$ cannot be equal to $[B]_o$. Hence, the time it takes to consume one-half of A is not the same as the time it takes to consume one-half of B. Because of this, we cannot define a general equation for the half-life of this type of second-order reaction.

Example 2.1.5.2: Half-Life of a Second-Order Reaciton

If the only reactant is the initial concentration of A, and it is equivalent to $[A]_0 = 4.50 \times 10^{-5}\ M$ and the reaction is a second order with a rate constant $k = 0.89 M^{-1} s^{-1}$. What is the half-life of this reaction?

Solution

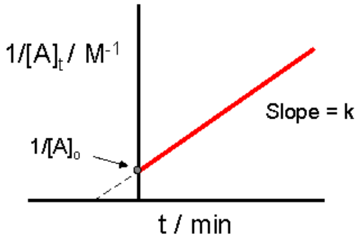
This is a direct application of Equation 2.1.5.5.

$$\begin{aligned}\frac{1}{k[A]_0} &= \frac{1}{(4.50 \times 10^{-5} M)(0.89 M^{-1} s^{-1})} \\ &= 2.50 \times 10^4\ s\end{aligned}$$

Summary

	$2A \rightarrow P$	$A + B \rightarrow P$
Differential Form	$-\frac{d[A]}{dt} = k[A]^2$	$-\frac{d[A]}{dt} = k[A][B]$
Integral Form	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$	$\frac{1}{[B]_o - [A]_o} \ln \frac{[B][A]_o}{[A][B]_o} = kt$
Half Life	$t_{1/2} = \frac{1}{k[A]_o}$	Cannot be easily defined; $t_{1/2}$ for A and B are different.

The graph below is the graph that tests if a reaction is second order. The reaction is second order if the graph has a straight line, as is in the example below.



Exercise 2.1.5.3

Given the following information, determine the order of the reaction and the value of k, the reaction constant.

Concentration (M)	Time (s)
1.0	10
0.50	20
0.33	30

*Hint: Begin by graphing

Answer

Make graphs of concentration vs. time (zeroth order), natural log of concentration vs. time (first order), and one over concentration vs. time (second order). Determine which graph results in a straight line. This graph reflects the order of the reaction. For this problem, the straight line should be in the 3rd graph, meaning the reaction is second order. The numbers should have are:

1/Concentration$^{(M-1)}$	Time (s)

1/Concentration$^{(M-1)}$	Time (s)
1	10
2	20
3	30

The slope can be found by taking the "rise" over the "run". This means taking two points, (10,1) and (20,2). The "rise" is the vertical distance between the points (2-1=1) and the "run" is the horizontal distance (20-10=10). Therefore the slope is 1/10=0.1. The value of k, therefore, is 0.1 $M^{-2}s^{-1}$.

Exercise 2.1.5.4

Using the following information, determine the half life of this reaction, assuming there is a single reactant.

Concentration (M)	Time (s)
2.0	0
1.3	10
0.9633	20

Answer

Determine the order of the reaction and the reaction constant, k, for the reaction using the tactics described in the previous problem. The order of the reaction is second, and the value of k is 0.0269 $M^{-2}s^{-1}$. Since the reaction order is second, the formula for $t_{1/2} = k^{-1}[A]_0^{-1}$. This means that the half life of the reaction is 0.0259 seconds.

Exercise 2.1.5.5

Given the information from the previous problem, what is the concentration after 5 minutes?

Answer

Convert the time (5 minutes) to seconds. This means the time is 300 seconds. Use the integrated rate law to find the final concentration. The final concentration is 0.1167 M.

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2.1.5.1: Pseudo-1st-order reactions

Under certain conditions, the 2nd order kinetics can be approximated as first-order kinetics. These **pseudo-1$^{\text{st}}$-order reactions** greatly simplify quantifying the reaction dynamics.

Introduction

A 2nd-order reaction can be challenging to follow mostly because the two reactants involved must be measured simultaneously. There can be additional complications because certain amounts of each reactant are required to determine the reaction rate, for example, which can make the cost of one's experiment high if one or both of the needed reactants are expensive. To avoid more complicated, expensive experiments and calculations, we can use the pseudo-1$^{\text{st}}$-order reaction, which involves treating a 2$^{\text{nd}}$ order reaction like a 1$^{\text{st}}$ order reaction.

In second-order reactions with two reactant species,

$$\mathrm{A+B\longrightarrow products}$$

the rate of disappearance of A is

$$\frac{d[A]}{dt}=-k[A][B]$$

as discussed previously (Case 2a), the integrated rate equation under the condition that [A] and [B] are not equal is

$$\frac{1}{[B]_o-[A]_o}\ln\frac{[B][A]_o}{[A][B]_o}=kt \tag{2.1.5.1.1}$$

However, when $[B]_0\gg[A]_0$, then $[B]_0\approx[B]$ and Equation 2.1.5.1.1becomes

$$\frac{1}{[B]_0-[A]_0}\ln\frac{[B][A]_0}{[B]_0[A]}\approx\frac{1}{[B]}\ln\frac{[A]_0}{[A]}=kt$$

or

$$[A]=[A]_0e^{-[B]kt}$$

This functional form of the decay kinetics is similar ot the first order kinetics and the system is said to operate under pseudo-first order kinetics. To reach a pseudo-1$^{\text{st}}$-order reaction, we can manipulate the initial concentrations of the reactants. One of the reactants, B, for example, would have a significantly higher concentration, while the other reactant, A, would have a significantly lower concentration. We can then assume that the concentration of reactant B effectively remains constant during the reaction because its consumption is so small that the change in concentration becomes negligible. Because of this assumption, we can multiply the reaction rate, k, with the reactant with assumed constant concentration, B, to create a new rate constant ($k'=k[B]$) that will be used in the new rate equation,

$$\text{Rate}=k'[A]$$

as the new rate constant so we can treat the 2$^{\text{nd}}$ order reaction as a 1$^{\text{st}}$ order reaction.

Overloading

One can also do the same by overloading the initial concentration of A so that it effectively remains constant during the course of the reaction For example, if one were to dump a liter of 5 M HCl into a 55 M ocean, the concentration of the mixture would be closer or equal to that of the ocean because there is so much water physically compared to the HCl. Even if the amount of water was one liter this would still be the case because 55 M is relatively large compared to 5 M.

If we have an instance where there are more than two reactants involved in a reaction, all we would have to do to make the reaction pseudo-1$^{\text{st}}$-order is to make the concentrations of all but one of the reactants very large. If there were three reactants, for example, we would make two of the three reactants be in excess (whether in amount or in concentration) and then monitor the dependency of the third reactant.

We can write the pseudo$^{\text{st}}$-order reaction equation as:

$$[A]=[A]_0e^{-[B]_0kt} \tag{2.1.5.1.2}$$

or

$$[A]=[A]_0e^{-k^{'}t}$$

where

- $[A]_o$ is the initial concentration of A,
- $[B]_o$ is the initial concentration of B,
- $k^{'}$ is the pseudo-1st-order reaction rate constant,
- k is the 2nd order reaction rate constant, and
- $[A]$ is the concentration of A at time t.

By using natural log to both sides of the pseudo-1st-order equation we get:

$$\ln\left(\frac{A}{A_0}\right)=-k[B]_0t$$

or

$$\ln\left(\frac{A}{A_0}\right)=-k^{'}t$$

✓ Example 2.1.5.1.1

If a 2nd order reaction has the rate equation $\text{Rate}=k[A][B]$, and the rate constant, k, is $3.67\;M^{-1}s^{-1}$, $[A]$ is $4.5\;M$ and $[B]$ is $99\;M$, what is the rate constant of its pseudo-1st-order reaction?

Solution

Because $[B]$ is in excess we multiply $99\;M$ with $3.67\;M^{-1}s^{-1}$

$$(99\;M)(3.67\;M^{-1}s^{-1})=363.33\;s^{-1}$$

✓ Example 2.1.5.1.2

If [A] = 55 M at 39 s, $[A]_o$ = 99 M, and $[B]_o$ = 1000 M, what is the 2nd order reaction rate constant?

Solution

Use the Equation 2.1.5.1.2

$$(55\text{ M}) = (99\text{ M})e^{-k'(1000M)(39s)}$$

$$k' = 1.507 \times 10^{-5}\text{ M}^{-1}\text{s}^{-1}$$

✓ Example 2.1.5.1.3

What is the concentration of A at time 45 s if $[A]_o$ = 1M, $[B]_o$ = 45 M, and 2nd order rate constant is 0.6 $M^{-1}s^{-1}$?

Solution

Use the Equation 2.1.5.1.2

$[A] = (1)e^{-(0.6\text{ M-1s-1})(45)}$

$[A] = 1.88 \times 10^{-12}$ M

✓ Example 2.1.5.1.4

What is the rate of a reaction if $[A]_o$ = 560 M, $[B]_o$ = 0.2M, and 2nd order rate constant is 0.1 $M^{-1}s^{-1}$?

Solution

Use the equation R = k'[A][B]

R = (0.1$M^{-1}s^{-1}$)(560M)(0.2M)

Rate = 11.2Ms^{-1}

Half-Life in a Pseudo-1st Order reaction

Half-life refers to the time required to decrease the concentration of a reactant by half, so we must solve for t. Here, $[B]$ will be the reactant in excess, and its concentration will stay constant. $[A]_o$ is the initial concentration of A; thus the half-life concentration of A is $0.5[A]_o$.

The pseudo-1st-order reaction equation can be written as:

$$[A] = [A]_o e^{-[B]kt} \quad or \quad \frac{[A]}{[A]_o} = e^{-k^{'}t}$$

By taking natural logs on both sides of the pseudo-1st-order equation, we get:

$$\ln\left(\frac{[A]}{[A]_o}\right) = k^{'}t$$

Because the concentration of A for a half-life $t_{1/2}$ is $1/2[A]_o$:

$$\ln\left(\frac{1/2[A]_o}{[A]_o}\right) = \ln\left(\frac{1}{2}\right) = -k^{'}t_{1/2}$$

Recalling that $k^{'} = k[B]$, $[B] \approx [B]_0$ and that $-\ln(1/2) = \ln 2$:

$$\ln(2) = k[B]_0 t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{k[B]_0}$$

✓ Example 2.1.5.1.5

What is the half-life of a reaction with $[A]_o$ = 109 M, $[B]_o$ = 1 M, k' = 45 $M^{-1}s^{-1}$?

Solution

Because [A] is in excess we can multiply the k' with $[A]_o$ to find k

(109M)(45$M^{-1}s^{-1}$) = 4905s^{-1}

$t_{1/2}$ = (ln0.5 / -k)

$t_{1/2}$ = 1.41 X 10^{-4}s

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2.1.6: Zero-Order Reactions

In some reactions, the rate is *apparently* independent of the reactant concentration. The rates of these **zero-order reactions** do not vary with increasing nor decreasing reactants concentrations. This means that the rate of the reaction is equal to the rate constant, k, of that reaction. This property differs from both first-order reactions and second-order reactions.

Origin of Zero Order Kinetics

Zero-order kinetics is *always* an artifact of the conditions under which the reaction is carried out. For this reason, reactions that follow zero-order kinetics are often referred to as pseudo-zero-order reactions. Clearly, a zero-order process cannot continue after a reactant has been exhausted. Just before this point is reached, the reaction will revert to another rate law instead of falling directly to zero as depicted at the upper left.

There are two general conditions that can give rise to zero-order rates:

1. Only a small fraction of the reactant molecules are in a location or state in which they are able to react, and this fraction is continually replenished from the larger pool.
2. When two or more reactants are involved, the concentrations of some are much greater than those of others

This situation commonly occurs when a reaction is catalyzed by attachment to a solid surface (*heterogeneous catalysis*) or to an enzyme.

✓ Example 1: Decomposition of Nitrous Oxide

Nitrous oxide will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 575 °C

$$2\,\mathrm{N_2O} \xrightarrow{\Delta,\,Ni} 2\,\mathrm{N_2(g)} + \mathrm{O_2(g)}$$

This reaction in the presence of a hot platinum wire (which acts as a catalyst) is zero-order, but it follows more conventional second order kinetics when carried out entirely in the gas phase.

$$2\,\mathrm{N_2O} \longrightarrow 2\,\mathrm{N_2(g)} + \mathrm{O_2(g)}$$

In this case, the N_2O molecules that react are limited to those that have attached themselves to the surface of the solid catalyst. Once all of the sites on the limited surface of the catalyst have been occupied, additional gas-phase molecules must wait until the decomposition of one of the adsorbed molecules frees up a surface site.

Enzyme-catalyzed reactions in organisms begin with the attachment of the substrate to the active site on the enzyme, leading to the formation of an *enzyme-substrate complex*. If the number of enzyme molecules is limited in relation to substrate molecules, then the reaction may appear to be zero-order.

This is most often seen when two or more reactants are involved. Thus if the reaction

$$A + B \rightarrow \text{products} \tag{1}$$

is first-order in both reactants so that

$$\text{rate} = k\,[A][B] \tag{2}$$

If B is present in *great excess*, then the reaction will appear to be zero order in B (and first order overall). This commonly happens when B is also the solvent that the reaction occurs in.

Differential Form of the Zeroth Order Rate Law

$$Rate = -\frac{d[A]}{dt} = k[A]^0 = k = constant \tag{3}$$

where $Rate$ is the reaction rate and k is the reaction rate coefficient. In this example, the units of k are M/s. The units can vary with other types of reactions. For zero-order reactions, the units of the rate constants are always M/s. In higher order reactions, k will have different units.

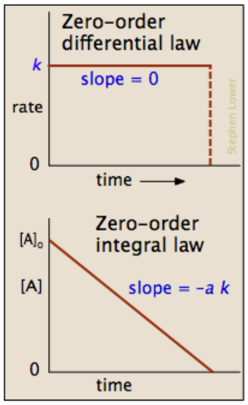

Figure 1: Rate vs. time (A) and Concentration vs. time for a zero order reaction.

Integrated Form of the Zeroth Order Rate Law

Integration of the differential rate law yields the concentration as a function of time. Start with the general rate law equations

$$Rate = k[A]^n \tag{4}$$

First, write the differential form of the rate law with $n = 0$

$$Rate = -\frac{d[A]^0}{dt} = k \tag{5}$$

then rearrange

$$d[A] = -kdt \tag{6}$$

Second, integrate both sides of the equation.

$$\int_{[A]_0}^{[A]} d[A] = -\int_0^t kdt \tag{7}$$

Third, solve for $[A]$. This provides the integrated form of the rate law.

$$[A] = [A]_0 - kt \tag{8}$$

The integrated form of the rate law allows us to find the population of reactant at any time after the start of the reaction.

Graphing Zero-order Reactions

$$[A] = -kt + [A]_0 \tag{9}$$

is in the form y = mx+b where slope = m = -k and the y- intercept = b = $[A]_0$

Zero-order reactions are *only* applicable for a very narrow region of time. Therefore, the linear graph shown below (Figure 2) is only realistic over a limited time range. If we were to extrapolate the line of this graph downward to represent all values of time for a given reaction, it would tell us that as time progresses, the concentration of our reactant becomes negative. We know that concentrations can never be negative, which is why zero-order reaction kinetics is applicable for describing a reaction for only brief window and must eventually transition into kinetics of a different order.

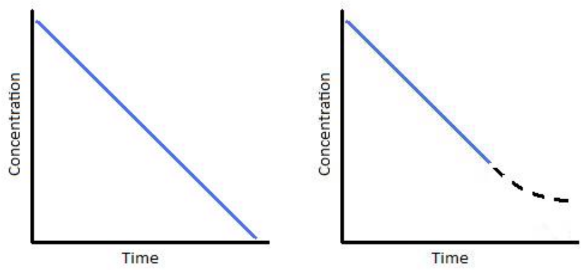

Figure 2*: (left) Concentration vs. time of a zero-order reaction. (Right) Concentration vs. time of a zero-order catalyzed reaction.*

To understand where the above graph comes from, let us consider a catalyzed reaction. At the beginning of the reaction, and for small values of time, the rate of the reaction is constant; this is indicated by the blue line in Figures 2; right. This situation typically happens when a catalyst is saturated with reactants. With respect to Michaelis-Menton kinetics, this point of catalyst saturation is related to the V_{max}. As a reaction progresses through time, however, it is possible that less and less substrate will bind to the catalyst. As this occurs, the reaction slows and we see a tailing off of the graph (Figure 2; right). This portion of the reaction is represented by the dashed black line. In looking at this particular reaction, we can see that reactions are ***not*** zero-order under all conditions. They are only zero-order for a limited amount of time.

If we plot rate as a function of time, we obtain the graph below (Figure 3). Again, this only describes a narrow region of time. The slope of the graph is equal to k, the rate constant. Therefore, k is constant with time. In addition, we can see that the reaction rate is completely independent of how much reactant you put in.

Figure 3*: Rate vs. time of a zero-order reaction.*

Relationship Between Half-life and Zero-order Reactions

The half-life. $t_{1/2}$, is a timescale in which each half-life represents the reduction of the initial population to 50% of its original state. We can represent the relationship by the following equation.

$$[A] = \frac{1}{2}[A]_o \tag{10}$$

Using the integrated form of the rate law, we can develop a relationship between zero-order reactions and the half-life.

$$[A] = [A]_o - kt \tag{11}$$

Substitute

$$\frac{1}{2}[A]_o = [A]_o - kt_{\frac{1}{2}} \tag{12}$$

Solve for $t_{1/2}$

$$t_{1/2} = \frac{[A]_o}{2k} \tag{13}$$

Notice that, for zero-order reactions, the half-life **depends** on the initial concentration of reactant and the rate constant.

Questions

1. Using the integrated form of the rate law, determine the rate constant *k* of a zero-order reaction if the initial concentration of substance A is 1.5 M and after 120 seconds the concentration of substance A is 0.75 M.
2. Using the substance from the previous problem, what is the half-life of substance A if its original concentration is 1.2 M?
3. If the original concentration is reduced to 1.0 M in the previous problem, does the half-life decrease, increase, or stay the same? If the half-life changes what is the new half-life?
4. Given are the rate constants *k* of three different reactions:

- Reaction A: k = 2.3 $M^{-1}s^{-1}$
- Reaction B: k = 1.8 Ms^{-1}
- Reaction C: k = 0.75 s^{-1}

Which reaction represents a zero-order reaction?

5. True/False: If the rate of a zero-order reaction is plotted as a function of time, the graph is a strait line where \(rate = k\ ).

Answers

1. The rate constant *k* is 0.00624 M/s
2. The half-life is 96 seconds.
3. Since this is a zero-order reaction, the half-life is dependent on the concentration. In this instance, the half-life is decreased when the original concentration is reduced to 1.0 M. The new half-life is 80 seconds.
4. Reaction B represents a zero-order reaction because the units are in M/s. Zero-order reactions always have rate constants that are represented by molars per unit of time. Higher order reactions, however, require the rate constant to be represented in different units.
5. True. When using the rate function $rate = k[A]^n$ with *n* equal to zero in zero-order reactions. Therefore, rate is equal to the rate constant *k*.

Summary

The kinetics of any reaction depend on the reaction mechanism, or rate law, and the initial conditions. If we assume for the reaction A -> Products that there is an initial concentration of reactant of $[A]_0$ at time t=0, and the rate law is an integral order in A, then we can summarize the kinetics of the zero-order reaction as follows:

Related Topics

Definition of a reaction rate

- Rate laws and rate constants
- The determination of the rate law
- Reaction Order
- First-order reactions
- Half-lives and Pharmacokinetics
- Second-order reactions

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2.2: Introduction to reaction kinetics- Basic rate laws

The kinetic theory of gases can be used to model the frequency of collisions between hard-sphere molecules, which is proportional to the reaction rate. Most systems undergoing a chemical reaction, however, are much more complex. The reaction rates may be dependent on specific interactions between reactant molecules, the phase(s) in which the reaction takes place, etc. The field of chemical kinetics is thus by-and-large based on empirical observations. From experimental observations, scientists have established that reaction rates almost always have a power-law dependence on the concentrations of one or more of the reactants. In the following sections, we will discuss different power laws that are commonly observed in chemical reactions.

0^{th} Order Reaction Kinetics

Consider a closed container initially filled with chemical species A. At $t=0$, a stimulus, such as a change in temperature, the addition of a catalyst, or irradiation, causes an irreversible chemical reaction to occur in which A transforms into product B:

$$a\mathrm{A} \longrightarrow b\mathrm{B} \tag{2.2.1}$$

The rate that the reaction proceeds, r, can be described as the change in the concentrations of the chemical species with respect to time:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = \frac{1}{b}\frac{d[\mathrm{B}]}{dt} \tag{2.2.2}$$

where $[\mathrm{X}]$ denotes the molar concentration of chemical species X with units of $\frac{\mathrm{mol}}{\mathrm{L}^3}$.

Let us first examine a reaction $\mathrm{A} \longrightarrow \mathrm{B}$ in which the reaction rate, r, is constant with time:

$$r = -\frac{d[\mathrm{A}]}{dt} = k \tag{2.2.3}$$

where k is a constant, also known as the rate constant with units of $\frac{\mathrm{mol}}{\mathrm{m}^3\mathrm{s}}$. Such reactions are called zeroth order reactions because the reaction rate depends on the concentrations of species A and B to the 0^{th} power. Integrating $[\mathrm{A}]$ with respect to T, we find that

$$[\mathrm{A}] = -kt + c_1 \tag{2.2.4}$$

At $t=0$, $[\mathrm{A}](0) = [\mathrm{A}]_0$. Plugging these values into the equation, we find that $c_1 = [\mathrm{A}]_0$. The final form of the equation is:

$$[\mathrm{A}] = [\mathrm{A}]_0 - kt \tag{2.2.5}$$

A plot of the concentration of species A with time for a 0^{th} order reaction is shown in Figure $2.2.1$, where the slope of the line is $-k$ and the y-intercept is $[\mathrm{A}]_0$. Such reactions in which the reaction rates are independent of the concentrations of products and reactants are rare in nature. An example of a system displaying 0^{th} order kinetics would be one in which a reaction is mediated by a catalyst present in small amounts.

1^{st} Order Reaction Kinetics

Experimentally, it is observed than when a chemical reaction is of the form

$$\sum_i \nu_i \mathrm{A}_i = 0 \tag{2.2.6}$$

the reaction rate can be expressed as

$$r = k \prod_{\text{reactants}} [\mathrm{A}_i]^{\nu_i} \tag{2.2.7}$$

where it is assumed that the stoichiometric coefficients ν_i of the reactants are all positive. Thus, or a reaction $\mathrm{A} \longrightarrow \mathrm{B}$, the reaction rate depends on $[\mathrm{A}]$ raised to the first power:

$$r = \frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{2.2.8}$$

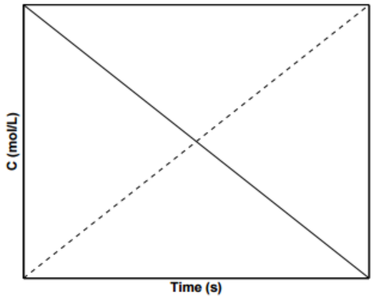

Figure 2.2.1: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 0^{th} order reaction.

For first order reactions, k has the units of $\frac{1}{\mathrm{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\mathrm{A}] = [\mathrm{A}]_0$, we arrive at the following equation:

$$[\mathrm{A}] = [\mathrm{A}]\, e^{-kt} \tag{2.2.9}$$

Figure 2.2.2 displays the concentration profiles for species A and B for a first order reaction. To determine the value of k from

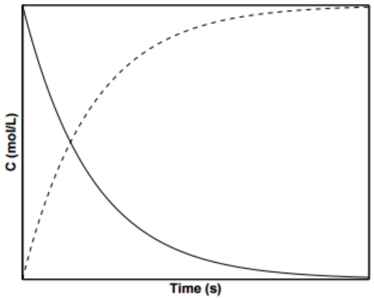

Figure 2.2.2: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 1^{st} order reaction.

experimental data, it is convenient to take the natural log of Equation 19.8:

$$\ln([\mathrm{A}]) = \ln([\mathrm{A}]_0) - kt \tag{2.2.10}$$

For a first order irreversible reaction, a plot of $\ln([\mathrm{A}])$ vs. t is straight line with a slope of $-k$ and a y-intercept of $\ln([\mathrm{A}]_0)$.

2^{nd} Order Reaction Kinetics

Another type of reaction depends on the square of the concentration of species A - these are known as second order reactions. For a second order reaction in which $2\mathrm{A} \longrightarrow \mathrm{B}$, we can write the reaction rate to be

$$r = -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2 \tag{2.2.11}$$

For second order reactions, k has the units of $\frac{\mathrm{m}^3}{\mathrm{mol}\cdot\mathrm{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\mathrm{A}] = [\mathrm{A}]_0$, we arrive at the following equation for the concentration of A over time:

$$[\mathrm{A}] = \frac{1}{2kt + \frac{1}{[\mathrm{A}]_0}} \tag{2.2.12}$$

Figure 2.2.3 shows concentration profiles of A and B for a second order reaction. To determine k from experimental data for

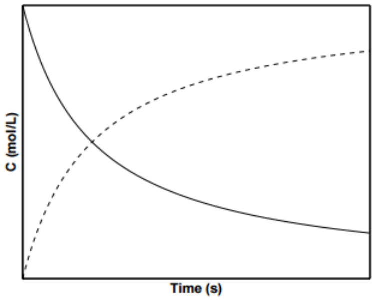

Figure 2.2.3: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 2^{nd} order reaction.

second-order reactions, it is convenient to invert Equation 19.11:

$$\frac{1}{[\mathrm{A}]}=\frac{1}{[\mathrm{A}]_0}+2kt \tag{2.2.13}$$

A plot of $1/[\mathrm{A}]$ vs. t will give rise to a straight line with slope k and intercept $1/[\mathrm{A}]_0$.

Second order reaction rates can also apply to reactions in which two species react with each other to form a product:

$$\mathrm{A}+\mathrm{B}\xrightarrow{k}\mathrm{C} \tag{2.2.14}$$

In this scenario, the reaction rate will depend on the concentrations of both A and B to the first order:

$$r=-\frac{d[\mathrm{A}]}{dt}=-\frac{d[\mathrm{B}]}{dt}=k[\mathrm{A}][\mathrm{B}] \tag{2.2.15}$$

In order to integrate the above equation, we need to write it in terms of one variable. Since the concentrations of A and B are related to each other via the chemical reaction equation, we can write:

$$[\mathrm{B}]=[\mathrm{B}]_0-([\mathrm{A}]_0-[\mathrm{A}])=[\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0 \tag{2.2.16}$$

$$\frac{d[\mathrm{A}]}{dt}=-k[\mathrm{A}]([\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0) \tag{2.2.17}$$

We can then use partial fractions to integrate:

$$kdt=\frac{d[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0)}=\frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\left(\frac{d[\mathrm{A}]}{[\mathrm{A}]}-\frac{d[\mathrm{A}]}{[\mathrm{B}]_0-[\mathrm{A}]_0+[\mathrm{A}]}\right) \tag{2.2.18}$$

$$kt=\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\ln\frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{B}][\mathrm{A}]_0} \tag{2.2.19}$$

Figure $2.2.4$ displays the concentration profiles of species A, B, and C for a second order reaction in which the initial concentrations of A and B are not equal.

Rate Laws for Elementary Reactions

In general, it is necessary to experimentally measure the concentrations of species over time in order to determine the apparent rate law governing the reaction. If the reactions are elementary reactions, (i.e. they cannot be expressed as a series of simpler reactions), then we can directly define the rate law based on the chemical equation. For example, an elementary

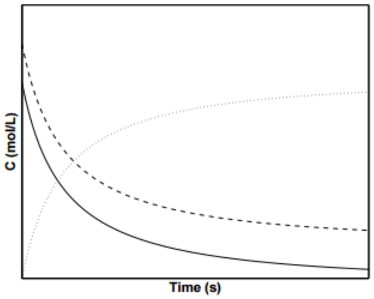

Figure 2.2.4: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{B}]$ (dashed line) and $[\mathrm{C}]$ (dotted line) over time for a 2^{nd} order reaction in which the initial concentrations of the reactants, $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$, are not equal.

reaction in which a single reactant transforms into a single product, is unimolecular reaction. These reactions follow 1^{st} order rate kinetics. An example of this type of reaction would be the isomerization of butane:

$$nC_4H_{10} \longrightarrow iC_4H_{10} \tag{2.2.20}$$

From the chemical reaction equation, we can directly write the rate law as

$$\frac{d\left[nC_4H_{10}\right]}{dt} = -k\left[nC_4H_{10}\right] \tag{2.2.21}$$

without the need to carry out experiments.

Elementary bimolecular reactions that involve two molecules interacting to form one or more products follow second order rate kinetics. An example would be the following reaction between a nitrate molecule and carbon monoxide to form nitrogen dioxide and carbon dioxide:

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \tag{2.2.22}$$

For the above elementary reaction, we can directly write the rate law as:

$$\frac{d\left[NO_3\right]}{dt} = -k\left[NO_3\right]\left[CO\right] \tag{2.2.23}$$

Trimolecular elementary reactions involving three reactant molecules to form one or more products are rare due to the low probability of three molecules simultaneously colliding with one another.

Reversible Reactions

Oftentimes, reactions are reversible, meaning that a reaction can proceed in both directions. An example of a reversible reaction is the isomerization of *cis*-1,2-dichloroethene to *trans*-1,2-dichloroethene. At equilibrium, both isomers are present, with their equilibrium concentrations determined by the rate at which the forward and reverse reaction take place.

Consider the following reversible reaction which follows first order rate kinetics in both directions, with rate constants k_1 and k_{-1} in the forward and reverse directions, respectively:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{2.2.24}$$

For the above reaction, we can write rate law for the reaction as:

$$\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{2.2.25}$$

If the concentration of species $\mathrm{B} = 0$ at the start of the reaction, then we can write:

$$[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}] \tag{2.2.26}$$

Equation 19.20 then becomes

$$\frac{d[\mathrm{A}]}{dt} = (k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_0 \tag{2.2.27}$$

Under equilibrium conditions, $d[\mathrm{A}]/dt = 0$. The equilibrium concentration of species A, $d[\mathrm{A}]_{\mathrm{eq}}$, can be calculated from the above expression as

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{k_{-1}}{k_1 + k_{-1}}[\mathrm{A}]_0 \tag{2.2.28}$$

Plugging Equation 19.23 into Equation 19.22 and integrating, we obtain the following expression:

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + c_1 e^{-(k_1+k_{-1})t} \tag{2.2.29}$$

where c_1 is a constant. Applying the initial condition that $[\mathrm{A}] = [\mathrm{A}]_0$ at $t = 0$,

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + \left([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}\right) e^{-(k_1+k_{-1})t} \tag{2.2.30}$$

From Equation 19.20, we can also write an expression for the equilibrium constant, K_c

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}} \tag{2.2.31}$$

In general, the equilibrium constant K_c is equal to the ratio of the forward and reverse rate constants. Consider the following bimolecular elementary reaction:

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} + \mathrm{D} \tag{2.2.32}$$

The forward and reverse reaction rates will be

$$r_{\text{forward}} = k_1 [\mathrm{A}][\mathrm{B}] \tag{2.2.33}$$

$$r_{\text{reverse}} = k_{-1} [\mathrm{C}][\mathrm{D}] \tag{2.2.34}$$

At equilibrium, $r_{\text{forward}} = r_{\text{reverse}}$, so

$$k_1 [\mathrm{A}]_{\mathrm{eq}} [\mathrm{B}]_{\mathrm{eq}} = k_{-1} [\mathrm{C}]_{\mathrm{eq}} [\mathrm{D}]_{\mathrm{eq}} \tag{2.2.35}$$

The equilibrium constant, K_c is given by

$$K_c = \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} \tag{2.2.36}$$

Plugging in Equation 19.30 into Equation 19.31, we arrive at

$$K_c = \frac{k_1}{k_{-1}} \tag{2.2.37}$$

The above equation is true for all reversible elementary reactions.

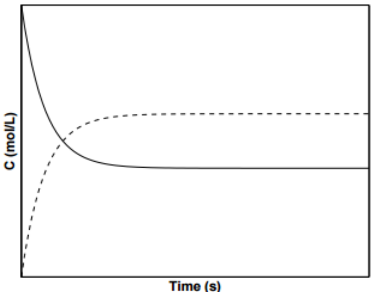

Figure 2.2.5: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a reversible reaction in which the forward and reverse reactions follow first order rate kinetics, with $k_1 > k_{-1}$

Relaxation Method to Determine Rate Constants

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. Consider the following reversible reaction:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{2.2.38}$$

The rate law can be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{B}] \tag{2.2.39}$$

Consider a system comprising A and B that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of A and B, $[\mathrm{A}]_{\text{eq},2}$ and $[\mathrm{B}]_{\text{eq},2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of A as

$$[\mathrm{A}] = [\mathrm{B}]_{\text{eq},1} - [\mathrm{B}] \tag{2.2.40}$$

The rate of change of species B can then be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\text{eq},1} - [\mathrm{B}]\right) - k_{-1}\,[\mathrm{B}] = k_1\,[\mathrm{B}]_{\text{eq},1} - (k_1 + k_{-1})\,[\mathrm{B}] \tag{2.2.41}$$

At equilibrium, $d\,[\mathrm{B}]\,/dt = 0$ and $[\mathrm{B}] = [\mathrm{B}]_{\text{eq},2}$, allowing us to write

$$k_1\,[\mathrm{B}]_{\text{eq},1} = (k_1 + k_{-1})\,[\mathrm{B}]_{\text{eq},2} \tag{2.2.42}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left([\mathrm{B}]_{\text{eq},2} - [\mathrm{B}]\right)} = (k_1 + k_{-1})\,dt \tag{2.2.43}$$

Integrating yields

$$-\ln\left([\mathrm{B}] - [\mathrm{B}]_{\text{eq},2}\right) = -\,(k_1 + k_{-1})\,t + C \tag{2.2.44}$$

We can rearrange the above equation in terms of B

$$[\mathrm{B}] = Ce^{-(k_1+k_{-1})t} + [\mathrm{B}]_{\text{eq},2} \tag{2.2.45}$$

At $t = 0$, $[\mathrm{B}] = [\mathrm{B}]_{\text{eq},1}$, so $C = [\mathrm{B}]_{\text{eq},1} - [\mathrm{B}]_{\text{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}] - [\mathrm{B}]_{\text{eq},2} = \left([\mathrm{B}]_{\text{eq},1} - [\mathrm{B}]_{\text{eq},2}\right)\,e^{-(k_1+k_{-1})t} \tag{2.2.46}$$

which can also be expressed as

$$\Delta\,[\mathrm{B}] = \Delta[\mathrm{B}]_0 e^{-(k_1+k_{-1})t} = \Delta[\mathrm{B}]_0 e^{-t/\tau} \tag{2.2.47}$$

where $\Delta\,[\mathrm{B}]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta\,[\mathrm{B}]\,/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-\,(k_1 + k_{-1})$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

2.2.1: Collision theory, transition state theory, and the prediction of rate laws and rate constants

Rate Law and Collision Theory

Consider the reaction

$$\mathrm{A}+\mathrm{B}\longrightarrow \mathrm{C} \tag{2.2.1.1}$$

In the last class, we regarded the rate law

$$r=k\,[\mathrm{A}]\,[\mathrm{B}] \tag{2.2.1.2}$$

as empirical. As it happens, we can actually derive this using the collision theory discussed in Lecture 6. Recall, from lecture 6, that the collision rate between two atoms or molecules in a system is

$$\gamma=\rho\sigma\,\langle|\mathbf{v}|\rangle \tag{2.2.1.3}$$

where ρ is the number density, σ is the collision cross section, and $\langle|\mathbf{v}|\rangle$ is the relative velocity between the two atoms or molecules. Now, if the two colliding atoms or molecules are different, and we are interested in the rate of collisions of atoms/molecules of type A with those of type B, then the collision rate must be written as

$$\gamma_{\mathrm{AB}}=\sigma_{\mathrm{AB}}\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{B}} \tag{2.2.1.4}$$

Here ρ_{B} is the density of atoms/molecules of type B, $|\mathbf{v}_{\mathrm{AB}}|=|\mathbf{v}_{\mathrm{B}}-\mathbf{v}_{\mathrm{A}}|$ is the relative speed between A and B, and σ_{AB} is the cross section between A and B, which, is given the average of arithmetic and geometric averages:

$$\sigma_{\mathrm{AB}}=\frac{1}{2}\left[\left(\frac{\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}}{2}\right)+\sqrt{\sigma_{\mathrm{A}}\sigma_{\mathrm{B}}}\right] \tag{2.2.1.5}$$

From the Maxwell-Boltzmann distribution,

$$\langle|\mathbf{v}_{\mathrm{AB}}|\rangle=\sqrt{\frac{8k_BT}{\pi\mu}} \tag{2.2.1.6}$$

where the reduced mass

$$\mu=\frac{m_{\mathrm{A}}m_{\mathrm{B}}}{m_{\mathrm{A}}+m_{\mathrm{B}}} \tag{2.2.1.7}$$

The collision rate γ_{AB} is the rate for the collision of one atom/molecule of A. If there are N_{A} atoms/molecules of A, then the total collision rate for A with B is

$$\gamma_{\mathrm{tot}}=N_{\mathrm{A}}\gamma_{\mathrm{AB}}=N_{\mathrm{A}}\sigma_{\mathrm{AB}}\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{B}} \tag{2.2.1.8}$$

However, the number density of A is $\rho_{\mathrm{A}}=N_{\mathrm{A}}/V$, so we can write the total collision rate as

$$\gamma_{\mathrm{tot}}=\sigma_{\mathrm{AB}}V\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{A}}\rho_{\mathrm{B}} \tag{2.2.1.9}$$

In a time interval dt, the number of collisions dN_{coll} is

$$dN_{\mathrm{coll}}=\gamma_{\mathrm{tot}}dt=\sigma_{\mathrm{AB}}V\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{A}}\rho_{\mathrm{B}}dt \tag{2.2.1.10}$$

Let P_{rxn} denote the probability that a collision between A and B leads to product C. The rate of decrease of N_{A} must then be

$$dN_{\mathrm{A}}=-P_{\mathrm{rxn}}dN_{\mathrm{coll}}=-\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}V\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{A}}\rho_{\mathrm{B}}dt \tag{2.2.1.11}$$

so that

$$\frac{dN_{\mathrm{A}}}{dt}=-\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}V\,\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\,\rho_{\mathrm{A}}\rho_{\mathrm{B}} \tag{2.2.1.12}$$

Note that the rate is

$$r=-\frac{d[\mathrm{A}]}{dt} \tag{2.2.1.13}$$

However, $[\mathrm{A}]$ is in units of moles/liter. The ratio $N_{\mathrm{A}}/(N_0V)$, where N_0 is Avogadro's number, has the proper units of moles/liter, if V is in liters. Thus,

$$\begin{aligned}\frac{d[\mathrm{A}]}{dt}&=\frac{d(N_{\mathrm{A}}/(N_0V))}{dt} && (2.2.1.14)\\ &=-\frac{1}{N_0V}\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}V\langle|\mathrm{v}_{\mathrm{AB}}|\rangle\rho_{\mathrm{A}}\rho_{\mathrm{B}} && (2.2.1.15)\\ &=-\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}N_0^{-1}\langle|\mathbf{v}_{\mathrm{AB}}|\rangle\rho_{\mathrm{A}}\rho_{\mathrm{B}} && (2.2.1.16)\end{aligned}$$

Since ρ_{A} has units of (molecules of A/liters), we can write $\rho_{\mathrm{A}}=N_0[\mathrm{A}]$, and similarly, $\rho_{\mathrm{B}}=N_0[\mathrm{B}]$. This gives

$$\frac{d[\mathrm{A}]}{dt}=-\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}N_0\langle|\mathbf{v}_{\mathrm{AB}}|\rangle[\mathrm{A}][\mathrm{B}]=-k[\mathrm{A}][\mathrm{B}] \tag{2.2.1.17}$$

where the rate constant is

$$k=\sigma_{\mathrm{AB}}P_{\mathrm{rxn}}N_0\langle|\mathbf{v}_{\mathrm{AB}}|\rangle \tag{2.2.1.18}$$

To determine the reaction probability P_{rxn}, consider the energy profile for the reaction in Figure 2.2.1.1 In the gas phase, the activation "energy", denote E_a in the figure is the potential energy at the top of the hill, which we denote as $\mathcal{E}^{\ddagger}$. If the reaction takes place in a condensed phase, such as in solution, then the activation "energy" is the free energy $\Delta G^{\ddagger}$.

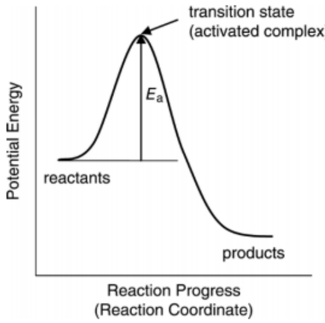

Figure 2.2.1.1: Illustration of a reaction energy profile.

If A and B are atoms, then P_{rxn} is the probability that the energy E_{AB} between A and B must be larger than this energy E_a in order for the collision to yield product C. If A and B are molecules, then A and B must also have the right orientation in addition to a sufficiently high energy. The probability that they have the right orientation is a fraction $f<1$, which we call the steric factor. When A and B are atoms, $f=1$. Generally, we can write

$$P_{\mathrm{rxn}}=fP(E_{\mathrm{AB}}>E_a) \tag{2.2.1.19}$$

The general probability distribution $p(E_{\mathrm{AB}})$ is just given by the Boltzmann distribution

$$p(E_{\mathrm{AB}})Ce^{-\beta E_{\mathrm{AB}}} \tag{2.2.1.20}$$

where C is a normalization constant. The normalization condition is

$$\int_0^\infty p(E_{\mathrm{AB}})\,dE_{\mathrm{AB}}=C\int_0^\infty e^{-\beta E_{\mathrm{AB}}}=-\frac{C}{\beta}e^{-\beta E_{\mathrm{AB}}}\Big|_0^\infty=1 \tag{2.2.1.21}$$

which gives $C=\beta=1/(k_BT)$. Thus,

$$p(E_{\mathrm{AB}})=\beta e^{-\beta E_{\mathrm{AB}}} \tag{2.2.1.22}$$

Now, the probability $P(E_{\mathrm{AB}}>E_a)$ that $E_{\mathrm{AB}}>E_a$ is

$$P(E_{\mathrm{AB}}>E_a)=\beta\int_{E_a}^\infty e^{-\beta E_{\mathrm{AB}}}\,dE_{\mathrm{AB}}=e^{-\beta E_a} \tag{2.2.1.23}$$

which gives the rate constant as

$$k = \sigma_{\mathrm{AB}} N_0 f e^{-\beta E_a} \langle |\mathbf{v}_{\mathrm{AB}}| \rangle = \sigma_{\mathrm{AB}} N_0 f e^{-\beta E_a} \left(\frac{8}{\beta \pi \mu} \right)^{1/2} \tag{2.2.1.24}$$

We see, generally, that

$$k = \mathrm{A} e^{-\beta E_a} \tag{2.2.1.25}$$

where E_a is the activation potential $\mathcal{E}^{\ddagger}$ in the gas phase and the activation free energy $\Delta G^{\ddagger}$ in condensed phases. This is known as the *Arrhenius law*.

Note that if we plot $\ln k$ vs. $1/T$, which is given by

$$\ln k = \ln \mathrm{A} - \frac{E_a}{k_B T} \tag{2.2.1.26}$$

the plot will be a line with slope $-E_a/k_B$. Such a plot is called an Arrhenius plot. Note, moreover, that if A and B are the same atom or molecule type, then the rate law we derived, would take the form of a second-order rate law

$$\frac{d\,[\mathrm{A}]}{dt} = -k[\mathrm{A}]^2 \tag{2.2.1.27}$$

Transition State Theory

In Figure $2.2.1.1$, the point at which we evaluate or measure E_a serves as a dividing line (also called a *dividing surface*) between reactants and products. At this point, we do not have $\mathrm{A}+\mathrm{B}$, and we do not have C. Rather, what we have is an activated complex of some kind called a *transition state* between reactants and products. The value of the reaction coordinate at the transition state is denoted $q^{\ddagger}$. Recall our notation x for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(\mathrm{x})$ of all of the coordinates and momenta, although typically, $q(\mathrm{x})$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms A and B undergoing a collision. An appropriate reaction coordinate could simply be the distance r between A and B. This distance is a function of the positions $\mathbf{r}_{\mathrm{A}}$ and $\mathbf{r}_{\mathrm{B}}$ of the two atoms, in that

$$q = r = |\mathbf{r}_{\mathrm{A}} - \mathbf{r}_{\mathrm{B}}| \tag{2.2.1.28}$$

When A and B are molecules, such as proteins, $q(\mathrm{x})$ is a much more complicated function of x.

Now, recall that the mechanical energy $\mathcal{E}(\mathrm{x})$ is given by

$$\mathcal{E}(\mathrm{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_1} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.2.1.29}$$

and is a sum of kinetic and potential energies. Transition state theory assumes the following:

1. We start a trajectory obeying this equation of motion with an initial condition x that makes $q(\mathrm{x}) = q^{\ddagger}$ and such that $\dot{q}(\mathrm{x}) > 0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
2. We follow the motion x_t of the coordinates and momenta in time starting from this initial condition x, which gives us a unique function $\mathrm{x}_t(\mathrm{x})$.
3. If $q(\mathrm{x}_t(\mathrm{x})) > q^{\ddagger}$ at time t, then the trajectory is designated as “reactive” and contributes to the reaction rate.

Define a function $\theta(y)$, which is 1 if $y \geq 0$ and 0 if $y < 0$. The function $\theta(y)$ is known as a *step function*.

We now define a *flux* of reactive trajectories $k(t)$ using statistical mechanics

$$k(t) = \frac{1}{hQ_r} \int_{q(\mathrm{x})=q^{\ddagger}} d\mathrm{x}\, e^{-\beta \mathcal{E}(\mathrm{x})} |\dot{q}(\mathrm{x})|\, \theta\left(q(\mathrm{x}_t(\mathrm{x})) - q^{\ddagger}\right) \tag{2.2.1.30}$$

where h is Planck’s constant. Here Q_r is the partition function of the reactants

$$Q_r = \int d\mathrm{x}\, e^{-\beta \mathcal{E}(\mathrm{x})} \theta\left(q^{\ddagger} - q(\mathrm{x})\right) \tag{2.2.1.31}$$

The meaning of Equation 2.2.1.30 is an ensemble average over a canonical ensemble of the product $|\dot{q}(\mathrm{x})|$ and $\theta\left(q(\mathrm{x}_t(\mathrm{x})) - q^{\ddagger}\right)$. The first factor in this product $|\dot{q}(\mathrm{x})|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q\left(\mathrm{x}_t\left(\mathrm{x}\right)\right)-q^\ddagger\right)$ requires that the trajectory of $q\left(\mathrm{x}_t\left(\mathrm{x}\right)\right)$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k\left(t\right)$ in Equation 2.2.1.30 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^\ddagger-q\left(\mathrm{x}\right)\right)$ measures the total number of microscopic states on the reactive side of the energy profile.

A plot of some examples of reactive flux functions $k\left(t\right)$ is shown in Figure $2.2.1.2$ These functions are discussed in greater detail in *J. Chem. Phys.* **95**, 5809 (1991). These examples all show that $k\left(t\right)$ decays at first but then finally reaches a plateau value. This plateau value is taken to be the true rate of the reaction under the assumption that eventually, all trajectories that will become reactive will have done so after a sufficiently long time. Thus,

$$k=\lim_{t\to\infty}k\left(t\right) \tag{2.2.1.32}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k\left(0\right)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})}=k\left(0\right) \tag{2.2.1.33}$$

$$=\frac{1}{Q_r}\int_{q(\mathrm{x})=q^\ddagger}d\mathrm{x}\,e^{-\beta\mathcal{E}(\mathrm{x})}\left|\dot{q}\left(\mathrm{x}\right)\right|\theta\left(q\left(\mathrm{x}\right)-q^\ddagger\right) \tag{2.2.1.34}$$

However, note that since we require $\dot{q}\left(\mathrm{x}\right)$ to initially be toward products, then by definition, at $t=0$, $q\left(\mathrm{x}\right)\geq q^\ddagger$, and the step function in the above expression is redundant. In addition, if $\dot{q}\left(\mathrm{x}\right)$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q\left(\mathrm{x}\right)$ is not curvilinear (and is true for some curvilinear coordinates $q\left(\mathrm{x}\right)$), and if $q\left(\mathrm{x}\right)$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})}=\frac{1}{hQ_r}\int d\mathrm{x}_{\mathbf{p}}e^{-\beta\sum_{i=1}^{N}\mathbf{p}_i^2/2m_i}\left|\dot{q}\left(\mathbf{p}_1,\ldots,\mathbf{p}_N\right)\right|\int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger}d\mathrm{x}_{\mathbf{r}}e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{2.2.1.35}$$

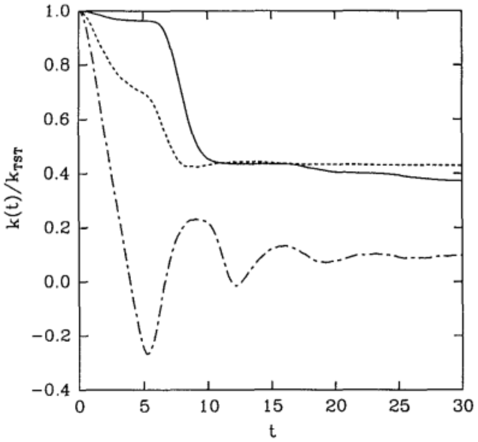

Figure 2.2.1.2: Examples of the reactive flux $k\left(t\right)$.

The integral

$$Z^\ddagger=\int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger}d\mathrm{x}_{\mathbf{r}}e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{2.2.1.36}$$

counts the number of microscopic states consistent with the condition $q\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)=q^\ddagger$ and is, therefore, a kind of partition function, and is denoted $Q^\ddagger$. On the other hand, because it is a partition function, we can derive a free energy $\Delta F^\ddagger$ from it

$$F^\ddagger\propto-k_BT\ln Z^\ddagger \tag{2.2.1.37}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r=Q_r^{(\mathrm{ideal})}Z_r \tag{2.2.1.38}$$

then we can take

$$Z_r=e^{-\beta F_r} \tag{2.2.1.39}$$

where F_r is the free energy of the reactants. Finally, setting $\dot{q} = p/\mu$, where μ is the associated mass, and p is the corresponding momentum of the reaction coordinate, then, canceling most of the momentum integrals between the numerator and $Q_r^{(\text{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{2.2.1.40}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\text{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{2.2.1.41}$$

Figure $2.2.1.2$ actually shows $k(t)/k^{(\text{TST})}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(\text{TST})}$. Hence, $k^{(\text{TST})}$ is always an upper bound to the true rate constant. Transition state theory assumes that any trajectory that initially moves toward products will be a reactive trajectory. For this reason, it overestimates the reaction rate. In reality, trajectories can cross the dividing surface several or many times before eventually proceeding either toward products *or* back toward reactants.

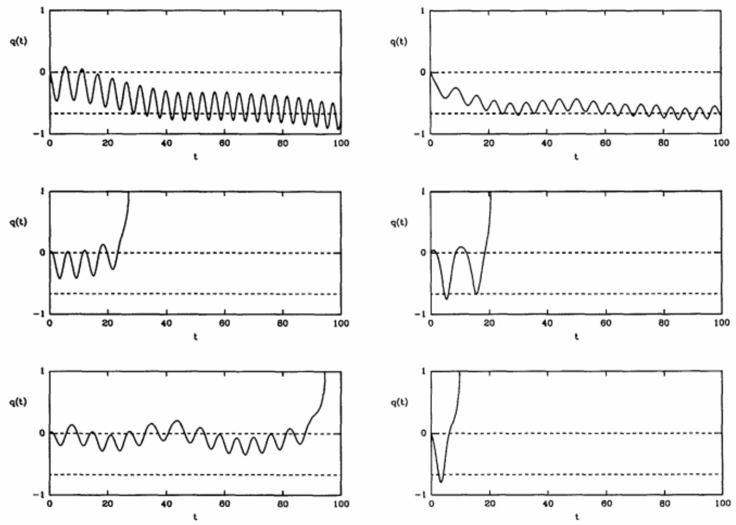

Figure $2.2.1.3$: Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

Figure $2.2.1.3$ shows that one can obtain trajectories of both types. Here, the dividing surface lies at $q = 0$. Left, toward $q = -1$ is the reactant side, and right, toward $q = 1$ is the product side. Because some trajectories return to reactants and never become products, the true rate is always less than $k^{(\text{TST})}$, and we can write

$$k = \kappa k^{(\text{TST})} \tag{2.2.1.42}$$

where the factor $\kappa < 1$ is known as the *transmission factor*. This factor accounts for multiple recrossings of the dividing surface and the fact that some trajectories do not become reactive ones.

2.2.2: Complex reaction mechanisms

A major goal in chemical kinetics is to determine the sequence of elementary reactions, or the reaction mechanism, that comprise complex reactions. For example, Sherwood Rowland and Mario Molina won the Nobel Prize in Chemistry in 1995 for proposing the elementary reactions involving chlorine radicals that contribute to the overall reaction of $O_3 \rightarrow O_2$ in the troposphere. In the following sections, we will derive rate laws for complex reaction mechanisms, including reversible, parallel and consecutive reactions.

Parallel Reactions

Consider the reaction in which chemical species A undergoes one of two irreversible first order reactions to form either species B or species C :

$$\mathrm{A} \stackrel{k_1}{\rightarrow} \mathrm{B} \tag{2.2.2.1}$$

$$\mathrm{A} \stackrel{k_2}{\rightarrow} \mathrm{C} \tag{2.2.2.2}$$

The overall reaction rate for the consumption of A can be written as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_2[\mathrm{A}] = -(k_1 + k_2)[\mathrm{A}] \tag{2.2.2.3}$$

Integrating $[\mathrm{A}]$ with respect to t, we obtain the following equation:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{2.2.2.4}$$

Plugging this expression into the equation for $\frac{d[\mathrm{B}]}{dt}$, we obtain:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{2.2.2.5}$$

Integrating $[\mathrm{B}]$ with respect to t, we obtain:

$$[\mathrm{B}] = -\frac{k_1[\mathrm{A}]_0}{k_1+k_2}\left(e^{-(k_1+k_2)t}\right) + c_1 \tag{2.2.2.6}$$

At $t = 0$, $[\mathrm{B}] = 0$. Therefore,

$$c_1 = \frac{k_1[\mathrm{A}]_0}{k_1+k_2} \tag{2.2.2.7}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{2.2.2.8}$$

Likewise,

$$[\mathrm{C}] = \frac{k_2[\mathrm{A}]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{2.2.2.9}$$

The ratio of $[\mathrm{B}]$ to $[\mathrm{C}]$ is simply:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2} \tag{2.2.2.10}$$

An important parallel reaction in industry occurs in the production of ethylene oxide, a reagent in many chemical processes and also a major component in explosives. Ethylene oxide is formed through the partial oxidation of ethylene:

$$2\ C_2H_4 + O_2 \xrightarrow{k_1} 2\ C_2H_4O \tag{2.2.2.11}$$

However, ethylene can also undergo a combustion reaction:

$$C_2H_4 + 3\ O_2 \xrightarrow{k_2} 2\ CO_2 + 2\ H_2O \tag{2.2.2.12}$$

To select for the first reaction, the oxidation of ethylene takes place in the presence of a silver catalyst, which significantly increases k_1 compared to k_2. Figure $2.2.2.1$ displays the concentration profiles for species A, B, and C in a parallel reaction in which $k_1 > k_2$.

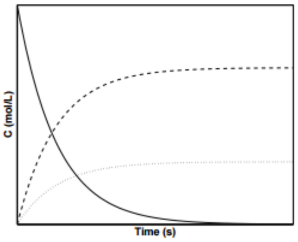

Figure $2.2.2.1$: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{B}]$ (dashed line) and $[\mathrm{C}]$ (dotted line) over time for a parallel reaction.

Consecutive Reactions

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, I, which then reacts to form the product, P:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{2.2.2.13}$$

We can write the reaction rates of species A, I and P as follows:

$$\frac{d\,[\mathrm{A}]}{dt} = -k_1\,[\mathrm{A}] \tag{2.2.2.14}$$

$$\frac{d\,[\mathrm{I}]}{dt} = k_1\,[\mathrm{A}] - k_2\,[\mathrm{I}] \tag{2.2.2.15}$$

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{I}] \tag{2.2.2.16}$$

As before, integrating $[\mathrm{A}]$ with respect to t leads to:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{2.2.2.17}$$

The concentration of species I can be written as

$$[\mathrm{I}] = \frac{k_1\,[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{2.2.2.18}$$

Then, solving for $[\mathrm{P}]$, we find that:

$$[\mathrm{P}] = [\mathrm{A}]_0 \left[1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right] \tag{2.2.2.19}$$

Figure $2.2.2.2$ displays the concentration profiles for species A, I, and P in a consecutive reaction in which $k_1 = k_2$. As can be seen from the figure, the concentration of species I reaches a maximum at some time, $t_{\max}$. Oftentimes, species I is the desired product. Returning to the oxidation of ethylene into ethylene oxide, it is important to note another reaction in which ethylene oxide can decompose into carbon dioxide and water through the following reaction

$$C_2H_4O + \frac{5}{2}\,O_2 \xrightarrow{k_3} 2\,CO_2 + 2\,H_2O \tag{2.2.2.20}$$

Thus, to maximize the concentration of ethylene oxide, the oxidation of ethylene is only allowed proceed to partial completion before the reaction is stopped.

Finally, in the limiting case when $k_2 \gg k_1$, we can write the concentration of P as

$$[\mathrm{P}] \approx [\mathrm{A}]_0 \left\{1 + \frac{1}{-k_2} k_2 e^{-k_1 t}\right\} = [\mathrm{A}]_0 \left(1 - e^{-k_1 t}\right) \tag{2.2.2.21}$$

Thus, when $k_2 \gg k_1$, the reaction can be approximated as $\mathrm{A} \rightarrow \mathrm{P}$ and the apparent rate law follows 1^{st} order kinetics.

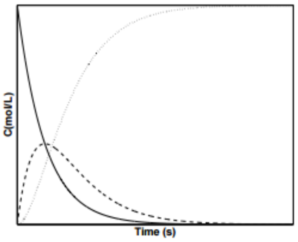

Figure 2.2.2.2: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for consecutive first order reactions.

Consecutive Reactions With an Equilibrium

Consider the reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{2.2.2.22}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{2.2.2.23}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{2.2.2.24}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{2.2.2.25}$$

The exact solutions of these is straightforward, in principle, but rather involved, so we will just state the exact solutions, which are

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\lambda}\left[(\lambda - k_1 + K)e^{-(k_1+K-\lambda)t/2} + (\lambda + k_1 - K)e^{-(k_1+K+\lambda)t/2}\right] \tag{2.2.2.26}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\lambda}\left[e^{-(k_1+K-\lambda)t/2} - e^{-(k_1+K+\lambda)t/2}\right] \tag{2.2.2.27}$$

$$[\mathrm{P}](t) = 2k_1k_2[\mathrm{A}]_0\left[\frac{2}{(k_1+K)^2 - \lambda^2} - \frac{1}{\lambda}\left(\frac{e^{-(k_1+K-\lambda)t/2}}{k_1+K-\lambda} - \frac{e^{-(k_1+K+\lambda)t/2}}{k_1+K+\lambda}\right)\right] \tag{2.2.2.28}$$

where

$$K = k_2 + k_{-1} \tag{2.2.2.29}$$

$$\lambda = \sqrt{(k_1 - K)^2 - 4k_1k_{-1}} \tag{2.2.2.30}$$

Steady-State Approximations

Consider the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{2.2.2.31}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{2.2.2.32}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{2.2.2.33}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{2.2.2.34}$$

These equations can be solved explicitly in terms of $[\mathrm{A}]$, $[\mathrm{I}]$, and $[\mathrm{P}]$, but the math becomes very complicated quickly. If, however, $k_2 + k_{-1} \gg k_1$ (in other words, the rate of consumption of I is much faster than the rate of production of I), we can make the approximation that the concentration of the intermediate species, I, is small and constant with time:

$$\frac{d[\mathrm{I}]}{dt} \approx 0 \tag{2.2.2.35}$$

Equation 21.22 can now be written as

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}]_{ss} - k_2[\mathrm{I}]_{ss} \approx 0 \tag{2.2.2.36}$$

where $[\mathrm{I}]_{ss}$ is a constant represents the steady state concentration of intermediate species, $[\mathrm{I}]$. Solving for $[\mathrm{I}]_{ss}$,

$$[\mathrm{I}]_{ss} = \frac{k_1}{k_{-1}+k_2}[\mathrm{A}] \tag{2.2.2.37}$$

We can then write the rate equation for species A as

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}]_{ss} = -k_1[\mathrm{A}] + k_{-1}\frac{k_1}{k_{-1}+k_2}[\mathrm{A}] = -\frac{k_1k_2}{k_{-1}+k_2}[\mathrm{A}] \tag{2.2.2.38}$$

Integrating,

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-\frac{k_1k_2}{k_{-1}+k_2}t} \tag{2.2.2.39}$$

Equation 21.28 is the same equation we would obtain for apparent 1^{st} order kinetics of the following reaction:

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{2.2.2.40}$$

where

$$k' = \frac{k_1k_2}{k_{-1}+k_2} \tag{2.2.2.41}$$

Figure $2.2.2.3$ displays the concentration profiles for species, A, I, and P with the condition that $k_2 + k_{-1} \gg k_1$. These types of reaction kinetics appear when the intermediate species, I, is highly reactive.

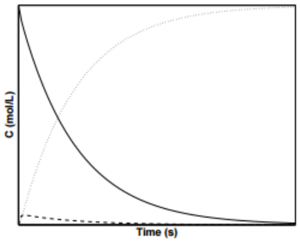

Figure $2.2.2.3$: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 + k_{-1} \gg k_1$.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN \tag{2.2.2.42}$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{2.2.2.43}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{2.2.2.44}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{2.2.2.45}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d\left[\mathrm{A}^*\right]}{dt} = k_1 [\mathrm{A}][\mathrm{M}] - k_{-1}\left[\mathrm{A}^*\right]_{ss}[\mathrm{M}] - k_2\left[\mathrm{A}^*\right]_{ss} \approx 0 \tag{2.2.2.46}$$

Solving for $\left[\mathrm{A}^*\right]$,

$$\left[\mathrm{A}^*\right] = \frac{k_1 [\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{2.2.2.47}$$

The reaction rates of species A and B can be written as

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_2\left[\mathrm{A}^*\right] = \frac{k_1 k_2 [\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{2.2.2.48}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2 [\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{2.2.2.49}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\mathrm{M}] \gg k_2$. Equation 21.33 then becomes

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{2.2.2.50}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\mathrm{M}] \ll k_2$. In this scenario, equation 21.33 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1 [\mathrm{A}][\mathrm{M}] \tag{2.2.2.51}$$

which follows second order rate kinetics, consistent with experimental observations.

Equilibrium Approximations

Consider again the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{2.2.2.52}$$

Now let us consider the situation in which $k_2 \ll k_1$ and k_{-1}. In other words, the conversion of I to P is slow and is the *rate-limiting step*. In this situation, we can assume that $[\mathrm{A}]$ and $[\mathrm{I}]$ are in equilibrium with each other. As we derived before for a reversible reaction in equilibrium,

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \approx \frac{[\mathrm{I}]}{[\mathrm{A}]} \tag{2.2.2.53}$$

or, in terms of $[\mathrm{I}]$,

$$[\mathrm{I}] = K_{\mathrm{eq}}[\mathrm{A}] \tag{2.2.2.54}$$

These conditions also result from the exact solution when we set $k_2 \approx 0$. When this is done, we have the approximate expressions from the exact solution:

$$K \approx k_{-1} \tag{2.2.2.55}$$

$$\lambda \approx \sqrt{\left(k_1 - k_{-1}\right)^2 + 4k_1 k_{-1}} = \sqrt{k_1^2 + 2k_1 k_{-1} + k_{-1}^2} = k_1 + k_{-1} \tag{2.2.2.56}$$

$$\lambda - k_1 + K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{2.2.2.57}$$

$$\lambda + k_1 - K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{2.2.2.58}$$

$$k_1 + K - \lambda \approx k_1 + k_{-1} - k_1 - k_{-1} = 0 \tag{2.2.2.59}$$

$$k_1 + K + \lambda \approx k_1 + k_{-1} + k_1 + k_{-1} = 2\left(k_1 + k_{-1}\right) \tag{2.2.2.60}$$

and the approximate solutions become

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\left(k_1 + k_{-1}\right)}\left[2k_{-1} + 2k_1 e^{-(k_1 + k_{-1})t}\right] \tag{2.2.2.61}$$

$$[\mathrm{I}](t) = \frac{k_1 [\mathrm{A}]_0}{\left(k_1 + k_{-1}\right)}\left[1 - e^{-(k_1 + k_{-1})t}\right] \tag{2.2.2.62}$$

In the long-time limit, when equilibrium is reached and transient behavior has decayed away, we find

$$\frac{[\mathrm{I}]}{[\mathrm{A}]} \equiv K_{\mathrm{eq}} \to \frac{k_1}{k_{-1}} \tag{2.2.2.63}$$

Plugging the above equation into the expression for $d[\mathrm{P}]/dt$,

$$\frac{d[\mathrm{P}]}{dt} = k_2 [\mathrm{I}] = k_2 K_{\mathrm{eq}} [\mathrm{A}] = \frac{k_1 k_2}{k_{-1}} [\mathrm{A}] \tag{2.2.2.64}$$

The reaction can thus be approximated as a 1^{st} order reaction

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{2.2.2.65}$$

with

$$k' = \frac{k_1 k_2}{k_{-1}} \tag{2.2.2.66}$$

Figure 2.2.2.4 displays the concentration profiles for species, A, I, and P with the condition that $k_2 \ll k_1 = k_{-1}$. When $k_1 = k_{-1}$, we expect $[\mathrm{A}] = [\mathrm{I}]$. As can be seen from the figure, after a short initial startup time, the concentrations of species A and I are approximately equal during the reaction.

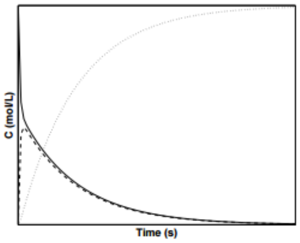

Figure 2.2.2.4: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 \ll k_1 = k_{-1}$.

2.2.3: Kinetics of catalysis

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst. *Homogeneous catalysis* refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure $2.2.3.1$shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

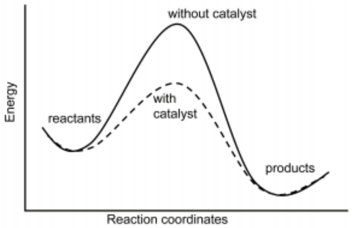

Figure $2.2.3.1$: Comparison of energy profiles with and without catalyst present.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P} \tag{2.2.3.1}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{2.2.3.2}$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A}+\mathrm{C} \xrightarrow{k_{\text{cat}}} \mathrm{P}+\mathrm{C} \tag{2.2.3.3}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{\text{cat}}[\mathrm{A}][\mathrm{C}] \tag{2.2.3.4}$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{\text{cat}} \gg k$), the first term can often be ignored.

Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}] \tag{2.2.3.5}$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S}+\mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^{+}+\mathrm{A}^{-} \tag{2.2.3.6}$$

$$\mathrm{S}H^{+}+H_2O \overset{k_2}{\rightarrow} \mathrm{P}+H_3O^{+} \tag{2.2.3.7}$$

$$H_3O^{+}+\mathrm{A}^{-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H+H_2O \tag{2.2.3.8}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt}=-k_1[\mathrm{S}][\mathrm{A}H]+k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right] \tag{2.2.3.9}$$

$$\frac{d[\mathrm{A}H]}{dt}=-k_1[\mathrm{S}][\mathrm{A}H]+k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right]-k_{-3}[\mathrm{A}H]+k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right] \tag{2.2.3.10}$$

$$\frac{d\left[\mathrm{S}H^+\right]}{dt}=k_1[\mathrm{S}][\mathrm{A}H]-k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right]-k_2\left[SH^+\right] \tag{2.2.3.11}$$

$$\frac{d\left[\mathrm{A}^-\right]}{dt}=k_1[\mathrm{S}][\mathrm{A}H]-k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right]-k_2\left[\mathrm{A}^-\right]\left[H_3O^+\right]+k_{-3}[\mathrm{A}H] \tag{2.2.3.12}$$

$$\frac{d[\mathrm{P}]}{dt}=k_2\left[SH^+\right] \tag{2.2.3.13}$$

$$\frac{d\left[H_3O^+\right]}{dt}=-k_2\left[SH^+\right]-k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right]+k_{-3}[\mathrm{A}H] \tag{2.2.3.14}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$ and $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d\left[\mathrm{S}H^+\right]}{dt}=k_1[\mathrm{S}][\mathrm{A}H]-k_{-1}\left[\mathrm{A}^-\right]\left[\mathrm{S}H^+\right]-k_2\left[SH^+\right]=0 \tag{2.2.3.15}$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$\left[SH^+\right]=\frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right]+k_2} \tag{2.2.3.16}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt}=k_2\left[SH^+\right]=\frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right]+k_2} \tag{2.2.3.17}$$

In the case where $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$, Equation 2.2.3.17can be written as

$$\frac{d[\mathrm{P}]}{dt}=k_1[\mathrm{S}][\mathrm{A}H] \tag{2.2.3.18}$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt}=\frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right]}=\frac{k_1k_2}{k_{-1}K}[\mathrm{S}]\left[H^+\right] \tag{2.2.3.19}$$

where K is the acid dissociation constant:

$$K=\frac{\left[\mathrm{A}^-\right]\left[H^+\right]}{[\mathrm{A}H]} \tag{2.2.3.20}$$

In this case, the reaction is hydrogen ion-catalyzed.

Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}(g)+\mathrm{S}(s)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{AS}(s) \tag{2.2.3.21}$$

$$\mathrm{AS}(s)\xrightarrow{k_2}\mathrm{P}(g)+\mathrm{S}(g) \tag{2.2.3.22}$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d[\mathrm{AS}]}{dt}=k_1[\mathrm{A}][\mathrm{S}]-k_{-1}[\mathrm{AS}]_{ss}-k_2[\mathrm{AS}]_{ss}=0 \tag{2.2.3.23}$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}]=\theta[\mathrm{S}]_0 \tag{2.2.3.24}$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}]=(1-\theta)[\mathrm{S}]_0 \tag{2.2.3.25}$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 2.2.3.23as

$$k_1[\mathrm{A}](1-\theta)[\mathrm{S}]_0-(k_{-1}+k_2)\theta[\mathrm{S}]_0=0 \tag{2.2.3.26}$$

Rearranging the above equation in terms of θ yields

$$\theta=\frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}]+k_{-1}+k_2} \tag{2.2.3.27}$$

The rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt}=k_2[\mathrm{AS}]_{ss}=k_2\theta[\mathrm{S}]_0=\frac{k_1k_2}{k_1[\mathrm{A}]+k_{-1}+k_2}[\mathrm{A}][\mathrm{S}]_0 \tag{2.2.3.28}$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

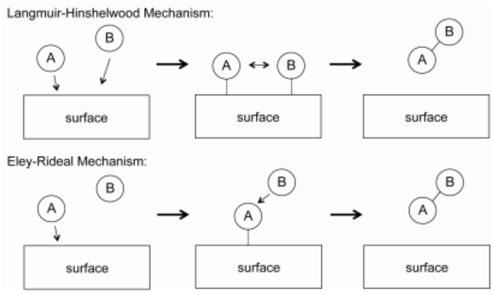

Figure 2.2.3.2: Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure $2.2.3.2$ In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}(g)+\mathrm{S}(s)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{AS}(s) \tag{2.2.3.29}$$

$$\mathrm{B}(g)+\mathrm{S}(s)\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\mathrm{BS}(s) \tag{2.2.3.30}$$

$$\mathrm{AS}(s)+\mathrm{BS}(s)\xrightarrow{k_3}\mathrm{P} \tag{2.2.3.31}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure $2.2.3.3$ In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}(g)+\mathrm{S}(s)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{AS}(s) \tag{2.2.3.32}$$

$$\mathrm{AS}\,(s)+\mathrm{B}\,(g)\xrightarrow{k_2}\mathrm{P}\,(g)+\mathrm{S}\,(s) \tag{2.2.3.33}$$

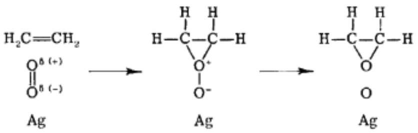

Figure 2.2.3.3: Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, *1]*

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species AS:

$$\frac{d\,[\mathrm{AS}]}{dt}=0=k_1\,[\mathrm{A}]\,[\mathrm{S}]-k_{-1}\,[\mathrm{AS}]_{ss}-k_2\,[\mathrm{AS}]_{ss}\,[\mathrm{B}] \tag{2.2.3.34}$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of AS and S in terms of a fraction of the total number of active sites, S_0 and rewrite the above equation as

$$0=k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0-k_{-1}\,[\mathrm{S}]_0-k_2\theta[\mathrm{S}]_0\,[\mathrm{B}] \tag{2.2.3.35}$$

Solving for θ yields

$$\theta=\frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}]+k_{-1}+k_2\,[\mathrm{B}]} \tag{2.2.3.36}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta=\frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}]+k_{-1}} \tag{2.2.3.37}$$

The rate of production of P can be expressed as

$$\frac{d\,[\mathrm{P}]}{dt}=k_2\,[\mathrm{AS}]_{ss}\,[\mathrm{B}]=k_2\theta[\mathrm{S}]_0\,[\mathrm{B}]=\frac{k_1k_2\,[\mathrm{A}]}{k_1\,[\mathrm{A}]+k_{-1}}\,[\mathrm{S}]_0\,[\mathrm{B}] \tag{2.2.3.38}$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal tok_1/k_{-1}

$$\frac{d\,[\mathrm{P}]}{dt}=Kk_2\,[\mathrm{B}]\,\frac{K\,[\mathrm{A}]}{K\,[\mathrm{A}]+1} \tag{2.2.3.39}$$

Michaelis-Menten Enzyme Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathrm{E}+\mathrm{S}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{ES}\xrightarrow{k_2}\mathrm{E}+\mathrm{P} \tag{2.2.3.40}$$

where E is the enzyme, ES is the enzyme-substrate complex, and P is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, \(\text{ES}|), is small and employ a steady-state approximation:

$$\frac{d\,[\mathrm{ES}]}{dt}=k_1\,[\mathrm{E}]\,[\mathrm{S}]-k_{-1}\,[\mathrm{ES}]_{ss}-k_2\,[\mathrm{ES}]_{ss}\approx 0 \tag{2.2.3.41}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0=[\mathrm{ES}]+[\mathrm{E}] \tag{2.2.3.42}$$

Plugging Equation 2.2.3.42into Equation 2.2.3.41, we obtain

$$0=k_1\left([\mathrm{E}]_0-[\mathrm{ES}]_{ss}\right)[\mathrm{S}]-k_{-1}[\mathrm{ES}]_{ss}+k_2[\mathrm{ES}]_{ss} \tag{2.2.3.43}$$

Solving for $[\mathrm{ES}]_{ss}$

$$[\mathrm{ES}]_{ss}=\frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}]+k_{-1}+k_2}=\frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}]+\dfrac{k_{-1}+k_2}{k_1}} \tag{2.2.3.44}$$

We can then write the reaction rate of the product as

$$\frac{d[\mathrm{P}]}{dt}=k_2[\mathrm{ES}]_{ss}=\frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}]+\dfrac{k_{-1}+k_2}{k_1}}=\frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}]+K_M} \tag{2.2.3.45}$$

where K_M is the Michaelis constant. Equation 2.2.3.45 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present $\left([\mathrm{S}] \gg K_M\right)$ Equation 2.2.3.45 reduces to

$$\frac{d[\mathrm{P}]}{dt}=r_{\max}=k_2[\mathrm{E}]_0 \tag{2.2.3.46}$$

which is a 0^{th} order reaction, since $[\mathrm{E}]_0$ is a constant. The value $k_2[\mathrm{E}]_0$ represents the maximum rate, $r_{\max}$, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 2.2.3.4 displays the dependence of the reaction rate on the substrate concentration, $[\mathrm{S}]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2[\mathrm{E}]_0$ at large values of $[\mathrm{S}]$.

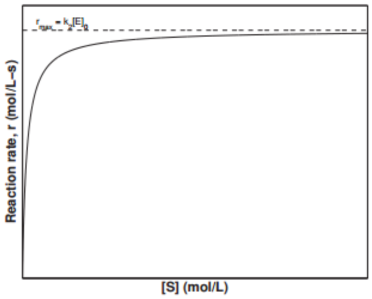

Figure 2.2.3.4: Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[\mathrm{S}]$. Rearranging Equation 2.2.3.45,

$$\frac{1}{r}=\frac{K_M+[\mathrm{S}]}{k_2[\mathrm{E}]_0[\mathrm{S}]}=\frac{K_M}{k_2[\mathrm{E}]_0}\frac{1}{[\mathrm{S}]}+\frac{1}{k_2[\mathrm{E}]_0} \tag{2.2.3.47}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2[\mathrm{E}]_0$ and y-intercept equal to $1/k_2[\mathrm{E}]_0$.

SECTION OVERVIEW

2.3: Chemical Kinetics II- Reaction Mechanisms

2.3.1: A Mechanism is a Sequence of Elementary Reactions

The mechanism of a reaction is a series of steps leading from the starting materials to the products. After each step, an intermediate is formed. The intermediate is short-lived, because it quickly undergoes another step to form the next intermediate. These simple steps are called elementary reactions. Because an overall reaction is composed of a series of elementary reaction, the overall rate of the reaction is somehow dependent on the rates of those smaller reactions. But how are the two related? Let's look at two cases. We'll keep it simple and both cases will be two-step reactions.

2.3.2: The Principle of Detailed Balance

The principle of **detailed balance** is formulated for kinetic systems which are decomposed into elementary processes (collisions, or steps, or elementary reactions): *At equilibrium, each elementary process should be equilibrated by its reverse process.* Lewis put forward this general principle in 1925:

> *Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.*[1]

According to Ter Haar, [2] the essence of the detailed balance is:

> *...at equilibrium the number of processes destroying situation A and creating situation B will be equal to the number of processes producing A and destroying B*

The principle of detailed balance was explicitly introduced for collisions by Ludwig Boltzmann. In 1872, he proved his H-theorem using this principle. The arguments in favor of this property are founded upon microscopic reversibility. In 1901, R. Wegscheider introduced the principle of detailed balance for chemical kinetics. In particular, he demonstrated that the irreversible cycles

$$A \rightarrow B \rightarrow C \ldots Y \rightarrow Z \tag{2.3.2.1}$$

are impossible and found explicitly the relations between kinetic constants that follow from the principle of detailed balance. This system is more accurately described thusly:

$$A \rightleftharpoons B \rightleftharpoons C \ldots Y \rightleftharpoons Z \tag{2.3.2.2}$$

2.3.3: Multiple Mechanisms are often Indistinguishable

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

2.3.4: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{2.3.4.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{2.3.4.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{2.3.4.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 2.3.4.1is proposed to be

$$A \xrightarrow{k_1} A^* \tag{2.3.4.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{2.3.4.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{2.3.4.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\,\cancel{[B]}}\right)\cancel{[B]} \tag{2.3.4.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

2.3.5: Rate Laws Do Not Imply Unique Mechanism

Because a proposed mechanism can only be valid if it is consistent with the rate law found experimentally, the rate law plays a central role in the investigation of chemical reaction mechanisms. The discussion above introduces the problems and methods associated with collecting rate data and with finding an empirical rate law that fits experimental concentration-*versus*-time data. We turn now to finding the rate laws that are consistent with a particular proposed mechanism. For simplicity, we consider reactions in closed constant-volume systems.

In principle, numerical integration can be used to predict the concentration at any time of each of the species in any proposed reaction mechanism. This prediction can be compared to experimental observations to see whether they are consistent with the proposed mechanism. To do the numerical integration, it is necessary to know the initial concentrations of all of the chemical species and to know, or assume, values of all of the rate constants. The initial concentrations are known from the procedure used to initiate the reaction. However, the rate constants must be determined by some iterative procedure in which initial estimates of the rate constants are used to predict concentration-*versus*-time data that can be compared to the experimental results to produce refined estimates.

In practice, we tailor our choice of reaction conditions so that we can use various approximations to test whether a proposed mechanism can explain the data. We now consider the most generally useful of these approximations.

In this discussion, we assume that the overall reaction goes to completion; that is, at equilibrium the concentration of the reactant whose concentration is limiting has become essentially zero. If the overall reaction involves more than one elementary step, then an intermediate compound is involved. A valid mechanism must include this intermediate, and more than one differential equation may be needed to characterize the time rate of change of all of the species involved in the reaction. We focus on conditions and approximations under which the rate of appearance of the final products in a multi-step reaction mechanism can be described by a single differential equation, the rate law.

We examine the application of these approximations to a particular reaction mechanism. When we understand the application of these approximations to this mechanism, the ways in which they can be used in other situations are clear.

Consider the following sequence of elementary steps

$$\mathrm{A}+\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\begin{aligned}\frac{d[A]}{dt}=\frac{d[B]}{dt}&=-k_1[A][B]+k_2\,[C]\\ \frac{d\,[C]}{dt}&=k_1[A][B]-k_2\,[C]-k_3\,[C]\\ \frac{d\,[D]}{dt}&=k_3\,[C]\end{aligned}$$

The general analytical solution for this system of coupled differential equations can be obtained, but it is rather complex, because $[C]$ increases early in the reaction, passes through a maximum, and then decreases at long times. In principle, experimental data could be fit to these equations. The numerical approach requires that we select values for k_1, k_2, k_3, $[A]_0$, $[B]_0$, $[C]_0$, and $[D]_0$, and then numerically integrate to get $[A]$, $[B]$, $[C]$, and $[D]$ as functions of time. In principle, we could refine our estimates of k_1, k_2, and k_3 by comparing the calculated values of one or more concentrations to the experimental ones. In practice, the approximate treatments we consider next are more expedient.

When we begin a kinetic study, we normally have a working hypothesis about the reaction mechanism, and we design our experiments to simplify the differential equations that apply to it. For the present example, we will assume that we always arrange the experiment so that $[C]_0=0$ and $[D]_0=0$. In consequence, at all times:

$$[A]_0=[A]+[C]+[D]\,.$$

Also, we restrict our considerations to experiments in which $[B]_0\gg[A]_0$. This exemplifies the use of **flooding**. The practical effect is that the concentration of B remains effectively constant at its initial value throughout the entire reaction, which simplifies the differential equations significantly. In the present instance, setting $[B]_0 \gg [A]_0$ means that the rate-law term $k_1[A][B]$ can be replaced, to a good approximation, by $k_{obs}[A]$, where $k_{obs} = k_1[B]_0$.

Once we have decided upon the reaction conditions we are going to use, whether the resulting concentration-*versus*-time data can be described by a single differential equation depends on the relative magnitudes of the rate constants in the several steps of the overall reaction. Particular combinations of relationships that lead to simplifications are often referred to by particular names; we talk about a combination that has a ***rate-determining step***, or one that involves a ***prior equilibrium***, or one in which a ***steady-state approximation*** is applicable. To see what we mean by these terms, let us consider some particular relationships that can exist among the rate constants in the mechanism above.

2.3.5.1: Case I

Suppose that $k_1[A][B] \gg k_2[C]$ and $k_3 \gg k_2$. We often describe this situation by saying, rather imprecisely, that the reaction to convert C to D is very fast and that the reaction to convert C back to A and B is very slow—compared to the reaction that forms C from A and B. When C is produced in these circumstances, it is converted to D so rapidly that we never observe a significant concentration of C in the reaction mixture. The formation of a molecule of C is tantamount to the formation of a molecule of D, and the reaction produces D at essentially the same rate that it consumes A or B. We say that the first step, $A+B \rightarrow C$, is the rate-determining step in the reaction. We have

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \approx \frac{d[D]}{dt}$$

The assumption that $k_1[A][B] \gg k_2[C]$ means that we can neglect the smaller term in the equation for $d[A]/dt$, giving the approximation

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[D]}{dt} = -k_1[A][B]$$

Letting $[D] = x$ and recognizing that our assumptions make $[C] \approx 0$, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Choosing $[B]_0 \gg [A]_0$ means that $k_1[B] \approx k_1[B]_0 = k_{I,obs}$. The rate equation becomes first-order:

$$\frac{dx}{dt} = k_{I,obs}\left([A]_0 - x\right)$$

Since $k_{I,obs}$ is not strictly constant, it is a pseudo-first-order rate constant. The disappearance of A is said to follow a pseudo-first-order rate equation.

The concept of a rate-determining step step is an **approximation**. In general, the consequence we have in mind when we invoke this approximation is that no intermediate species can accumulate to a significant concentration if it is produced by the rate-determining step or by a step that occurs after the rate-determining step. We do not intend to exclude the accumulation of a species that is at equilibrium with another product. Thus, in the mechanism

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \rightleftharpoons \mathrm{C}$$

we suppose that the conversion of A to B is rate-determining and that the interconversion of B and C is so rapid that their concentrations always satisfy the equilibrium relationship

$$K = \frac{[C]}{[B]}.$$

For the purpose at hand, we do not consider B to be an intermediate; B is a product that happens to be at equilibrium with the co-product, C.

2.3.5.2: Case II

Suppose that $k_1[A][B] \gg k_3[C]$. In this case $A+B \rightarrow C$ is fast compared to the rate at which C is converted to D, and we say that $C \rightarrow D$ is the rate-determining step. We can now distinguish three sub-cases depending upon the way $[C]$ behaves during the course of the reaction.

Case IIa: Suppose that $k_1[A][B] \gg k_3[C]$ and $k_3 \gg k_2$. Then $A+B \rightarrow C$ is rapid and essentially quantitative. That is, within a short time of initiating the reaction, all of the stoichiometrically limiting reactant is converted to C. Letting $[D] = x$ and recognizing that our assumptions make $[A] \approx 0$, the mass-balance condition,

$$[A]_0 = [A] + [C] + [D]$$

becomes

$$[C] = [A]_0 - x.$$

After a short time, the rate at which D is formed becomes

$$\frac{d[D]}{dt} = k_3 [C]$$

or

$$\frac{dx}{dt} = k_3 \left([A]_0 - x \right)$$

The disappearance of C and the formation of D follow a first-order rate law.

Case IIb: If the forward and reverse reactions in the first elementary process are rapid, then this process may be effectively at equilibrium during the entire time that D is being formed. (This is the case that $k_1[A][B] \gg k_3[C]$ and $k_2 \gg k_3$.) Then, throughout the course of the reaction, we have

$$K_{eq} = [C]/[A][B]$$

Letting $[D] = x$ and making the further assumption that $[A] \gg [C] \approx 0$ throughout the reaction, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Substituting into the equilibrium-constant expression, we find

$$[C] = K_{eq}[B]_0 \ \left([A]_0 - x\right)$$

Substituting into $d[D]/dt = k_3[C]$ we have

$$\frac{dx}{dt} = k_3 K_{eq}[B]_0 \ \left([A]_0 - x\right) = k_{IIa,obs} \left([A]_0 - x\right)$$

where $k_{IIa,obs} = k_3 K_{eq}[B]_0$. The disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is a composite quantity that is directly proportional to $[B]_0$.

Case IIc: If we suppose that the first step is effectively at equilibrium during the entire time that D is being produced (as in case IIb) but that $[C]$ is not negligibly small compared to $[A]$, we again have $K_{eq} = [C]/[A][B]$. With $[D] = x$, the mass-balance condition becomes $[A] = [A]_0 - [C] - x$. Eliminating $[A]$ between the mass-balance and equilibrium-constant equations gives

$$[C] = \frac{K_{eq}[B]_0 \left([A]_0 - x\right)}{1 + K_{eq}[B]_0}$$

so that $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_3 K_{eq}[B]_0}{1 + K_{eq}[B]_0}\right) \left([A]_0 - x\right) = k_{IIc,obs} \left([A]_0 - x\right)$$

The formation of D follows a pseudo-first-order rate equation. (The disappearance of A is also pseudo-first-order, but the pseudo-first-order rate constant is different.) As in Case IIb, the pseudo-first-order rate constant, $k_{IIc,obs}$, is a composite quantity, but now its dependence on $[B]_0$ is more complex. The result for Case IIc reduces to that for Case IIb if $K_{eq}[B]_0 \ll 1$.

2.3.5.3: Case III

In the cases above, we have assumed that one or more reactions are intrinsically much slower than others are. The differential equations for this mechanism can also become much simpler if all three reactions proceed at similar rates, but do so in such a way that the concentration of the intermediate is always very small, $[C] \approx 0$. If the concentration of C is always very small, then we expect the graph of $[C]$ versus time to have a slope, $d[C]/dt$, that is approximately zero. In this case, we have

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C] \approx 0$$

so that

$$[C] = \frac{k_1[A][B]}{k_2 + k_3}$$

With $[D] = x$, $d\,[D]/dt = k_3\,[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_1 k_3 [B]_0}{k_2 + k_3}\right)([A]_0 - x) = k_{III,obs}\,([A]_0 - x)$$

As in the previous cases, the disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is again a composite quantity, which depends on $[B]_0$ and the values of all of the rate constants.

Case III illustrates the ***steady-state approximation***, in which we assume that the concentration of an intermediate species is much smaller than the concentrations of other species that affect the reaction rate. Under these circumstances, we can be confident that the time-derivative of the intermediate's concentration is negligible compared to the reaction rate, so that it is a good approximation to set it equal to zero. The idea is simply that, if the concentration is always small, its time-derivative must also be small. If the graph of the intermediate's concentration versus time is always much lower than that of other participating species, then its slope will be much less.

Equating the time derivative of the steady-state intermediate's concentration to zero produces an algebraic expression that involves the intermediate's concentration. Solving this expression for the concentration of the steady-state intermediate makes it possible to greatly simplify the set of simultaneous differential equations that is predicted by the mechanism. When there are multiple intermediates to which the approximation is applicable, remarkable simplifications can result. This often happens when the mechanism involves free-radical intermediates.

The name "steady-state approximation" is traditional. When we use it, we do so on the understanding that the "state" which is approximately "steady" is the concentration of the intermediate, not the state of the system. Since a net reaction is occurring, the state of the system is distinctly not constant.

2.3.6: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

2.3.6.1: General Mechanism

The schematic reaction $A+M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A+M \rightleftharpoons A^{*}+M \tag{2.3.6.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^{*} \xrightarrow{k_2} P \tag{2.3.6.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 2.3.6.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^{*}]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^{*}][M]} - \underset{\text{(forward second step)}}{k_2[A^{*}]} \tag{2.3.6.3}$$

According to the steady-state approximation,

$$\frac{d[A^{*}]}{dt} \approx 0 \tag{2.3.6.4}$$

Therefore the rate of production of A^* (first term in Equation 2.3.6.3) equals the rate of consumption (second and third terms in Equation 2.3.6.3):

$$k_1[A][M] = k_{-1}[A^{*}][M] + k_2[A^{*}] \tag{2.3.6.5}$$

Solving for $[A^*]$, it is found that

$$[A^{*}] = \frac{k_1[A][M]}{k_{-1}[M]+k_2} \tag{2.3.6.6}$$

The overall reaction rate is (Equation 2.3.6.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{2.3.6.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 2.3.6.6 into Equation 2.3.6.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1k_2[A][M]}{k_{-1}[M]+k_2} \tag{2.3.6.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 2.3.6.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 2.3.6.1)
2. There is a time delay Δt between collision and reaction (Equation 2.3.6.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 2.3.6.1)

Example 29.6.1 : Dissociation of

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M]=[N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1k_2[N_2O_5]^2}{k_{-1}[N_2O_5]+k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

  $$\text{Rate} = k_1[N_2O_5]^2$$

  which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

  $$\text{Rate} = \frac{k_1k_2[N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

  which is *first order* with

  $$k_{obs} = \frac{k_2k_2}{k_{-1}}.$$

Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5](mol/m^{-3})$	10	25	50

> Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

2.3.6.2: Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d\,[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{2.3.6.9}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{2.3.6.10}$$

$$\mathrm{A}^* \overset{k_2}{\rightarrow} \mathrm{B} \tag{2.3.6.11}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d\,[\mathrm{A}^*]}{dt} = k_1\,[\mathrm{A}]\,[\mathrm{M}] - k_{-1}[\mathrm{A}^*]_{ss}\,[\mathrm{M}] - k_2[\mathrm{A}^*]_{ss} \approx 0 \tag{2.3.6.12}$$

Solving for $[\mathrm{A}^*]$,

$$[\mathrm{A}^*] = \frac{k_1\,[\mathrm{M}]\,[\mathrm{A}]}{k_2 + k_{-1}\,[\mathrm{M}]} \tag{2.3.6.13}$$

The reaction rates of species A and B can be written as

$$-\frac{d\,[\mathrm{A}]}{dt} = \frac{d\,[\mathrm{B}]}{dt} = k_2\,[\mathrm{A}^*] = \frac{k_1 k_2\,[\mathrm{M}]\,[\mathrm{A}]}{k_2 + k_{-1}\,[\mathrm{M}]} = k_{\mathrm{obs}}\,[\mathrm{A}] \tag{2.3.6.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2\,[\mathrm{M}]}{k_2 + k_{-1}\,[\mathrm{M}]} \tag{2.3.6.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}\,[\mathrm{M}] \gg k_2$. Equation 2.3.6.14then becomes

$$-\frac{d\,[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{2.3.6.16}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}\,[\mathrm{M}] \ll k_2$. In this scenario, Equation 2.3.6.14 becomes

$$-\frac{d\,[\mathrm{A}]}{dt} = k_1\,[\mathrm{A}]\,[\mathrm{M}] \tag{2.3.6.17}$$

which follows second order rate kinetics, consistent with experimental observations.

2.3.6.3: References

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2.3.7: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{2.3.7.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{2.3.7.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{2.3.7.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{2.3.7.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2]+\frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation $2.3.7.1$)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

2.3.8: A Catalyst Affects the Mechanism and Activation Energy

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst.

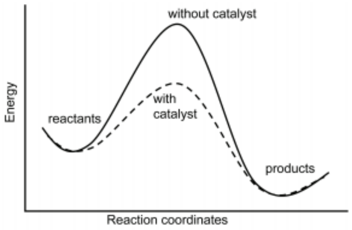

Figure 29.8.1 : Comparison of energy profiles with and without catalyst present.

Homogeneous catalysis refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 29.8.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A}+\mathrm{C} \xrightarrow{k_{\text{cat}}} \mathrm{P}+\mathrm{C}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{\text{cat}}[\mathrm{A}][\mathrm{C}]$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{\text{cat}} \gg k$), the first term can often be ignored.

2.3.8.1: Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}]$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S}+\mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{2.3.8.1}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{2.3.8.2}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{2.3.8.3}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[SH^+][\mathrm{A}^-] \tag{2.3.8.4}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[SH^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{2.3.8.5}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[SH^+][\mathrm{A}^-] - k_2[SH^+] \tag{2.3.8.6}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[SH^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{2.3.8.7}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[SH^+] \tag{2.3.8.8}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[SH^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{2.3.8.9}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[SH^+] = 0$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[SH^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[SH^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 29.8.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H]$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+]$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]}$$

In this case, the reaction is hydrogen ion-catalyzed.

2.3.8.2: Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}(g) + \mathrm{S}(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}(s)$$

$$\mathrm{AS}(s) \xrightarrow{k_2} \mathrm{P}(g) + \mathrm{S}(g)$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d[\mathrm{AS}]}{dt}=k_1[\mathrm{A}][\mathrm{S}]-k_{-1}[\mathrm{AS}]_{ss}-k_2[\mathrm{AS}]_{ss}=0$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}]=\theta[\mathrm{S}]_0$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}]=(1-\theta)[\mathrm{S}]_0$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 29.8.23 as

$$k_1[\mathrm{A}](1-\theta)[\mathrm{S}]_0-(k_{-1}+k_2)\theta[\mathrm{S}]_0=0$$

Rearranging the above equation in terms of θ yields

$$\theta=\frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}]+k_{-1}+k_2}$$

The rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt}=k_2[\mathrm{AS}]_{ss}=k_2\theta[\mathrm{S}]_0=\frac{k_1k_2}{k_1[\mathrm{A}]+k_{-1}+k_2}[\mathrm{A}][\mathrm{S}]_0$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

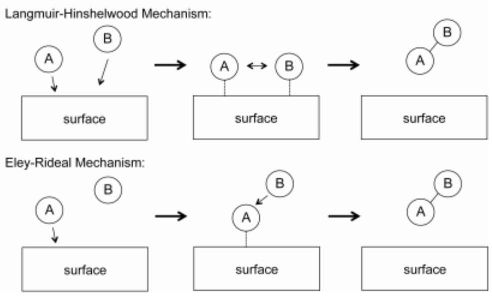

Figure 29.8.2 : Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure 29.8.2 . In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}(g)+\mathrm{S}(s)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{AS}(s)$$

$$\mathrm{B}(g)+\mathrm{S}(s)\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\mathrm{BS}(s)$$

$$\mathrm{AS}(s)+\mathrm{BS}(s)\xrightarrow{k_3}\mathrm{P}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure 29.8.3 . In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}(g)+\mathrm{S}(s)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{AS}(s)$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \xrightarrow{k_2} \mathrm{P}\,(g) + \mathrm{S}\,(s)$$

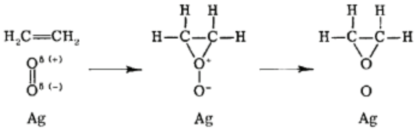

Figure 29.8.3 : Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, 1]

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species AS:

$$\frac{d\,[\mathrm{AS}]}{dt} = 0 = k_1\,[\mathrm{A}]\,[\mathrm{S}] - k_{-1}\,[\mathrm{AS}]_{ss} - k_2\,[\mathrm{AS}]_{ss}\,[\mathrm{B}]$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of AS and S in terms of a fraction of the total number of active sites, S_0 and rewrite the above equation as

$$0 = k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0 - k_{-1}\,[\mathrm{S}]_0 - k_2\theta[\mathrm{S}]_0\,[\mathrm{B}]$$

Solving for θ yields

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1} + k_2\,[\mathrm{B}]}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1}}$$

The rate of production of P can be expressed as

$$\frac{d\,[\mathrm{P}]}{dt} = k_2[\mathrm{AS}]_{ss}\,[\mathrm{B}] = k_2\theta[\mathrm{S}]_0\,[\mathrm{B}] = \frac{k_1k_2\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1}}[\mathrm{S}]_0\,[\mathrm{B}]$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal tok_1/k_{-1}

$$\frac{d\,[\mathrm{P}]}{dt} = Kk_2\,[\mathrm{B}]\,\frac{K\,[\mathrm{A}]}{K\,[\mathrm{A}] + 1}$$

Contributors and Attributions

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2.3.9: The Michaelis-Menten Mechanism for Enzyme Catalysis

Enzymes are biological catalysts and functional proteins. Enzymes contain specificity in its protein structure in order to have its specialized function. It usually contains more than one subunit and they are critical to sustain life. Enzymes can increase the chemical reactions in living cells. However, enzymes are not consumed in the reaction and their main function is to assist in bringing the substrates together so they can undergo normal reaction faster.

The first enzyme was found in the process of fermentation in milk and alcohol during the nineteenth century. Later in the early 1830s, the term enzyme was used to replace the term ferment. Some scientists believe that ferments must contain living cells and some think ferments could be non-living cells. Finally, in the 1920s, Sumner purified the structure of enzyme and then properties of enzyme then was more clearly understood. Until today, enzymes are still the popular research field that many people are subject to study.

2.3.9.1: Michaelis-Menten Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathrm{E}+\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E}+\mathrm{P}$$

where E is the enzyme, ES is the enzyme-substrate complex, and P is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, ES, is small and employ a steady-state approximation:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} - k_2[\mathrm{ES}]_{ss} \approx 0 \tag{2.3.9.1}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{2.3.9.2}$$

Plugging Equation 2.3.9.2into Equation 2.3.9.1, we obtain

$$0 = k_1([\mathrm{E}]_0 - [\mathrm{ES}]_{ss})[\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} + k_2[\mathrm{ES}]_{ss} \tag{2.3.9.3}$$

Solving for $[\mathrm{ES}]_{ss}$

$$[\mathrm{ES}]_{ss} = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \dfrac{k_{-1}+k_2}{k_1}} \tag{2.3.9.4}$$

We can then write the reaction rate of the product as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_{ss} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \dfrac{k_{-1}+k_2}{k_1}} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_M} \tag{2.3.9.5}$$

where K_M is the Michaelis constant. Equation 2.3.9.5 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present $([\mathrm{S}] \gg K_M)$ Equation 2.3.9.5reduces to

$$\frac{d[\mathrm{P}]}{dt} = r_{\max} = k_2[\mathrm{E}]_0 \tag{2.3.9.6}$$

which is a 0^{th} order reaction, since $[\mathrm{E}]_0$ is a constant. The value $k_2[\mathrm{E}]_0$ represents the maximum rate, $r_{\max}$, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 29.9.4 displays the dependence of the reaction rate on the substrate concentration, $[\mathrm{S}]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2[\mathrm{E}]_0$ at large values of $[\mathrm{S}]$.

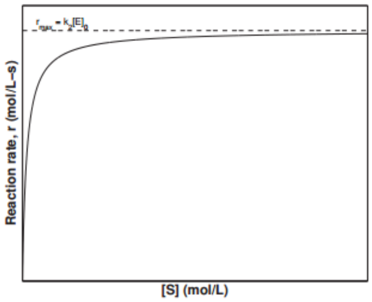

Figure 29.9.4 : Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[\mathrm{S}]$. Rearranging Equation 2.3.9.5,

$$\frac{1}{r} = \frac{K_M + [\mathrm{S}]}{k_2[\mathrm{E}]_0[\mathrm{S}]} = \frac{K_M}{k_2[\mathrm{E}]_0}\frac{1}{[\mathrm{S}]} + \frac{1}{k_2[\mathrm{E}]_0} \tag{2.3.9.7}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2[\mathrm{E}]_0$ and y-intercept equal to $1/k_2[\mathrm{E}]_0$.

Contributors and Attributions

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2.3.10: Predicting Rate Laws from Proposed Mechanisms

Because a proposed mechanism can only be valid if it is consistent with the rate law found experimentally, the rate law plays a central role in the investigation of chemical reaction mechanisms. The discussion above introduces the problems and methods associated with collecting rate data and with finding an empirical rate law that fits experimental concentration-*versus*-time data. We turn now to finding the rate laws that are consistent with a particular proposed mechanism. For simplicity, we consider reactions in closed constant-volume systems.

In principle, numerical integration can be used to predict the concentration at any time of each of the species in any proposed reaction mechanism. This prediction can be compared to experimental observations to see whether they are consistent with the proposed mechanism. To do the numerical integration, it is necessary to know the initial concentrations of all of the chemical species and to know, or assume, values of all of the rate constants. The initial concentrations are known from the procedure used to initiate the reaction. However, the rate constants must be determined by some iterative procedure in which initial estimates of the rate constants are used to predict concentration-*versus*-time data that can be compared to the experimental results to produce refined estimates.

In practice, we tailor our choice of reaction conditions so that we can use various approximations to test whether a proposed mechanism can explain the data. We now consider the most generally useful of these approximations.

In this discussion, we assume that the overall reaction goes to completion; that is, at equilibrium the concentration of the reactant whose concentration is limiting has become essentially zero. If the overall reaction involves more than one elementary step, then an intermediate compound is involved. A valid mechanism must include this intermediate, and more than one differential equation may be needed to characterize the time rate of change of all of the species involved in the reaction. We focus on conditions and approximations under which the rate of appearance of the final products in a multi-step reaction mechanism can be described by a single differential equation, the rate law.

We examine the application of these approximations to a particular reaction mechanism. When we understand the application of these approximations to this mechanism, the ways in which they can be used in other situations are clear.

Consider the following sequence of elementary steps

$$\mathrm{A}+\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\begin{aligned}\frac{d[A]}{dt}=\frac{d[B]}{dt}&=-k_1[A][B]+k_2\,[C]\\ \frac{d\,[C]}{dt}&=k_1[A][B]-k_2\,[C]-k_3\,[C]\\ \frac{d\,[D]}{dt}&=k_3\,[C]\end{aligned}$$

The general analytical solution for this system of coupled differential equations can be obtained, but it is rather complex, because $[C]$ increases early in the reaction, passes through a maximum, and then decreases at long times. In principle, experimental data could be fit to these equations. The numerical approach requires that we select values for k_1, k_2, k_3, $[A]_0$, $[B]_0$, $[C]_0$, and $[D]_0$, and then numerically integrate to get $[A]$, $[B]$, $[C]$, and $[D]$ as functions of time. In principle, we could refine our estimates of k_1, k_2, and k_3 by comparing the calculated values of one or more concentrations to the experimental ones. In practice, the approximate treatments we consider next are more expedient.

When we begin a kinetic study, we normally have a working hypothesis about the reaction mechanism, and we design our experiments to simplify the differential equations that apply to it. For the present example, we will assume that we always arrange the experiment so that $[C]_0=0$ and $[D]_0=0$. In consequence, at all times:

$$[A]_0=[A]+[C]+[D]\,.$$

Also, we restrict our considerations to experiments in which $[B]_0\gg[A]_0$. This exemplifies the use of **flooding**. The practical effect is that the concentration of B remains effectively constant at its initial value throughout the entire reaction, which simplifies the differential equations significantly. In the present instance, setting $[B]_0 \gg [A]_0$ means that the rate-law term $k_1[A][B]$ can be replaced, to a good approximation, by $k_{obs}[A]$, where $k_{obs} = k_1[B]_0$.

Once we have decided upon the reaction conditions we are going to use, whether the resulting concentration-*versus*-time data can be described by a single differential equation depends on the relative magnitudes of the rate constants in the several steps of the overall reaction. Particular combinations of relationships that lead to simplifications are often referred to by particular names; we talk about a combination that has a ***rate-determining step***, or one that involves a ***prior equilibrium***, or one in which a ***steady-state approximation*** is applicable. To see what we mean by these terms, let us consider some particular relationships that can exist among the rate constants in the mechanism above.

Case I

Suppose that $k_1[A][B] \gg k_2[C]$ and $k_3 \gg k_2$. We often describe this situation by saying, rather imprecisely, that the reaction to convert C to D is very fast and that the reaction to convert C back to A and B is very slow—compared to the reaction that forms C from A and B. When C is produced in these circumstances, it is converted to D so rapidly that we never observe a significant concentration of C in the reaction mixture. The formation of a molecule of C is tantamount to the formation of a molecule of D, and the reaction produces D at essentially the same rate that it consumes A or B. We say that the first step, $A+B \rightarrow C$, is the rate-determining step in the reaction. We have

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \approx \frac{d[D]}{dt}$$

The assumption that $k_1[A][B] \gg k_2[C]$ means that we can neglect the smaller term in the equation for $d[A]/dt$, giving the approximation

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[D]}{dt} = -k_1[A][B]$$

Letting $[D]=x$ and recognizing that our assumptions make $[C] \approx 0$, the mass-balance condition, $[A]_0 = [A]+[C]+[D]$, becomes $[A] = [A]_0 - x$. Choosing $[B]_0 \gg [A]_0$ means that $k_1[B] \approx k_1[B]_0 = k_{I,obs}$. The rate equation becomes first-order:

$$\frac{dx}{dt} = k_{I,obs}\left([A]_0 - x\right)$$

Since $k_{I,obs}$ is not strictly constant, it is a pseudo-first-order rate constant. The disappearance of A is said to follow a pseudo-first-order rate equation.

The concept of a rate-determining step step is an **approximation**. In general, the consequence we have in mind when we invoke this approximation is that no intermediate species can accumulate to a significant concentration if it is produced by the rate-determining step or by a step that occurs after the rate-determining step. We do not intend to exclude the accumulation of a species that is at equilibrium with another product. Thus, in the mechanism

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \rightleftharpoons \mathrm{C}$$

we suppose that the conversion of A to B is rate-determining and that the interconversion of B and C is so rapid that their concentrations always satisfy the equilibrium relationship

$$K = \frac{[C]}{[B]}.$$

For the purpose at hand, we do not consider B to be an intermediate; B is a product that happens to be at equilibrium with the co-product, C.

Case II

Suppose that $k_1[A][B] \gg k_3[C]$. In this case $A+B \rightarrow C$ is fast compared to the rate at which C is converted to D, and we say that $C \rightarrow D$ is the rate-determining step. We can now distinguish three sub-cases depending upon the way $[C]$ behaves during the course of the reaction.

Case IIa: Suppose that $k_1[A][B] \gg k_3[C]$ and $k_3 \gg k_2$. Then $A+B \rightarrow C$ is rapid and essentially quantitative. That is, within a short time of initiating the reaction, all of the stoichiometrically limiting reactant is converted to C. Letting $[D]=x$ and recognizing that our assumptions make $[A] \approx 0$, the mass-balance condition,

$$[A]_0 = [A] + [C] + [D]$$

becomes

$$[C] = [A]_0 - x.$$

After a short time, the rate at which D is formed becomes

$$\frac{d[D]}{dt} = k_3 [C]$$

or

$$\frac{dx}{dt} = k_3 ([A]_0 - x)$$

The disappearance of C and the formation of D follow a first-order rate law.

Case IIb: If the forward and reverse reactions in the first elementary process are rapid, then this process may be effectively at equilibrium during the entire time that D is being formed. (This is the case that $k_1[A][B] \gg k_3 [C]$ and $k_2 \gg k_3$.) Then, throughout the course of the reaction, we have

$$K_{eq} = [C]/[A][B]$$

Letting $[D] = x$ and making the further assumption that $[A] \gg [C] \approx 0$ throughout the reaction, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Substituting into the equilibrium-constant expression, we find

$$[C] = K_{eq}[B]_0 \ ([A]_0 - x)$$

Substituting into $d[D]/dt = k_3 [C]$ we have

$$\frac{dx}{dt} = k_3 K_{eq}[B]_0 \ ([A]_0 - x) = k_{IIa,obs} \ ([A]_0 - x)$$

where $k_{IIa,obs} = k_3 K_{eq}[B]_0$. The disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is a composite quantity that is directly proportional to $[B]_0$.

Case IIc: If we suppose that the first step is effectively at equilibrium during the entire time that D is being produced (as in case IIb) but that $[C]$ is not negligibly small compared to $[A]$, we again have $K_{eq} = [C]/[A][B]$. With $[D] = x$, the mass-balance condition becomes $[A] = [A]_0 - [C] - x$. Eliminating $[A]$ between the mass-balance and equilibrium-constant equations gives

$$[C] = \frac{K_{eq}[B]_0 \left([A]_0 - x\right)}{1 + K_{eq}[B]_0}$$

so that $d[D]/dt = k_3 [C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_3 K_{eq}[B]_0}{1 + K_{eq}[B]_0}\right) ([A]_0 - x) = k_{IIc,obs} \ ([A]_0 - x)$$

The formation of D follows a pseudo-first-order rate equation. (The disappearance of A is also pseudo-first-order, but the pseudo-first-order rate constant is different.) As in Case IIb, the pseudo-first-order rate constant, $k_{IIc,obs}$, is a composite quantity, but now its dependence on $[B]_0$ is more complex. The result for Case IIc reduces to that for Case IIb if $K_{eq}[B]_0 \ll 1$.

Case III

In the cases above, we have assumed that one or more reactions are intrinsically much slower than others are. The differential equations for this mechanism can also become much simpler if all three reactions proceed at similar rates, but do so in such a way that the concentration of the intermediate is always very small, $[C] \approx 0$. If the concentration of C is always very small, then we expect the graph of $[C]$ versus time to have a slope, $d[C]/dt$, that is approximately zero. In this case, we have

$$\frac{d[C]}{dt} = k_1[A][B] - k_2 [C] - k_3 [C] \approx 0$$

so that

$$[C]=\frac{k_1[A][B]}{k_2+k_3}$$

With $[D]=x$, $d[D]/dt=k_3[C]$ becomes

$$\frac{dx}{dt}=\left(\frac{k_1k_3[B]_0}{k_2+k_3}\right)\left([A]_0-x\right)=k_{III,obs}\left([A]_0-x\right)$$

As in the previous cases, the disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is again a composite quantity, which depends on $[B]_0$ and the values of all of the rate constants.

Case III illustrates the ***steady-state approximation***, in which we assume that the concentration of an intermediate species is much smaller than the concentrations of other species that affect the reaction rate. Under these circumstances, we can be confident that the time-derivative of the intermediate's concentration is negligible compared to the reaction rate, so that it is a good approximation to set it equal to zero. The idea is simply that, if the concentration is always small, its time-derivative must also be small. If the graph of the intermediate's concentration versus time is always much lower than that of other participating species, then its slope will be much less.

Equating the time derivative of the steady-state intermediate's concentration to zero produces an algebraic expression that involves the intermediate's concentration. Solving this expression for the concentration of the steady-state intermediate makes it possible to greatly simplify the set of simultaneous differential equations that is predicted by the mechanism. When there are multiple intermediates to which the approximation is applicable, remarkable simplifications can result. This often happens when the mechanism involves free-radical intermediates.

The name "steady-state approximation" is traditional. When we use it, we do so on the understanding that the "state" which is approximately "steady" is the concentration of the intermediate, not the state of the system. Since a net reaction is occurring, the state of the system is distinctly not constant.

2.3.E: Chemical Kinetics II- Reaction Mechanisms (Exercises)

CHAPTER OVERVIEW

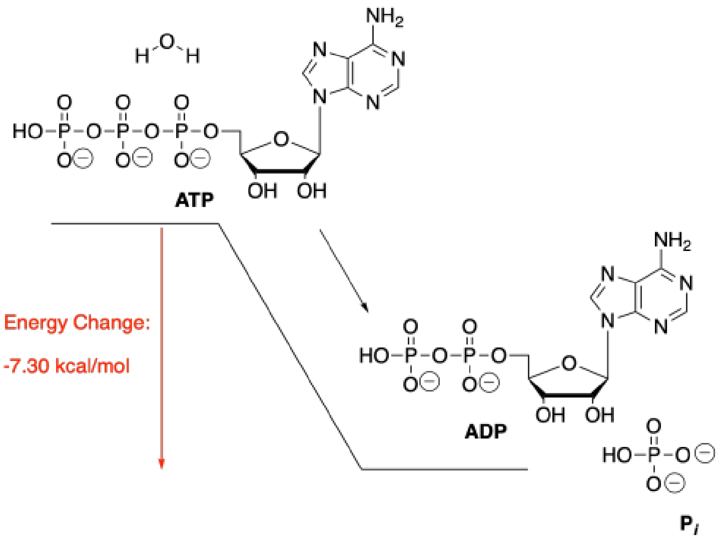
3: Chemical Thermodynamics

3.1: Introduction to Thermodynamics

Thermodynamics is the study of the relationship between heat (or energy) and work. In other words, thermodynamics looks at how we can put energy into a system (whether it is a machine or a molecule) and make it do work. Alternatively, we might be able to do some work on a system and make it produce energy (like spinning the turbines in a power station to produce electricity).

In chemistry, we sometimes speak more broadly about "energetics" of reactions (rather than thermodynamics), because energy given off during a reaction may simply be lost to the surroundings without doing useful work. Nevertheless, the ideas are the same: energy can be added to a set of molecules in order to produce a reaction, or a reaction can occur between a set of molecules in order to release energy.

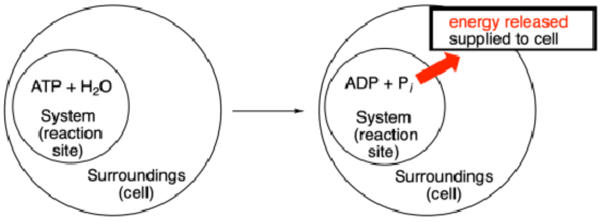
A classic example of reaction energetics is the hydrolysis of ATP to ADP in biology. This reaction is used in the cell as a source of energy; the energy released from the reaction is frequently coupled to other processes that could not occur without the added energy.



The hydrolysis of ATP, or the addition of water to ATP in order to break ATP into two, smaller molecules, gives off energy. That energy can be used by the cell to carry out other processes that would cost energy. One molecule of ADP and one molecule of inorganic phosphate, sometimes abbreviated as Pi, are also produced.

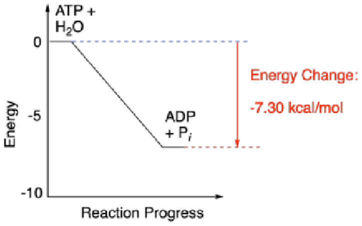
- Energy can be given off by a chemical reaction.
- That energy can be used to power other reactions that require energy.

In the cell, ATP is produced in high levels in the mitochondria. Because it is a relatively small molecule, it can be transported easily to other areas of the cell where energy may be needed. The ATP can be hydrolysed on site, providing energy for the cell to use for other reactions.



Note that the scheme above uses some thermodynamics jargon. The place where the reaction takes place, or the molecules participating in the reaction, are called "the system". Energy is supplied to "the surroundings", meaning places or molecules other than those directly involved in this reaction.

There are a couple of other ways in which energetics of reactions are commonly depicted. The energetic relationship between ATP plus water and ADP plus phosphate shown above is really a simplified graph of energy versus reaction progress (sometimes called reaction coordinate). This type of graph shows changes in energy over the course of a reaction. The energy of the system at the beginning of the reaction is shown on the left, and the energy at the end of the reaction is shown on the right. This type of graph is sometimes referred to as a reaction profile.

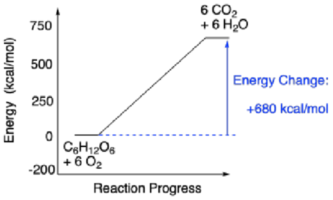


Another common way of discussing energetics is to include energy as a reactant or product in an equation describing the reaction. An equation for a reaction shows what the starting materials were for the reaction, and what they turned into after the reaction. The things that reacted together in the reaction are called the "reactants". They are written on the left hand side of the arrow that says a reaction took place. The things that the reactants turned into are called the "products". They show up on the right hand side of the arrow.

$$ATP + H_2O \rightarrow ADP + P_i + \text{energy} \tag{3.1.1}$$

For the hydrolysis of ATP, energy is simply included as one of the products of the reaction, since the reaction releases energy.

Alternatively, the energetic observation about ATP can be turned around, since there are evidently some reactions that cost energy. Probably the most well-know reaction of this type is the conversion of carbon dioxide to carbohydrates such as glucose. This conversion actually results from a long series of different reactions that happen one after another. Overall, the process requires a lot of energy. This energy is supplied in part by ATP, generated with assistance from photosystem I and II, which are arrays of molecules that interact with sunlight. A simplified reaction profile for carbohydrate synthesis is shown below.



- Energy can be consumed by a chemical reaction.
- Reactions that consume energy need an energy source in order to occur.

Again, this energetic relationship can be thought of in the form of a balanced reaction.

$$\text{energy} + 6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + O_2 \tag{3.1.2}$$

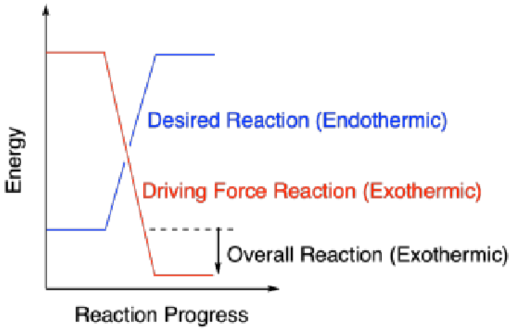
In this case, energy is a reactant, not a product. It is one of the key ingredients needed to make the reaction happen.

Reactions that produce energy, like ATP hydrolysis, are referred to as exothermic reactions (or sometimes exergonic, meaning roughly the same thing). In reaction profiles, these reactions go downhill in energy as the reaction occurs from the left side of the diagram to the right. On the other hand, reactions that cost energy (the ones that go uphill on the reaction profile, like carbohydrate synthesis) are referred to as endothermic (or sometimes endergonic).

It is useful to think of reactions as "going downhill" or "going uphill" because one of these situations should seem inherently easier than the other (especially if you've ever been skiing). Exothermic reactions (the downhill ones) occur very easily; endothermic reactions do not (those are the uphill ones).

- Systems always go to lower energy if possible.

Reactions that are energetically "uphill" cannot happen easily by themselves. Those reactions must be powered by other reactions that are going downhill. The energy traded between these reactions keeps chemical reactions going, in cells and other important places. Sometimes, a process that is used to supply energy for another reaction is thought of as the "driving force" of the reaction. Without the driving force, the desired reaction would not be able to occur.

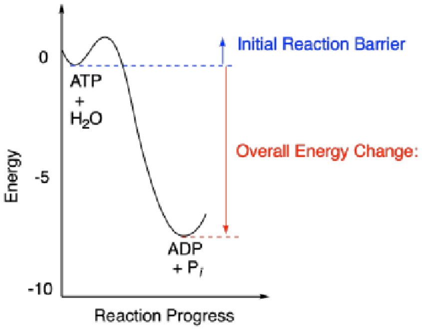


In general, a reaction will occur if more than enough energy is supplied. Excess energy does not hurt on the macroscopic scale. However, if not enough energy is supplied to make up for an endothermic reaction, the reaction is not likely to happen.

Energy is a lot like money. It can be passed from one set of hands to another. Doing so often helps get things done.

There is one problem with the use of chemical reactions as sources of energy. If ATP hydrolysis releases energy, and if the release of energy is always favoured, why doesn't it happen spontaneously? In other words, why don't all the ATP molecules in all the cells in all the organisms in the whole world just slide downhill into ADP right now? What is stopping them?

Fortunately, all reactions have barriers that stop them from happening until they are ready to go. A reaction barrier is an initial investment of energy needed to get things started. Reaction barriers occur for a variety of physical reasons: two molecules may need to get oriented in the right direction to react with each other, or a bond may have to be broken to get the reaction going, costing an initial outlay of energy.



The reaction barriers of reactions influence how quickly reactions happen. High barriers slow reactions down a lot. Low barriers allow them to happen more easily. The study of reaction barriers, and how quickly reactions can occur, is called chemical kinetics.

Thermodynamics, on the other hand, is really concerned with the overall energy change from the beginning of a reaction to the end. It compares the energies of two sets of molecules to each other: the energies of the reactants and the energies of the products.

Contributors and Attributions

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3.2: Bond Energies

Bond energies are limited in their application for the reasons discussed earlier. They were:

- values are for gases only
- many values are averages

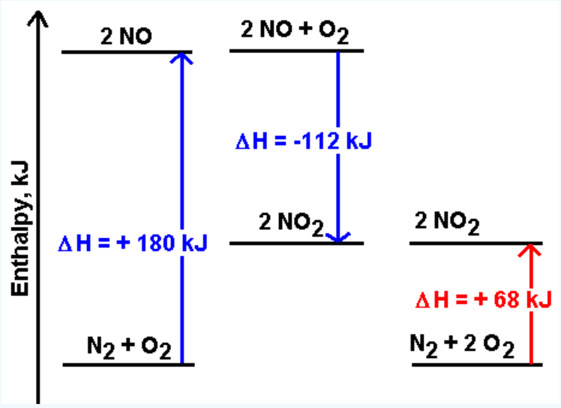
These are serious drawbacks if you want energy information about most reactions. Fortunately there is another way. Remember in our definition of enthalpy (H) we said it was a "state function". The net enthalpy change (ΔH --which is the only kind of enthalpy quantity we can measure) is independent of path. What does this mean?

If a process can be carried out in a single step, the enthalpy change for that step will be the same as for a series of steps which add up to give the same overall step.

Example 3.2.1: Additive of Heats

The diagram shows two possible pathways for one reaction:

$$N_2 + 2O_2 \rightarrow 2NO_2 \tag{3.2.1}$$



The direct reaction of the elements nitrogen and oxygen in a 1:2 molar ratio will produce 2 moles of nitrogen dioxide and absorb 68 kJ. But it is also possible to begin with the same elements under different conditions (like a 1:1 molar ratio) and produce 2 moles of nitrogen monoxide. This process absorbs 180 kJ.

The nitrogen monoxide can then react with additional oxygen to form 2 moles of nitrogen dioxide. This process releases 112 kJ.

The sum of the two reactions involving nitrogen monoxide gives the production of nitrogen dioxide:

$$180\ kJ + N_2 + O - 2 \rightarrow 2NO \tag{3.2.2}$$

$$\underline{2NO + O_2 \rightarrow 2NO_2 + 112\ kJ} \tag{3.2.3}$$

$$68\ kJ + N_2 + 2O_2 \rightarrow 2NO_2 \tag{3.2.4}$$

And because that is true, the enthalpy changes are also additive:

$$180\ kJ + (-112\ kJ) = 68\ kJ \tag{3.2.5}$$

So with a sufficiently ambitious catalog of reaction enthalpy changes it is sometimes possible to calculate--rather than measure--the enthalpy change for a new reaction.

Example 3.2.2: Heat of Reaction

Give the following data:

$$H_2 + ½O_2 \rightarrow H_2O + 286\ kJ \tag{3.2.6}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 + 77\ kJ \tag{3.2.7}$$

$$N_2 + 3O_2 + H_2 \rightarrow 2HNO_3 + 348\ kJ \tag{3.2.8}$$

Calculate ΔH_{rxn} for

$$2N_2 + 5O_2 \rightarrow 2N_2O_5 \tag{3.2.9}$$

Solution

To begin these problems, concentrate on the items in the balanced equation you want. Where are they found in the data available?

$$H_2 + ½O_2 \rightarrow H_2O + 286\ kJ \tag{3.2.10}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 + 77\ kJ \tag{3.2.11}$$

$$N_2 + 3O_2 + H_2 \rightarrow 2HNO_3 + 348\ kJ \tag{3.2.12}$$

Once these are located, the equations needs to be adjusted so that the substances appear in the same amount as in the desired reaction and on the same sides.

$$H_2 + ½O_2 \rightarrow H_2O + 286\ kJ \tag{3.2.13}$$

$$2 \times (2HNO_3 + 77\ kJ \rightarrow N_2O_5 + 2H_2O) \tag{3.2.14}$$

$$2 \times (N_2 + 3O_2 + H_2 \rightarrow 2HNO_3 + 348\ kJ) \tag{3.2.15}$$

Notice that this procedure did not fix the O_2 entirely. However, there are also things that we need to get rid of so that the equations will add up to give the desired reaction of H_2, H_2O, and HNO_3. If the first reaction is reversed and doubles, this will happen:

$$2 \times (H_2O + 572\ kJ \rightarrow 2H_2 + O_2) \tag{3.2.16}$$

$$2 \times (2HNO_3 + 77\ kJ \rightarrow N_2O_5 + 2H_2O \tag{3.2.17}$$

$$2 \times (N_2 + 3O_2 + H_2 \rightarrow 2HNO_3 + 348\ kJ) \tag{3.2.18}$$

Multiply all this out to get

$$2H_2O + 572\ kJ \rightarrow\ 2\cancel{H_2} + O_2 \tag{3.2.19}$$

$$4HNO_3 + 154\ kJ \rightarrow 2N_2O_5 + 2H_2O \tag{3.2.20}$$

$$2N_2 + O_2 + 2H_2 \rightarrow 4HNO_3 + 696\ kJ \tag{3.2.21}$$

Then we add and simplify, much like we do with a series of half reactions

$$2\cancel{H_2O} + 572\ kJ \rightarrow\ 2\cancel{H_2} +\ \cancel{O_2} \tag{3.2.22}$$

$$4\cancel{HNO_3} + 154\ kJ \rightarrow 2N_2O_5 +\ 2\cancel{H_2O} \tag{3.2.23}$$

$$\underline{2N_2 +\ \cancel{6}O_2 +\ 2\cancel{H_2} \rightarrow\ 4\cancel{HNO_3} + 696\ kJ} \tag{3.2.24}$$

$$30\ kJ + 2N_2 + 5O_2 \rightarrow 2N_2O_5 \tag{3.2.25}$$

So what's the advantage? Theoretically every reaction can be "rewritten" as a series of processes involving elements forming individual compounds. It does not matter whether the reaction actually occurs that way, of course, because the enthalpies are additive (Hess's Law). The heats of formation represent those reactions and therefore can be used in their place to determine the overall enthalpy change in a reaction based on a mathematical statement.

This additivity of heats of reaction (or reaction enthalpies) is generally known as Hess's Law. But it is also possible to state the equivalent of Hess's Law in purely mathematical terms with the introduction of an additional concept: **standard enthalpy of formation.**

If elements in their standard states (normal atmospheric pressure) and 25^oC are defined as having no enthalpy of formation (i.e., it takes no energy to get an element the way it would normally be), then all compounds will have some enthalpy change associated with their formation from those elements.

For example, when liquid water is formed from gaseous hydrogen and oxygen, we can write the following thermochemical equation:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\ +\ 285.8\ kJ \tag{3.2.26}$$

The 285.8 kJ is the enthalpy of formation for liquid water: **the energy released when one mole of liquid water forms from its elements.**

The fact that the value is on the products side of the reaction shows this is an exothermic process. The value can also be written separately (as in a table). By convention, a negative sign is then applied to show that there is a net loss of enthalpy in the system as the reactants become products. That means heat is released to the surroundings. So we can say $\Delta H_f^o = -285.8\ kJ/mol$ of water. All kinds of enthalpies of formation have been tabulated (Table T1).

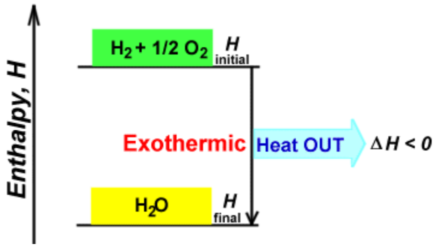


Figure: Example of an exothermic reaction with heat transferred to the surrounding ($\delta H < 0$)

For an endothermic reaction the enthalpy of reaction would be written on the reactant side:

$$177.8 kJ\ +\ CaCO_3 \rightarrow CaO + CO_2 \tag{3.2.27}$$

And when written in a table, the value would be $\Delta H_{rxn} = +177.8\ kJ/mol$. All "heats of reaction" are molar and therefore proportional. Stoichiometric amounts of heat can be determined for a given amount of starting material just as any other stoichiometric calculation would be done.

✓ Example 3.2.2: Acid/base neutralization

The thermochemical equation for the acid/base neutralization reaction of hydrochloric acid with barium hydroxide solution is

$$2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O + 118\ kJ \tag{3.2.28}$$

How much heat is produces if 34.5 g of HCl reacts with a stoichiometric amount of Barium hydroxide?

Solution

Step 1: Balance the Equation

Given and confirmed

Step 2: Find number of moles of

$$(34.5\ g) \times \frac{1\ mol}{36.5\ g} = 0.945\ mol\ HCl \tag{3.2.29}$$

Step 3: Use ration to find kJ

$$(0.945\ mol\ HCl) \times \frac{118\ kJ}{2\ mol\ HCl} = 55.8\ kJ \tag{3.2.30}$$

So what's the advantage? Theoretically every reaction can be "rewritten" as a series of processes involving elements forming individual compounds. It does not matter whether the reaction actually occurs that way, of course, because the enthalpies are additive (Hess's Law). The heats of formation represent those reactions and therefore can be used in their place to determine the overall enthalpy change in a reaction based on a mathematical statement.

$$\sum \Delta H^o_{f\ products} - \sum \Delta H^o_{f\ reactants} = \Delta H_{rxn} \tag{3.2.31}$$

That looks fearsome but it simply says that the overall enthalpy change for a reaction is the difference between the heat content of the products and the heat content of the reactants. If the products end up with more stored energy than the reactants, the enthalpy change will be positive (endothermic). If the products end up with less stored energy than the reactants, the enthalpy change will be negative (exothermic).

✓ Example 3.2.3: Thermite Reaction

Thermite is a generic term for a mixture of metal and metal oxide used to generate tremendous heat. During the reaction one metal is reduced and the other is oxidized. The classic thermite mixture consists of iron(III) oxide and aluminum:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \tag{3.2.32}$$

- The heat of formation for iron(III) oxide is -826 kJ/mol.
- The heat of formation for aluminum oxide is -1676 kJ/mol.

How much energy is released in this reaction?

Solution

$$\Delta H_{rxn} = -1676\ kJ - (-826\ kJ) = -850 \text{ kJ/mol of either oxide} \tag{3.2.33}$$

The notion of looking at the enthalpy change as reflective of "stored energy" is important and suggestive. Observation indicates that chemically "stable" compounds tend to have very negative heats of formation. Carbon dioxide (-393.5 kJ/mol) and water (-285.5 kJ/mol) would be examples, but by no means the most extreme. Oxides of metals like iron(III) oxide and aluminum oxide have very negative heats of formation.

In contrast, chemically "unstable" compounds tend to have rather positive heats of formation. These very reactive substances have energy stored within their bonds. Silver fulminate, $Ag_2C_2N_2O_2$, is a good example. The heat of formation is +180 kJ/mol.

✓ Example 3.2.4: Silver fulminate

Silver fulminate is one of a series of compounds containing transition metals and the "fulminate" group. All of the compounds are very unstable. When silver fulminate decomposes it does so according to the following reaction:

$$Ag_2C_2N_2O_2 \rightarrow 2Ag + N_2 + 2CO \tag{3.2.34}$$

- The heat of formation for silver fulminate is +180 kJ/mol.
- The heat of formation for carbon monoxide is -110.5 kJ/mol.

How much energy is released in this reaction? If 0.0009 g of silver fulminate decomposes (as in the "Whipper Snappers" fireworks), how much energy is released?

Solution

$$\Delta H_{rxn} = 2(-110.5kJ) - 180kJ = -401\ kJ/mol \tag{3.2.35}$$

So

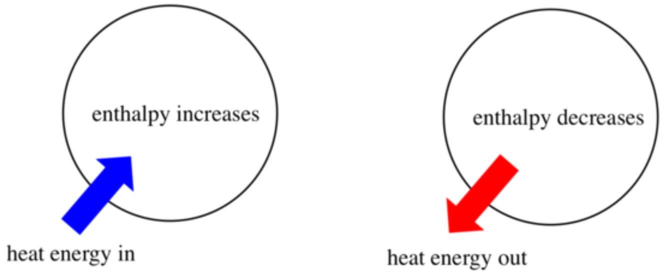
$0.0009\ g$of silver fulminate is 3×10^{-6} moles.

$$(3 \times 10^{-6} mol) \times (401\ kJ/mol) = 0.001\ kJ \tag{3.2.36}$$

Information like this seems to indicate that there might be a "preference" in Nature for reactions in which the enthalpy change is negative---loss of energy seems to breed chemical "stability". Substances which don't meet that criterion tend to react until they do. Or do they?

3.2.1: Enthalpy Changes in Reactions

Thermodynamics is the study of the relationship between heat (or energy) and work. Enthalpy is a central factor in thermodynamics. It is the heat content of a system. The heat that passes into or out of the system during a reaction is the enthalpy change. Whether the enthalpy of the system increases (i.e. when energy is added) or decreases (because energy is given off) is a crucial factor that determines whether a reaction can happen.



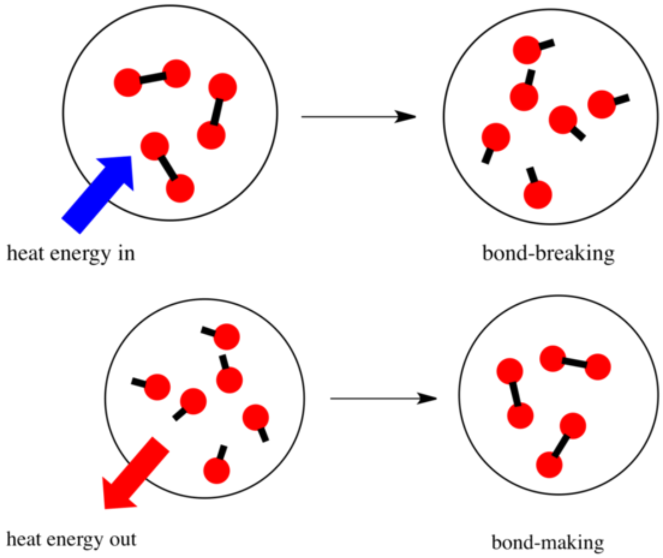
Sometimes, we call the energy of the molecules undergoing change the "internal enthalpy". Sometimes, we call it the "enthalpy of the system." These two phrases refer to the same thing. Similarly, the energy of the molecules that do not take part in the reaction is called the *"external enthalpy*" or the *"enthalpy of the surroundings"*.

Roughly speaking, the energy changes that we looked at in the introduction to thermodynamics were changes in enthalpy. We will see in the next section that there is another energetic factor, entropy, that we also need to consider in reactions. For now, we will just look at enthalpy.

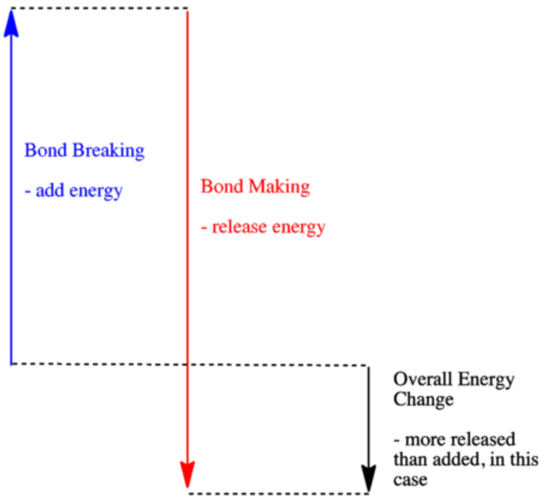
- Enthalpy is the heat content of a system.
- The enthalpy change of a reaction is roughly equivalent to the amount of energy lost or gained during the reaction.
- A reaction is favored if the enthalpy of the system decreases over the reaction.

That last statement is a lot like the description of energetics on the previous page. If a system undergoes a reaction and gives off energy, its own energy content decreases. It has less energy left over if it gave some away. Why does the energy of a set of molecules change when a reaction occurs? To answer that, we need to think about what happens in a chemical reaction.

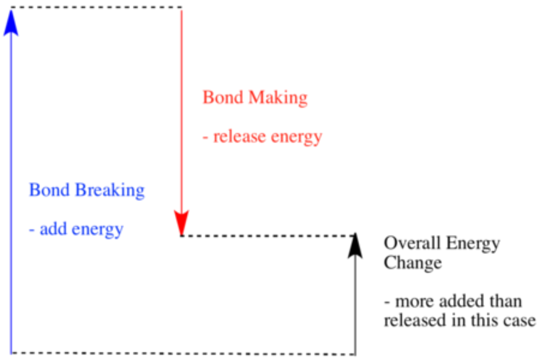
In a reaction, there is a change in chemical bonding. Some of the bonds in the reactants are broken, and new bonds are made to form the products. It costs energy to break bonds, but energy is released when new bonds are made.



Whether a reaction is able to go forward may depend on the balance between these bond-making and bond-breaking steps.



- A reaction is exothermic if more energy is released by formation of new bonds than is consumed by breaking old bonds.
- A reaction is exothermic if weaker bonds are traded for stronger ones.
- A reaction is endothermic if bond-breaking costs more energy than what is provided in bond-making.



Bond energies (the amount of energy that must be added in order to break a bond) are an important factor in determining whether a reaction will occur. Bond strengths are not always easy to predict, because the strength of a bond depends on a number of factors. However, lots of people have done lots of work measuring bond strengths, and they have collected the information in tables, so if you need to know how strong a bond is, you can just look up the information you need.

Bond	Bond Energy (kcal/mol)	Bond	Bond Energy (kcal/mol)
H-H	104	O-H	111
C-C	83	C-H	99
O=O	119	N-H	93
N=N	226	C=O	180

For example, suppose you wanted to know whether the combustion of methane were an exothermic or endothermic reaction. I am going to guess that it's exothermic, because this reaction (and others like it) is used to provide heat for lots of homes by burning natural gas in furnaces.

The "combustion" of methane means that it is burned in air, so that it reacts with oxygen. The products of burning hydrocarbons are mostly carbon dioxide and water. The carbon atom in methane (CH_4) gets incorporated into a carbon dioxide molecule. The hydrogen atoms get incorporated into water molecules. There are four hydrogen atoms in methane, so that's enough to make two molecules of H_2O.

- Four C-H bonds must be broken in the combustion of methane.
- Four new O-H bonds are made when the hydrogens from methane are added into new water molecules.

- Two new C=O bonds are made when the carbon from methane is added into a CO_2 molecule.

The other piece of the puzzle is the oxygen source for the reaction. Oxygen is present in the atmosphere mostly as O_2. Because we need two oxygen atoms in the CO_2 molecule and two more oxygen atoms for the two water molecules, we need a total of four oxygen atoms for the reaction, which could be provided by two O_2 molecules.

- Two O=O bonds must be broken to provide the oxygen atoms for the products.

Altogether, that's four C-H and two O=O bonds broken, plus two C=O and four O-H bonds made. That's 4 x 99 kcal/mol for the C-H bonds and 2 x 119 kcal/mol for the O=O bonds, a total of 634 kJ/mol added. The reaction releases 2 x 180 kcal/mol for the C=O bonds and 4 x 111 kcla/mol for the OH bonds, totaling 804 kcal/mol. Overall, there is 170 kcal/mol more released than is consumed.

That means the reaction is exothermic, so it produces heat. It's probably a good way to heat your home.

Problem TD2.1.

Compare the combustion of ethane to the combustion of methane.

1. Write a reaction for the combustion of ethane, CH_3CH_3, to carbon dioxide and water.
2. How many carbon dioxide molecules would be produced from one molecule of ethane?
3. How many water molecules would be produced from one molecule of ethane?
4. How many oxygen molecules would be needed to provide oxygen atoms to accomplish the steps in questions (b) and (c)?
5. How much energy is consumed / produced by the reaction? Compare this result to the one for methane.

Problem TD2.2.

The Haber-Bosch process is used to make ammonia for fertilizer. It employs the reaction of hydrogen gas (H_2) with atmospheric nitrogen (N_2) in a 3:1 ratio to produce ammonia (NH_3).

1. Write a reaction for the Haber-Bosch process.
2. How many ammonia molecules would be produced from one molecule of nitrogen?
3. How much energy is consumed / produced by the reaction?

Contributors and Attributions

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3.2.2: Enthalpy Changes in Reactions II

This page deals with the basic ideas about energy changes during chemical reactions, including simple energy diagrams and the terms exothermic and endothermic.

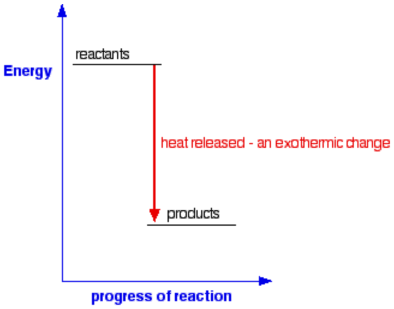
Energy changes during chemical reactions

Obviously, lots of chemical reactions give out energy as heat. Getting heat by burning a fuel is a simple example, but you will probably have come across lots of others in the lab. Other reactions need a continuous supply of heat to make them work. Splitting calcium carbonate into calcium oxide and carbon dioxide is a simple example of this.

Any chemical reaction will involve breaking some bonds and making new ones. Energy is needed to break bonds, and is given out when the new bonds are formed. It is very unlikely that these two processes will involve exactly the same amount of energy - and so some energy will either be absorbed or released during a reaction.

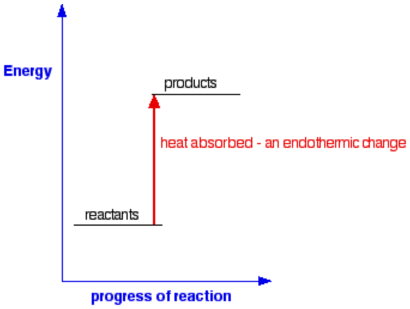
- A reaction in which heat energy is given off is said to be exothermic.
- A reaction in which heat energy is absorbed is said to be endothermic.

You can show this on simple energy diagrams. For an exothermic change:



Notice that in an exothermic change, the products have a lower energy than the reactants. The energy that the system loses is given out as heat. The surroundings warm up.

For an endothermic change:



This time the products have a higher energy than the reactants. The system absorbs this extra energy as heat from the surroundings.

Expressing exothermic and endothermic changes in numbers

Here is an exothermic reaction, showing the amount of heat evolved:

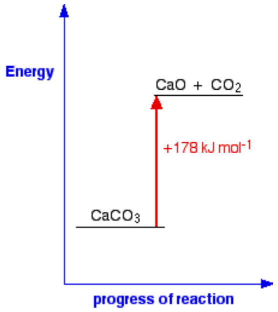
$$C + O_2 \rightarrow CO_2 \quad \Delta H = -394 \text{kJ}\, mol^{-1} \tag{3.2.2.1}$$

This shows that 394 kJ of heat energy are evolved when equation quantities of carbon and oxygen combine to give carbon dioxide. The mol^{-1} (per mole) refers to the whole equation in mole quantities. How do you know that heat is evolved? That is shown by the negative sign.

You always think of the energy change during a reaction from the point of view of the reactants. The reactants (carbon and oxygen) have lost energy during the reaction. When you burn carbon in oxygen, that is the energy which is causing the surroundings to get hotter. And here is an endothermic change:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = +178 \text{kJ}\, mol^{-1} \tag{3.2.2.2}$$

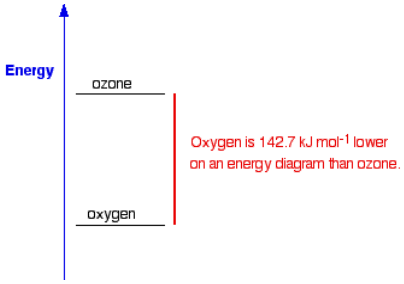
In this case, 178 kJ of heat are absorbed when 1 mole of calcium carbonate reacts to give 1 mole of calcium oxide and 1 mole of carbon dioxide. You can tell that energy is being absorbed because of the plus sign. A simple energy diagram for the reaction looks like this:



The products have a higher energy than the reactants. Energy has been gained by the system - hence the plus sign. Whenever you write values for any energy change, you must always write a plus or a minus sign in front of it.

Energetic Stability

Chemists often express statements that something is energetically more stable than something else. For example, that oxygen, O_2, is more energetically stable than ozone, O_3. What does this mean? If you plot the positions of oxygen and ozone on an energy diagram, it looks like this:



The lower down the energy diagram something is, the more energetically stable it is. If ozone converted into ordinary oxygen, heat energy would be released, and the oxygen would be in a more energetically stable form than it was before. So why does not ozone immediately convert into the more energetically stable oxygen?

Similarly, if you mix gasoline and air at ordinary temperatures (when you are filling up a car, for example), why does not it immediately convert into carbon dioxide and water? It would be much more energetically stable if it turned into carbon dioxide and water - you can tell that, because lots of heat is given out when gasoline burns in air. But there is no reaction when you mix the two.

For any reaction to happen, bonds have to be broken, and new ones made. Breaking bonds takes energy. There is a minimum amount of energy needed before a reaction can start - activation energy. If the molecules don't, for example, hit each other with enough energy, then nothing happens. We say that the mixture is kinetically stable, even though it may be energetically unstable with respect to its possible products.

So a gasoline/air mixture at ordinary temperatures does not react, even though a lot of energy would be released if the reaction took place. gasoline and air are energetically unstable with respect to carbon dioxide and water - they are much higher up the energy diagram. But a gasoline and air mixture is kinetically stable at ordinary temperatures, because the activation energy barrier is too high.If you expose the mixture to a flame or a spark, then you get a major fire or explosion. The initial flame supplies activation energy. The heat given out by the molecules that react first is more than enough to supply the activation energy for the next molecules to react - and so on.

The moral of all this is that you should be very careful using the word "stable" in chemistry!

Contributors and Attributions

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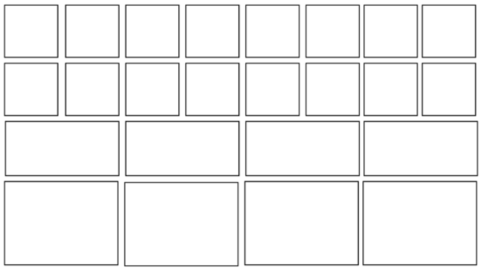
3.2.3: Entropy Changes in Reactions

Entropy is another important aspect of thermodynamics. Enthalpy has something to do with the energetic content of a system or a molecule. Entropy has something to do with how that energy is stored. We sometimes speak of the energy in a system as being "partitioned" or divided into various "states". How this energy is divided up is the concern of entropy.

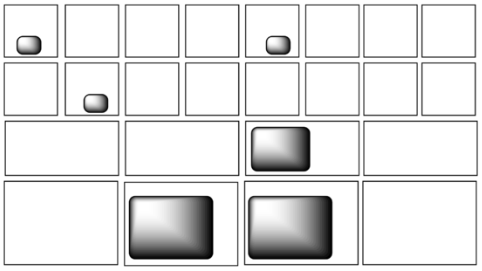
By way of analogy, picture a set of mailboxes. You may have a wall of them in your dormitory or your apartment building. The mailboxes are of several different sizes: maybe there are a few rows of small ones, a couple of rows of medium sized ones, and a row of big mailboxes on the bottom.



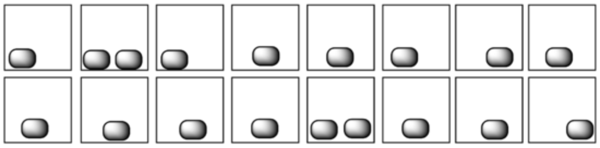
Instead of putting mail in these boxes, we're going to use them to hold little packages of energy. Later on, you might take the energy packages out of your own mailbox and use them to take a trip to the mall or the gym. But how does the mail get to your mailbox in the first place?

The energy packages don't arrive in your molecular dormitory with addresses on them. The packages come in different sizes, because they contain different amounts of energy, but other than that there is no identifying information on them.

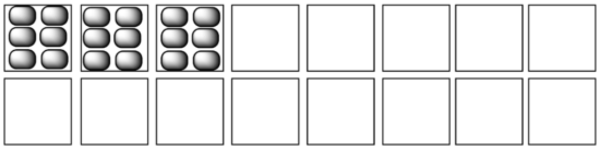
Some of the packages don't fit into some of the mailboxes, because some of the packages are too big and some of the mailboxes are smaller than the others. The energy packages need to go into mailboxes that they will fit into.



Still, there are an awful lot of mailboxes that most of the energy packages could still fit into. There needs to be some system of deciding where to put all of these packages. It turns out that, in the molecular world, there is such a system, and it follows a pretty simple rule. When a whole pile of energy packages arrive, the postmaster does her best to put one package into every mailbox. Then, when every mailbox has one, she starts putting a second one into each box, and so on.



It didn't have to be that way. It could have been the case that all the energy was simply put into the first couple of mailboxes and the rest were left empty. In other words, the rule could have been that all the energy must be sorted into the same place, instead of being spread around. But that's not how it is.



- Energy is always partitioned into the maximum number of states possible.

Entropy is the sorting of energy into different modes or states. When energy is partitioned or sorted into additional states, entropy is said to increase. When energy is bundled into a smaller number of states, entropy is said to decrease. Nature's bias is towards an increase in entropy.

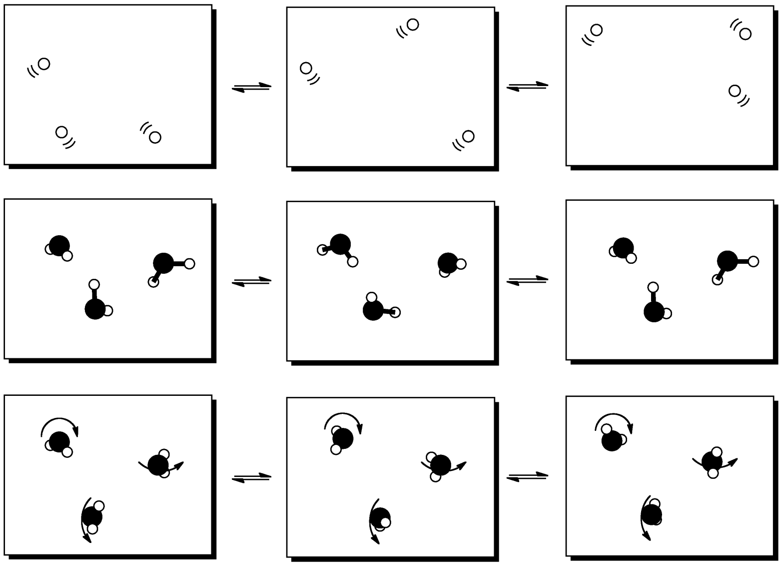
This is a fundamental law of the universe; there is no reason that can be used to explain why nature prefers high entropy to low entropy. Instead, increasing entropy is itself the basic reason for a wide range of things that happen in the universe.

Entropy is popularly described in terms of "disorder". That can be a useful idea, although it doesn't really describe what is happening energetically.

A better picture of entropy can be built by looking at how a goup of molecules might sort some energy that is added to them. In other words, what are some examples of "states" in which energy can be sorted?

If you get more energy -- maybe by eating breakfast -- one of the immediate benefits is being able to increase your physical activity. You have more energy to move around, to run, to jump. A similar situation is true with molecules.

Molecules have a variety of ways in which they can move, if they are given some energy. They can zip around; this kind of motion is usually called translation. They can tumble and roll; this kind of motion is referred to as rotation. Also, they can wiggle, letting their bonds get longer and shorter by moving individual atoms around a little bit. This type of motion is called vibration.

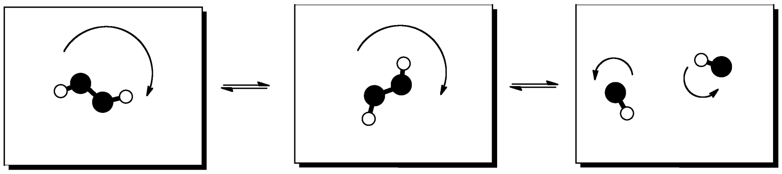


When molecules absorb extra energy, they may be able to sort the energy into rotational, vibrational and translational states. This only works with energy packages of a certain size; other packages would be sorted into other kinds of states. However, these are just a few examples of what we mean by states.

Okay, so energy is stored in states, and it is sorted into the maximum possible number of states. But how does entropy change in a reaction? We know that enthalpy may change by breaking or forming certain bonds, but how does the energy get sorted again?

The changes in internal entropy during a reaction are often very small. In other words, the energy remaining at the end of the reaction gets sorted more or less the way it was before the reaction. However, there are some very common exceptions.

The most common case in which internal entropy changes a lot is when the number of molecules involved changes between the start of the reaction and the end of the reaction. Maybe two molecules react together to form one, new molecule. Maybe one molecule splits apart to make two, new molecules.



If one molecule splits apart in the reaction, entropy generally increases. Two molecules can rotate, vibrate and translate (or tumble, wiggle and zip around) independently of each other. That means the number of states available for partitioning energy increases when one molecule splits into two.

- Entropy generally increases when a reaction produces more molecules than it started with.
- Entropy generally decreases when a reaction produces fewer molecules than it started with.

Apart from a factor like a change in the number of molecules involved, internal entropy changes are often fairly subtle. They are not as easy to predict as enthalpy changes.

Nevertheless, there may sometimes be a trade-off between enthalpy and entropy. If a reaction splits a molecule into two, it seems likely that an increase in enthalpy will be involved, so that the bond that held the two pieces together can be broken. That's not favourable. However, when that happens, we've just seen that there will be an increase in entropy, because energy can then be sorted into additional modes in the two, independent molecules.

So we have two different factors to balance. There is a tool we often use to decide which factor wins out. It's called free energy, and we will look at it next.

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3.2.4: Free Energy and Equilibrium

The balance between reactants and products in a reaction will be determined by the free energy difference between the two sides of the reaction. The greater the free energy difference, the more the reaction will favor one side or the other. The smaller the free energy difference, the closer the mixture will get to equal parts reactants and products (loosely speaking).

Exactly where the balance lies in an equilibrium reaction is described by the equilibrium constant. The equilibrium constant is just the ratio of products to reactants, once the reaction has settled to equilibrium. That's the point at which the forward and reverse reactions are balanced, so that the ratio of products to reactants is unchanging.

- A reaction has reached equilibrium when the reaction has stopped progressing (i.e., no change in concentrations although at a microscopic level both forward and reverse reactions occur), so that the amount of reactants that have turned into products remains constant, and the amount of reactants left over stays constant.
- The equilibrium constant is the ratio of products to reactants when the reaction has reached equilibrium.

The equilibrium constant could be a large number (like a thousand). That means that there are much more products than reactants at equilibrium. It could also be a very small fraction (like one millionth). That would indicate that the reaction does not proceed very far, producing only a tiny amount of products at equilibrium.

- Every reaction has an equilibrium constant
- A very large equilibrium constant (in the millions or billions) means the reaction goes "to completion", with all reactants essentially converted into products
- A tiny equilibrium (very close to zero) constant means the reaction hardly moves forward at all.
- A modest equilibrium constant (close to one, or as close to one as numbers like 0.01 or 100) is considered to be a true equilibrium reaction, in which there is a significant amount of both products and reactants.

The equilibrium constant is related to the free energy change of the reaction by the expression:

$$K = e^{-\Delta G/RT} \tag{3.2.4.1}$$

or

$$\ln K = -\frac{\Delta G}{RT} \tag{3.2.4.2}$$

in which T is the temperature in Kelvin and R is the "gas constant" (1.986 cal/K mol). Remember, e is just a number that occurs frequently in mathematical relationships in nature (sort of like π); it has a value of about 2.718. This expression for K does make some assumptions about the conditions that we won't worry about; we are using a slightly simplified model.

Relating Gibbs energy and the equilibrium

Let's look at the form of this relationship between free energy and the equilibrium constant. First, we will see how we deal with endergonic versus exergonic reactions. The free energy changes in opposite directions in these two cases, and we usually deal with opposites by giving one quantity a positive sign and one quantity a negative sign. A reaction in which the free energy increases is given a positive value for its free energy. On the other hand, if free energy decreases over the course of the reaction, we show that by using a negative number for the value of the free energy.

If ΔG is negative, the exponent in the relationship becomes positive (because it is multiplied by -1 in the expression). Since e to a positive power will usually be a number greater than one, the relationship suggests there are more products than reactants. That's good, because the reaction is exergonic, and we expect the reaction to go forward. What's more, the larger the value of ΔG, the more product-favored the reaction will be.

- $10^{\text{large number}}$ is a large number.
- $10^{\text{small number}}$ is a smaller number.

However, if ΔG is a positive number, then the exponent in the relationship becomes negative. An number with a negative exponent, by the rules of exponents, is the same as the inverse of the number with a positive exponent of the same size.

In other words, $10^{-2} = 1 / 10^2$.

- $10^{\text{negative number}}$ is a fraction.

That means if ΔG is positive, the equilibrium constant becomes a fraction. That's because that positive value of ΔG is multiplied by -1 in the expression, becoming negative, and then it's placed in the exponent. That's good, because a positive value of ΔG corresponds to an endergonic reaction, which does not favor product formation.

Other factors

There are other factors in the expression relating ΔG to the equilibrium constant. One of them, R, is just a "fudge factor"; it's the number that, when placed in the expression, makes the relationship agree with reality.

Moreover, it is a constant, so it does not change. However, the other factor is temperature, which does change. That means that the equilibrium constant **may** change with different temperatures. Overall, the effect of temperature is to make the exponent in the expression a smaller number. That's because the free energy is divided by the temperature and the gas constant; the resulting number becomes the exponent in the relationship. At the extreme, a high temperature could make the exponent into a very, very small number, something close to zero. What happens then?

- $10^0 = 1$
- $e^0 = 1$

As the exponent gets smaller and smaller, the equilibrium constant could approach 1. That means there would be more or less equal amounts of products and reactants in our simplified approach.

However, the fact that there is a temperature factor in the expression for ΔG itself means that there is a limit to how small K will get as the temperature increases. At some point, the two values for temperature cancel out altogether and the expression becomes K = e (ΔS/R). At that point, the equilibrium constant is independent of temperature and is based only on internal entropy differences between the two sides of the reaction.

This relationship is useful because of its predictive value. Qualtitatively, it confirms ideas we had already developed about thermodynamics.

- Highly exergonic reactions (large, negative/decreasing ΔG) favor products.
- Highly endergonic reactions (large, positive/increasing ΔG) favor reactants.
- Reactions with small free energy changes lead to equilibrium mixtures of both products and reactants.

Problems

TD6.1. Arrange the following series of numbers from the largest quantity to the smallest, from left to right.

A. 10^5 10^4 10^6
B. 2^3 2^6 2^2
C. 3^3 3^0 3^2
D. e^2 e^1 e^4
E. 10^{-1} 10^{-5} 10^{-3}
F. 1 / 10 1 / 25 1 / 50
G. $2^{0.5}$ $2^{0.1}$ $2^{0.9}$

Problem TD6.2. Given the following free energy differences, arrange the corresponding equilibrium constants from largest to smallest.

A. 25 kcal/mol 17 kcal/mol 9 kcal/mol
B. 16 kcal/mol 19 kcal/mol 21 kcal/mol
C. 7 kcal/mol 22 kcal/mol 13 kcal/mol
D. -17 kcal/mol -3 kcal/mol -8 kcal/mol
E. -17 kcal/mol 3 kcal/mol -8 kcal/mol

Problem TD6.3: What is the value of the equilibrium constant at 300K in the following cases? (1 kcal = 1000 cal)

A. ΔG = 3 kcal /mol
B. ΔG = -2 kcal/mol
C. ΔG = -5 kcal /mol
D. ΔG = 15 kcal/mol
E. ΔG = -10 kcal/mol

F. The free energy increases by 8 kcal/mol over the reaction.
G. The free energy decreases by 1 kcal/mol over the reaction.

Problem TD6.4. In which of the cases in TD6.3. do you think there would be significant amounts of both products and reactants at equilibrium?

Problem TD6.5. The mathematical expression for the equilibrium constant says that K will get smaller at higher temperatures. Explain this phenomenon without the mathematical expression in terms of what you know about temperature and energy.

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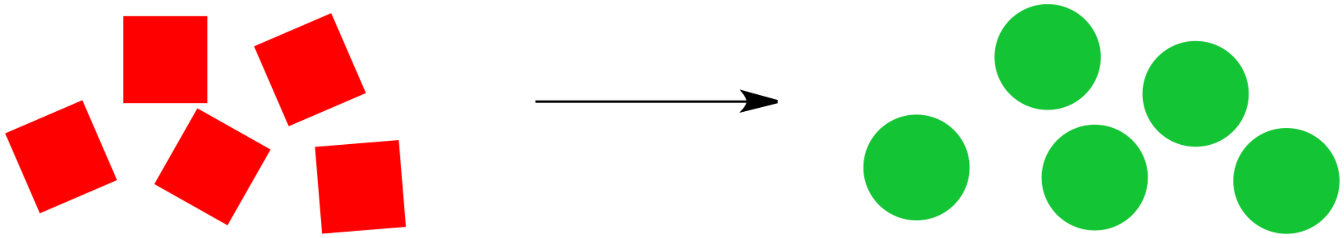
3.2.5: Free Energy Changes in Reactions

Entropy and enthalpy are two of the basic factors of thermodynamics. Enthalpy has something to do with the energetic content of a system or a molecule. Entropy has something to do with how that energy is stored.

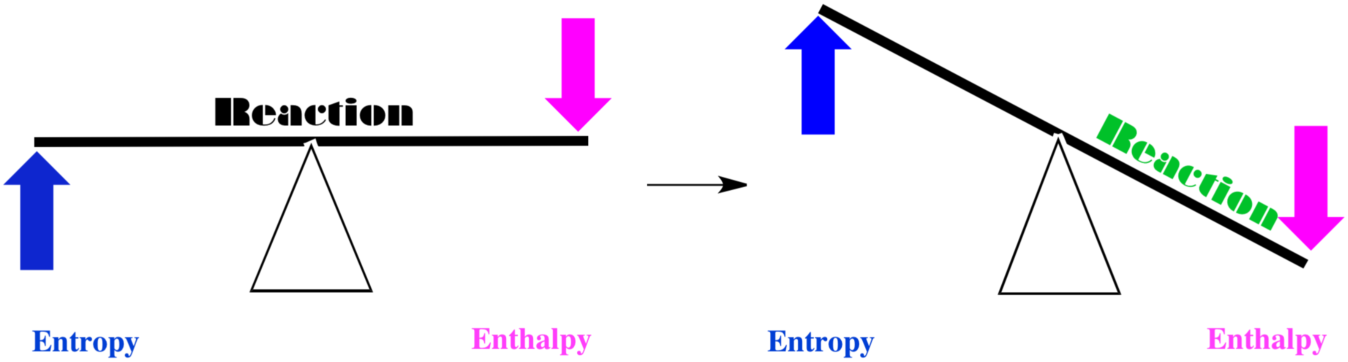
- **A reaction is favored if enthalpy decreases:** There is a bias in nature toward decreasing enthalpy in a system. Reactions can happen when enthalpy is transferred to the surroundings.
- **A reaction is favored if entropy increases:** There is also a bias in nature toward increasing entropy in a system. Reactions can happen when entropy increases.

Consider the cartoon reaction below. Red squares are being converted to green circles, provided the reaction proceeds from left to right as shown.

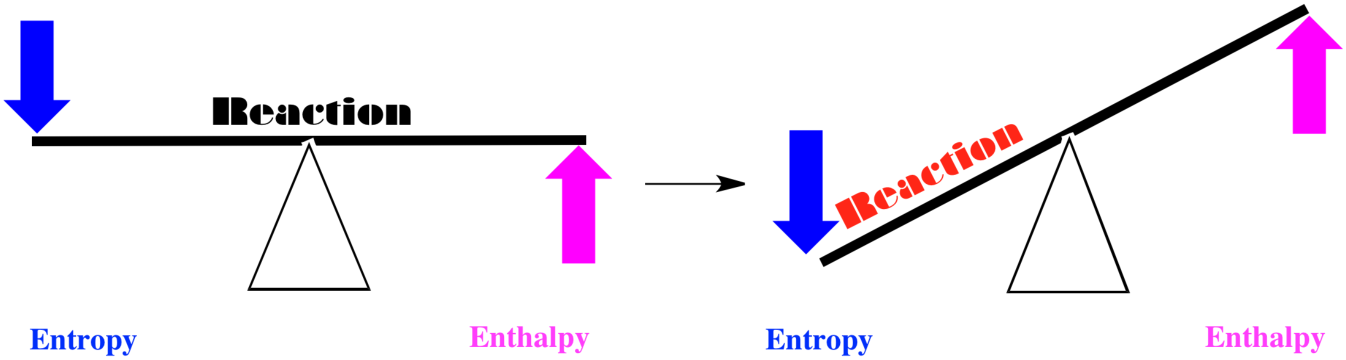


Whether or not the reaction proceeds to the right depends on the balance between enthalpy and entropy. There are several combinations possible.

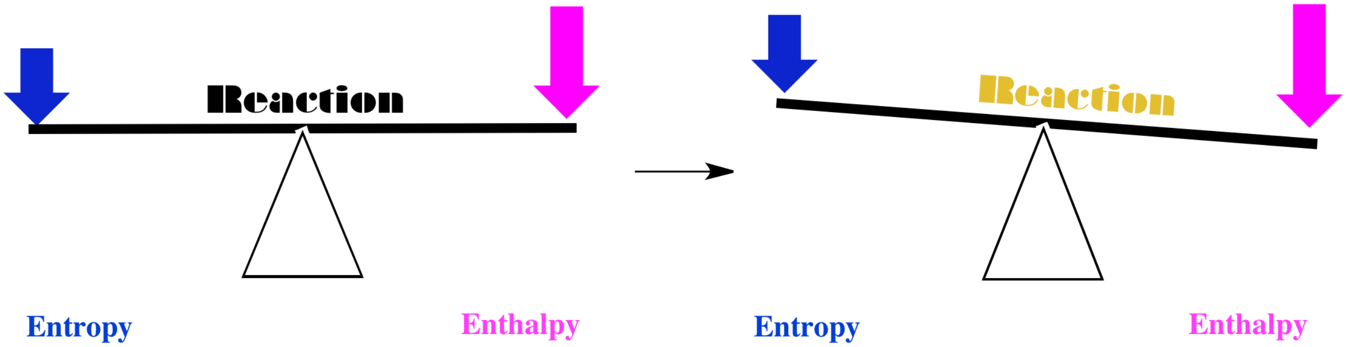
In one case, maybe entropy increases when the red squares turn into green circles, and the enthalpy decreases. If we think of the balance between these two factors, we come to a simple conclusion. Both factors tilt the balance of the reaction to the right. In this case, the red squares will be converted into green circles.



Alternatively, maybe entropy decreases when the red squares turn into green circles, and enthalpy increases. If we think of the balance between these two factors, we come to another simple conclusion. Both factors tilt the balance of the reaction to the left. In this case, the red squares will remain just as they are.



Having two factors may lead to complications. For example, what if enthalpy decreases, but so does entropy? Does the reaction happen, or doesn't it? In that case, we may need quantitation to make a decision. How much does the enthalpy decrease? How much does the entropy decrease? If the effect of the enthalpy decrease is greater than that of the entropy decrease, the reaction may still go forward.



The combined effects of enthalpy and entropy are often combined in what is called "free energy." Free energy is just a way to keep track of the sum of the two effects. Mathematically, the symbol for the internal enthalpy change is "ΔH" and the symbol for the internal entropy change is "ΔS." Free energy is symbolized by "ΔG," and the relationship is given by the following expression:

$$\Delta G = \Delta H - T\Delta S \tag{3.2.5.1}$$

T in this expression stands for the temperature (in Kelvin, rather than Celsius or Fahrenheit). The temperature acts as a scaling factor in the expression, putting the entropy and enthalpy on equivalent footing so that their effects can be compared directly.

How do we use free energy? It works the same way we were using enthalpy earlier (that's why the free energy has the same sign as the enthalpy in the mathematical expression, whereas the entropy has an opposite sign). If free energy decreases, the reaction can proceed. If the free energy increases, the reaction can't proceed.

- A reaction is favored if the free energy of the system decreases.
- A reaction is not favored if the free energy of the system increases.

Because free energy takes into consideration both the enthalpy and entropy changes, we don't have to consider anything else to decide if the reaction occurs. Both factors have already been taken into account.

Remember the terms "endothermic" and "exothermic" from our discussion of enthalpy. Exothermic reactions were favored (in which enthalpy decreases). Endothermic ones were not. In free energy terms, we say that exergonic reactions are favored(in which free energy decreases). Endergonic ones (in which free energy increases) are not.

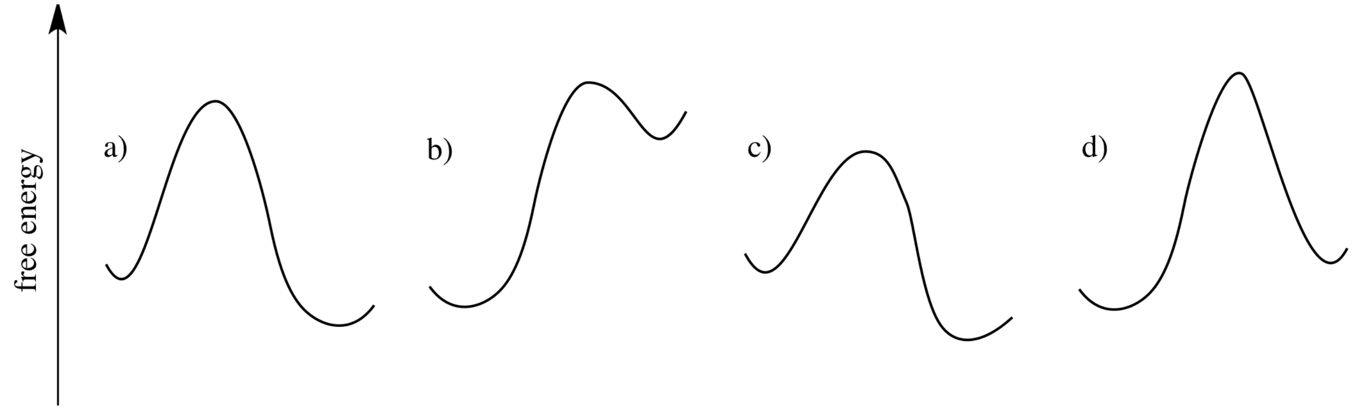
Problem TD4.1.

Imagine a reaction in which the effects of enthalpy and entropy are opposite and almost equally balanced, so that there is no preference for whether the reaction proceeds or not. Looking at the expression for free energy, how do you think the situation will change under the following conditions:

1. the temperature is very cold (0.09 K)
2. the temperature is very warm (500 K)

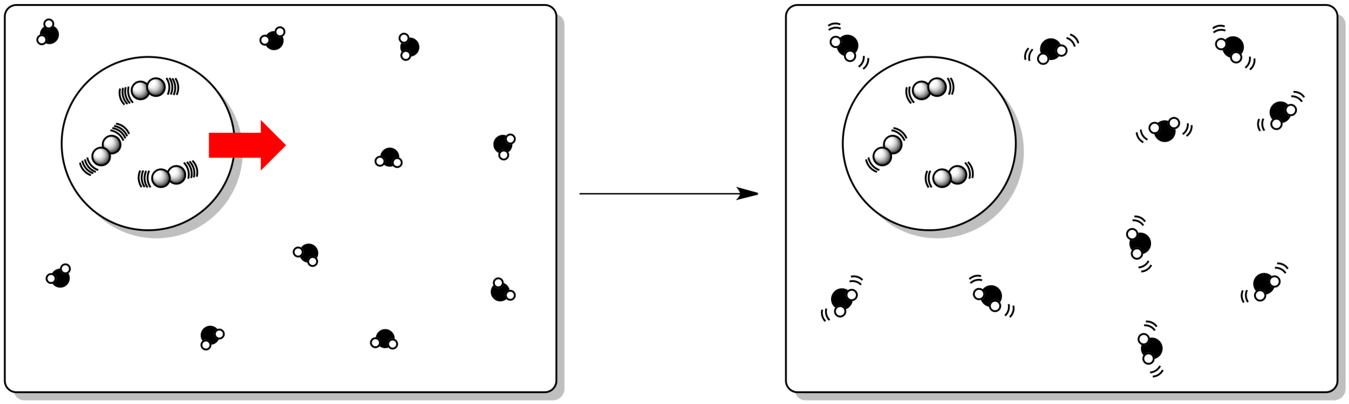
Problem TD4.2.

Which of the following reaction profiles describe reactions that will proceed? Which ones describe reactions that will not proceed?



How Entropy Rules Thermodynamics

Sometimes it is said that entropy governs the universe. As it happens, enthalpy and entropy changes in a reaction are partly related to each other. The reason for this relationship is that if energy is added to or released from the system, it has to be partitioned into new states. Thus, an enthalpy change can also have an effect on entropy.

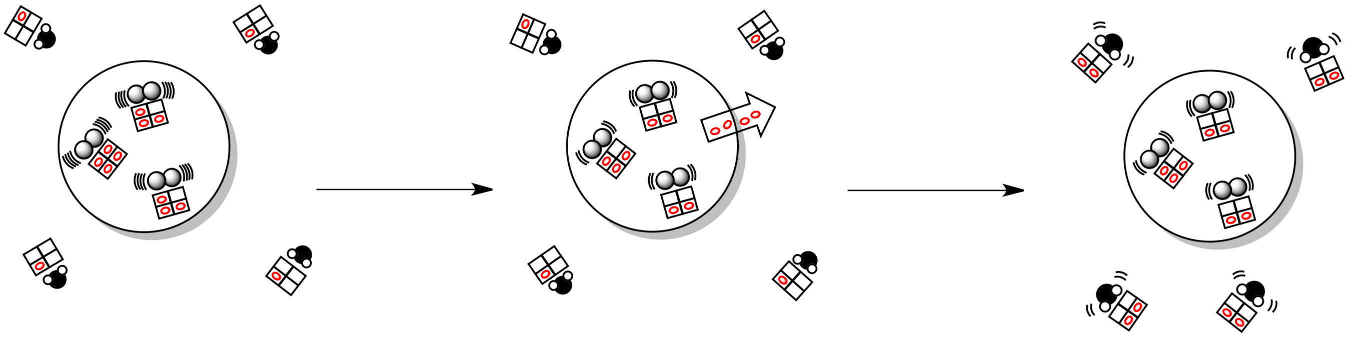


Specifically, the internal enthalpy change that we discussed earlier has an effect on the entropy of the surroundings. So far, we have just considered internal entropy changes.

- In an exothermic reaction, the external entropy (entropy of the surroundings) increases.
- In an endothermic reaction, the external entropy (entropy of the surroundings) decreases.

Free energy takes into account both the entropy of the system and the entropy changes that arise because of heat exchange with the surroundings. Together, the system and the surroundings are called "the universe". That's because the system is just everything involved in the reaction, and the surroundings are everything that isn't involved in the reaction.

Enthalpy changes in the system lead to additional partitioning of energy. We might visualize that with the mailbox analogy we used for entropy earlier. In this case, each molecule has its own set of mailboxes, into which it sorts incoming energy.



Looked at in this way, thermodynamics boils down to one major consideration, and that is the combined entropy of both the system and its surroundings (together known as the universe).

- For a reaction to proceed, the entropy of the universe must increase.

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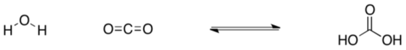
3.2.6: Reversibility and Le Chatelier

Sometimes, there is not a big difference in energy between reactants and products of a reaction. What happens then? Does the reaction go forward, because it will not cost a lot of energy? Or does it not proceed, because there isn't enough driving force? For example, one simple reaction that occurs all the time is the reaction of water with carbon dioxide. This is a reaction that happens when carbon dioxide dissolves in lakes, rivers and oceans. It even happens in your own bloodstream.



Water reacts with carbon dioxide to form carbonic acid. However, carbonic acid also decomposes spontaneously in water. It reacts to form carbon dioxide and water.

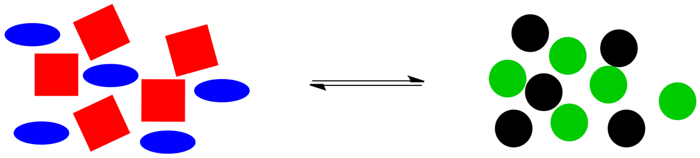
In other words, this is a reaction that can go either direction. It can go forwards or backwards. It is an example of an equilibrium reaction. An equilibrium reaction is one that is energetically balanced, so that it really isn't favored to go in either direction. Equilibrium reactions are extremely important in nature, partly because of the forward and reverse capabilities that they offer. In essence, they are reactions with an "undo" button. The reaction can proceed in one direction when needed, and it can proceed in the other direction when needed.

However, there are some inherent limitations involved. Frequently, equilibrium reactions only proceed "partway". That is, a group of molecules will start to produce products. However, at some point those products will begin reverting to the starting materials again. Eventually the system will settle out as a mixture of reactants and products.

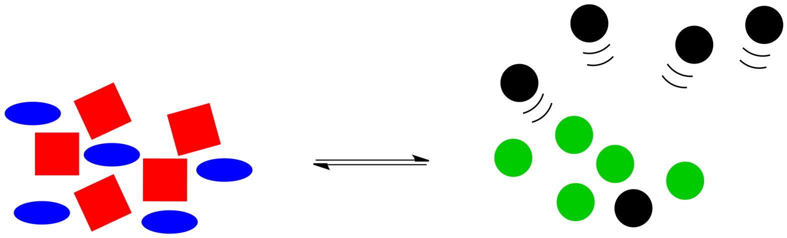
What if it's really important that we have the products of the reaction at one point, with none of the reactants? And if later on we need the reactants, but not any of the products? It would be useful if there were a way to control the direction of an equilibrium reaction, so that we could "push" it to one side or the other.

Control of equilibrium reactions can be remarkably simple. It follows a rule that was observed by Henri le Châtelier (ah-REE luh shah-tell-YAY), a French industrial chemist, around 1900. Le Chatelier noticed that equilibrium reactions often shift direction if the conditions of the reaction are changed. In general, adding any product of the reaction shifts the balance back toward the reactants. If any product of the reaction is added, the reaction makes more starting materials. Thus, adding more carbonic acid to a carbon dioxide - water - carbonic acid mixture would result in reverse reaction, producing more water and carbon dioxide. Adding more carbon dioxide, on the other hand, would lead to production of more carbonic acid.

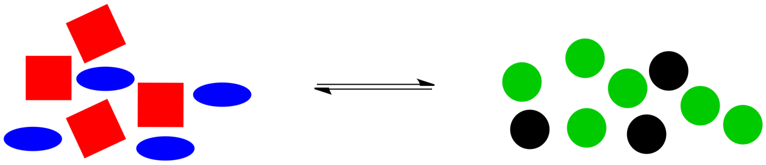
Here is a cartoon illustration of "le Châtelier's Principle" at work. Suppose red squares and blue ovals can react together to make black circles and green circles. Maybe there is a natural equilibrium in this reaction, so that the two piles of shapes are roughly equal in size.



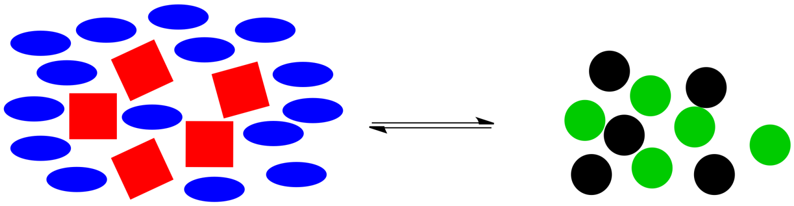
What would happen if something knocked this system off balance? For example, maybe black circles are highly elusive, and they just wander away as soon as they are formed. The system won't be in equilibrium anymore, because without those black circles, the balance will be upset, with not enough things on the right side for the number of things on the left.



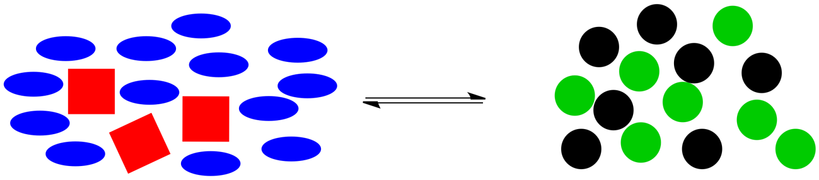
Le Chatelier noticed that nature automatically corrects for such changes. If some of the black circles disappear, the reaction will kick into action again, using up some red squares and blue ellipses to produce more green and black circles. The exact numbers of shapes won't return to exactly the same as before, because some of the black circles have still gone missing, but the system will have shifted to use up more reactants on the left and to produce more products on the right, so that the overall ratio between right and left is restored.



Alternatively, maybe we found a way to make the black circles stay where they are. Instead, we have dumped in a bunch of extra blue ellipses. Once again, the system is knocked off balance. This time, there is too much stuff on the left, compared to the amount on the right side.

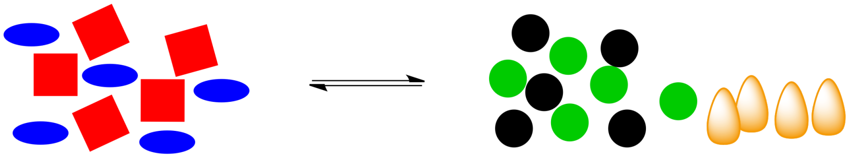


The reaction goes into action again. It uses up some of those extra blue ellipses (and, at the same time, some of the red squares) to produce more black and green circles, bringing the system back to the original ratio of right side shapes to left side shapes.

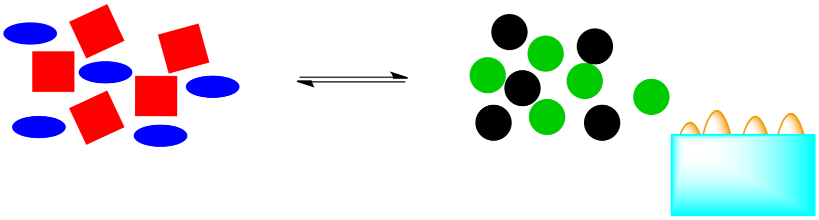


In general, if molecules are added to a system, the reaction will shift to bring the system back into equilibrium. If molecules are removed from the system, the reaction will also shift to bring the system back into equilibrium. Furthermore, because heat can be consumed by (or produced by) reactions, temperature can sometimes be used to shift equilibria. If a reaction is exothermic, heat is a product of the reaction. Adding more heat will result in the reaction shifting to produce more reactants. Cooling the reaction (removing heat) would do the opposite: the reaction would shift to produce more heat, and more products.

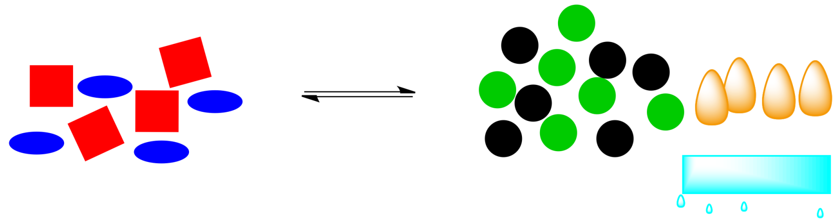
In the cartoon, we have a shape-shifting reaction again, but this time the reaction releases energy (those are orange flames, symbolic of the heat produced).



What happens if that energy is removed? For example, if heat is removed through addition of a pale blue ice cube, what will be the effect on the system?



Those orange energy shapes (the "flames") were a part of the system. If they are removed, the system will have to shift in order to restore them. If the reaction pushes to the right again, more energy will be released, bringing the system back into equilibrium.



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3.3: Describing a Reaction - Energy Diagrams and Transition States

Objectives

After completing this section, you should be able to

- sketch the reaction energy diagram for a single-step reaction, given some indication of whether the reaction is fast or slow, exothermic or endothermic.
- interpret the reaction energy diagram for a single-step process (e.g., use the diagram to decide whether the reaction is exothermic or endothermic).
- suggest possible transition-state structures for simple one-step processes.
- assess the likelihood of a reaction occurring at room temperature, given the value of the activation energy $\Delta G^{\ddagger}$.

Key Terms

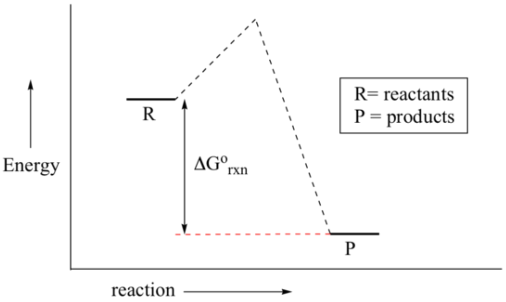
Make certain that you can define, and use in context, the key terms below.

- activation energy, $\Delta G^{\ddagger}$
- reaction energy diagram
- transition state

Study Notes

You may have been taught to use the term “activated complex” rather than “transition state,” as the two are often used interchangeably. Similarly, the activation energy of a reaction is often represented by the symbol E_{act} or E_{a}.

You may recall from general chemistry that it is often convenient to describe chemical reactions with energy diagrams. In an energy diagram, the vertical axis represents the overall energy of the reactants, while the horizontal axis is the ‘reaction coordinate’, tracing from left to right the progress of the reaction from starting compounds to final products. The energy diagram for a typical one-step reaction might look like this:



Despite its apparent simplicity, this energy diagram conveys some very important ideas about the thermodynamics and kinetics of the reaction. Recall that when we talk about the **thermodynamics** of a reaction, we are concerned with the difference in energy between reactants and products, and whether a reaction is ‘downhill’ (exergonic, energy releasing) or ‘uphill (endergonic, energy absorbing). When we talk about **kinetics**, on the other hand, we are concerned with the *rate* of the reaction, regardless of whether it is uphill or downhill thermodynamically.

First, let’s review what this energy diagram tells us about the thermodynamics of the reaction illustrated by the energy diagram above. The energy level of the products is *lower* than that of the reactants. This tells us that the change in standard Gibbs Free Energy for the reaction ($\Delta G^{\circ}_{\text{rnx}}$) is negative. In other words, the reaction is exergonic, or ‘downhill’. Recall that the $\Delta G^{\circ}_{\text{rnx}}$ term encapsulates both $\Delta H^{\circ}_{\text{rnx}}$, the change in enthalpy (heat) and $\Delta S^{\circ}_{\text{rnx}}$, the change in entropy (disorder):

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where T is the absolute temperature in Kelvin. For chemical processes where the entropy change is small (~0), the enthalpy change is essentially the same as the change in Gibbs Free Energy. Energy diagrams for these processes will often plot the enthalpy (H) instead of Free Energy for simplicity.

The standard Gibbs Free Energy change for a reaction can be related to the reaction's equilibrium constant (\(K_{eq}_) by a simple equation:

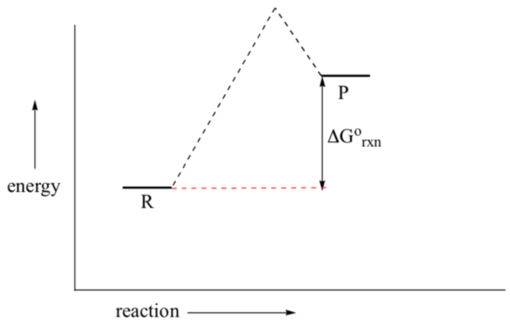
$$\Delta G^\circ = -RT \ln K_{eq}$$

where:

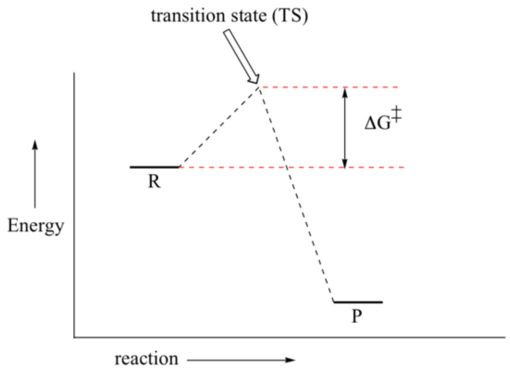
- K_{eq} = [product] / [reactant] at equilibrium
- R = 8.314 $J \times K^{-1} \times mol^{-1}$ *or* 1.987 $cal \times K^{-1} \times mol^{-1}$
- T = temperature in Kelvin (K)

If you do the math, you see that a negative value for ΔG°_{rnx} (an exergonic reaction) corresponds - as it should by intuition - to K_{eq} being greater than 1, an equilibrium constant which favors product formation.

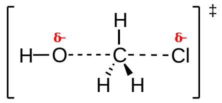
In a hypothetical endergonic (energy-absorbing) reaction the products would have a higher energy than reactants and thus ΔG°_{rnx} would be positive and K_{eq} would be less than 1, favoring reactants.



Now, let's move to kinetics. Look again at the energy diagram for exergonic reaction: although it is ‘downhill’ overall, it isn’t a straight downhill run.



First, an ‘energy barrier’ must be overcome to get to the product side. The height of this energy barrier, you may recall, is called the ‘**activation energy’** ($\Delta G^\ddagger$). The activation energy is what determines the kinetics of a reaction: the higher the energy hill, the slower the reaction. At the very top of the energy barrier, the reaction is at its **transition state** (TS), which is the point at which the bonds are in the process of breaking and forming. The transition state is an ‘**activated complex’**: a transient and dynamic state that, unlike more stable species, does not have any definable lifetime. It may help to imagine a transition state as being analogous to the exact moment that a baseball is struck by a bat. Transition states are drawn with dotted lines representing bonds that are in the process of breaking or forming, and the drawing is often enclosed by brackets. Here is a picture of a likely transition state for a substitution reaction between hydroxide and chloromethane:



Note that this species is absent from the chemical equation (that is it is neither a reactant nor product)

$$\mathrm{CH_3Cl + HO^- \rightarrow CH_3OH + Cl^-}$$

This reaction involves a collision between *two* molecules: for this reason, we say that it has **second order kinetics**. The **rate expression** for this type of reaction is:

$$\text{rate} = k[\text{reactant 1}][\text{reactant 2}]$$

... which tells us that the rate of the reaction depends on the **rate constant** k as well as on the concentration of *both* reactants. The rate constant can be determined experimentally by measuring the rate of the reaction with different starting reactant concentrations. The rate constant depends on the activation energy, of course, but also on temperature: a higher temperature means a higher *k* and a faster reaction, all else being equal. This should make intuitive sense: when there is more heat energy in the system, more of the reactant molecules are able to get over the energy barrier.

Here is one more interesting and useful expression. Consider a simple reaction where the reactants are A and B, and the product is AB (this is referred to as a **condensation reaction**, because two molecules are coming together, or condensing). If we know the rate constant k for the forward reaction and the rate constant $k_{reverse}$ for the reverse reaction (where AB splits apart into A and B), we can simply take the quotient to find our equilibrium constant K_{eq}:

$$A + B \rightleftharpoons AB$$

with

$$K_{eq} = \frac{[AB]}{[A][B]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$$

This too should make some intuitive sense; if the forward rate constant is higher than the reverse rate constant, equilibrium should lie towards products.

3.3.1: Potential Energy Surfaces

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths), the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concepts that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy. This creates a smooth energy “landscape” and chemistry can be viewed from a topology perspective (of particles evolving over "valleys""and passes").

Potential Energy Curves (1-D Potential Energy Surfaces)

The PES is the energy of a molecule as a function of the positions of its nuclei r. This energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning “no interaction”. At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond.

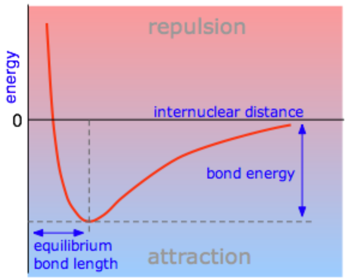


Figure $3.3.1.1$: A potential Energy Curve for a covalent bond.

The internuclear distance at which the potential energy minimum occurs defines the **bond length**. This is more correctly known as the *equilibrium* bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of *RT*, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the *van Der Waals force* that holds argon atoms together in its liquid and solid forms.

Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy Quantum theory tells us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two: $E = V + K$. The relation between them is surprisingly simple: $K = -0.5V$. This means that when a chemical bond forms (an exothermic process with $\Delta E < 0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $-\Delta E$ has half the magnitude of the fall in potential energy.

Mathematical definition and computation

The geometry of a set of atoms can be described by a vector, r, whose elements represent the atom positions. The vector r could be the set of the Cartesian coordinates of the atoms, or could also be a set of inter-atomic distances and angles. Given r, the energy as a function of the positions, $V(r)$, is the value of $V(r)$ for all values of r of interest. Using the landscape analogy from the introduction, $V(r)$ gives the height on the "energy landscape" so that the concept of a potential energy surface arises. An example is the PES for water molecule (Figure $3.3.1.1$) that show the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°

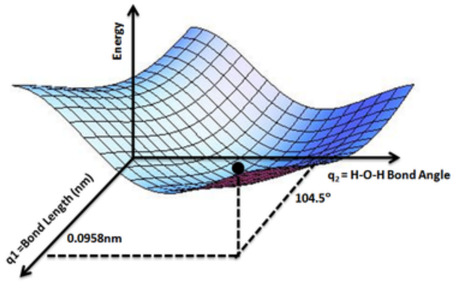


Figure 3.3.1.2: PES for water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958nm and H-O-H bond angle of 104.5°. of Wikipedia (Credit: Aimnature).

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (e.g., x, y,and z or r, θ and phi in Cartesian and Spherical coordinates) or *degrees of freedom*. However, a reaction and hence the corresponding PESs do not depend of the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degree of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3N-6 \tag{3.3.1.1}$$

where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactants). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding. See Calculate Number of Vibrational Modes to get a more details picture of how this applies to calculating the number of vibrations in a molecule

To study a chemical reaction using the PES as a function of atomic positions, it is necessary to calculate the energy for **every atomic** arrangement of interest. Methods of calculating the energy of a particular atomic arrangement of atoms are well described in the computational chemistry article, and the emphasis here will be on finding approximations of $(V(r)$ to yield fine-grained energy-position information.

For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$H+H_2 \rightarrow H_2+H \tag{3.3.1.2}$$

system as a function of the **three** H-H distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large scale representations of the surface to be feasible.

Application of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product). Three

- PES do not show kinetic energy, only potential energy.
- At T = 0 K (no KE), species will want to be at the lowest possible potential energy, (i.e., at a minimum on the PES).
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a **saddle point**, which we call that saddle point a transition-state structure.

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

Contributors and Attributions

- Wikipedia
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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3.3.2: The Potential-Energy Surface Can Be Calculated Using Quantum Mechanics

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths), the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concept that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction has associated with it a unique potential energy. This creates a smooth energy "landscape" and chemistry can be viewed from a topology perspective of particles evolving as they pass through potential energy "valleys" and "passes".

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

3.3.2.1: Potential Energy Curves (2-D Potential Energy Surfaces)

The energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning "no interaction". At distances of several atomic diameters, attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond (Figure $3.3.2.1$).

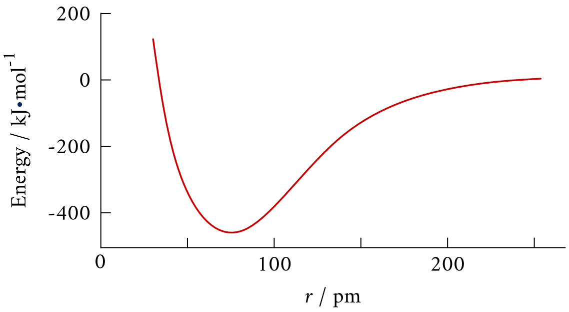

Figure $3.3.2.1$: A potential energy curve for the covalent bond in a H_2 molecule. The distance r is the distance between the nuclei of the two H atoms. (CC BY-NC; Ümit Kaya via LibreTexts)

The internuclear distance at which the potential energy minimum occurs defines the **bond length**. This is more correctly known as the *equilibrium* bond length because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of *RT*, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the *van der Waals force* that holds argon atoms together in their liquid and solid forms.

Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy quantum theory tell us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two: $E = V + K$. The relation between them is surprisingly simple: $K = -0.5V$. This means that when a chemical bond forms (an exothermic process with $\Delta E < 0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $-\Delta E$ has half the magnitude of the decrease in potential energy.

3.3.2.2: Mathematical Definition and Computation of a Potential Energy Surface

The geometry of a set of atoms can be described by a vector, r, whose elements represent the atom positions. The vector r could be the set of the Cartesian coordinates of the atoms, or could also be a set of inter-atomic distances and angles. Given r, the energy as a function of the positions, $V(r)$, is the value of $V(r)$ for all values of r of interest. Using the landscape analogy from the introduction, $V(r)$ gives the height on the "energy landscape" so that the concept of a potential energy surface arises. An example is the PES for water molecule (Figure $3.3.2.2$) that shows the energy minimum corresponding to optimized molecular structure for water- O-H bond lengths of 0.0958 nm and H-O-H bond angle of 104.5°

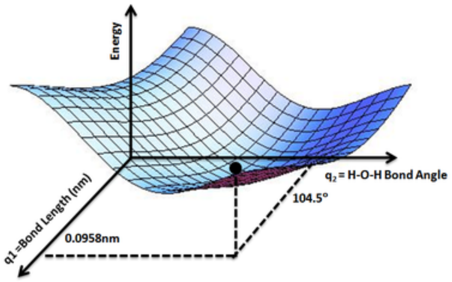

Figure $3.3.2.2$: PES for water molecule showing the energy minimum corresponding to optimized molecular structure for water- O-H bond lengths of 0.0958nm and H-O-H bond angle of 104.5°. of Wikipedia (Credit: Aimnature).

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (e.g., x, y,and z or r, θ and phi in Cartesian and Spherical coordinates) or *degrees of freedom*. However, a reaction and hence the corresponding PESs do not depend on the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degrees of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3N-6$$

where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactant). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding. See Calculate Number of Vibrational Modes to get a more detailed picture of how this applies to calculating the number of vibrations in a molecule

To study a chemical reaction using the PES as a function of atomic positions, it is necessary to calculate the energy for **every atomic** arrangement of interest. Methods of calculating the energy of a particular atomic arrangement of atoms are well known. For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$\mathrm{H}+\mathrm{H}_2 \longrightarrow \mathrm{H}_2+\mathrm{H} \tag{3.3.2.1}$$

a system that is described by a function of the **three** $\mathrm{H-H}$ distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large-scale representations of the surface to be feasible.

3.3.2.3: Applications of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and **saddle points** correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product).

3.3.2.3.1: A Hypothetical Endothermic Reaction PES

Figure $3.3.2.3$ shows an example of a PES for a hypothetical reaction system, with the corresponding 2-D energy contour map projected on the plane below. The contour map shows isolines of potential energy, using color to differentiate between high and low energies. In this figure, the highest potential energy is indicated with red, and as the color changes along the ROYGBIV scale, the potential energy decreases until violet is reached, indicating the lowest potential energy. In the PES, the z axis represents the potential energy, with the energy of the plane in the PES defined as 0 kJ. The color scheme of the PES has the same meaning as that of the 2-D contour map - red is high potential energy and violet is low potential energy.

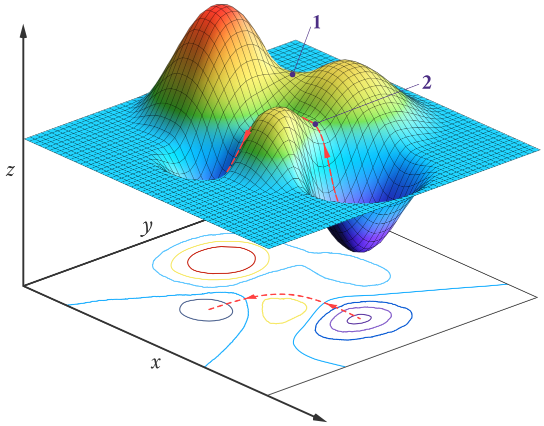

Figure $3.3.2.3$: A 2-D contour map and corresponding Potential Energy Surface for a hypothetical endothermic reaction. See the text for a detailed explanation. (CC BY-NC; Ümit Kaya via LibreTexts)

Before the reaction, the reactants are found at (or near) the energy minimum on the right. (The deep well in the PES and the smallest, violet oval in the contour map.) As the reaction proceeds, the reactants are shown following the minimum energy pathway toward the products, as designated by the dashed red line. The point "2" designates the transition state at the saddle point, the highest energy point of the reaction process. The reaction then moves on to form the products, which sit in the potential energy well on the left. (Designated by the shallower well on the PES and by the dark blue oval on the left in the contour map.) Because the potential energy of the reactants is greater than the potential energy of the products, this reaction is an endothermic reaction. The point "1" represents a second, higher energy saddle point which is the transition state for an alternative reaction that is possible for this set of chemicals.

3.3.2.3.2: The Exchange Reaction H_A + H_BH_C ⇒ H_AH_B + H_C

A specific application of a PES is the mapping of the reaction shown in equation $3.3.2.1$, the exchange of hydrogen atoms in an H_2 molecule. In this map, the individual H atoms are labeled as

$$H_A + H_BH_C \rightarrow H_AH_B + H_C$$

We must take into account the collision angle between the H_A atom and the H_BH_C molecule. If we fix this collision angle at 180°, we are able to plot a PES that is dependent on the two parameters of R_{BC} and R_{AB}. The resulting PES (figure $3.3.2.4a$) and energy contour map (figure $3.3.2.4b$) show us that if the particles are far enough apart, the potential energy of the reaction system starts out being described by the potential energy curve for the H_BH_C molecule, and ends up being described by the potential energy curve of the H_AH_B molecule. Individually, these curves both have appearances similar to the curve shown in Figure $3.3.2.1$. The PES and the energy contour map show the symmetrical nature of the potential energy changes that occur in this exchange process that involves products that are equivalent to the reactants.

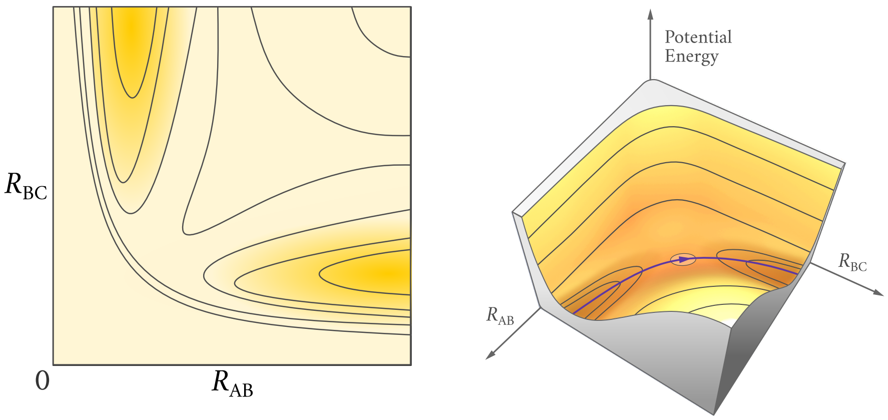

Figure $3.3.2.4a$: (left) The potential energy contour map for the exchange reaction $H_A + H_B H_C \rightarrow H_A H_B + H_C$. The x-axis is R_{AB}, the interatomic distance between H_A and H_B. These two atoms begin very far apart, but end up being bonded together. The y-axis is R_{BC}, the interatomic distance between H_B and H_C. These two atoms start out bonded together but end up separated and far apart. The darker the color, the lower the potential energy. (right) The 3-D potential energy surface for the exchange reaction $H_A + H_B H_C \rightarrow H_A H_B + H_C$. The darker the color, the lower the potential energy. (CC BY-NC; Ümit Kaya via LibreTexts)

As the H_A atom more closely approaches the $H_B H_C$ molecule, the interactions between these particles begin to affect the potential energy of the system. There are many possible potential energy pathways that the reaction could follow. Figure $3.3.2.5$ shows the energy contour map for three possible reaction pathways:

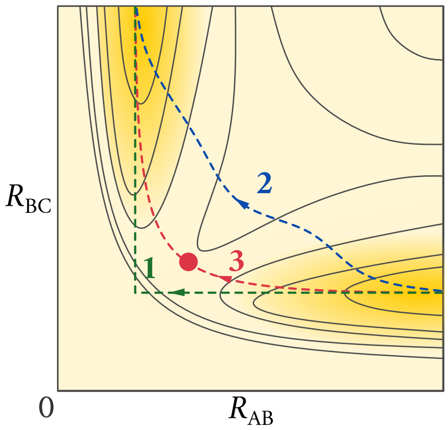

Figure $3.3.2.5$: An energy contour map showing three possible reaction pathways for the reaction

$$H_A + H_B H_C \rightarrow H_A H_B + H_C$$

(CC BY-NC; Ümit Kaya via LibreTexts)

In pathway 1, the $H_B H_C$ bond length R_{BC} is held constant as the distance R_{AB} decreases. This type of interaction would lead to a continually increasing potential energy for the system as the H_A atom moves closer and closer to the $H_B H_C$ molecule. Eventually, the new $H_A H_B$ molecule would form, and the H_C atom would break off and would move farther and farther away.

Pathway 2 shows a second possible reaction pathway in which the $H_B H_C$ bond length R_{BC} increases even though the H_A atom is still relatively far away. This pathway is unlikely because it requires a great deal of potential energy to stretch the $H_B H_C$ bond before the attractive force from the H_A atom influences this bond lengthening.

As the particles travel along Pathway 3, the reactants still must pass through a potential energy maximum at the saddle point, but this local maximum is the lowest energy barrier separating reactants from products. As noted above, this saddle point is called the transition state structure (designated by the red dot in pathway 3). This is the structure that is equally poised to return to the reactants or move forward to form products. Pathway 3 is the minimum energy pathway, and thus the one most likely to be followed during a successful reaction.

It is sometimes useful to create energy contour maps that include information about the vibrational state of reactants and products, as shown in figure 3.3.2.6.

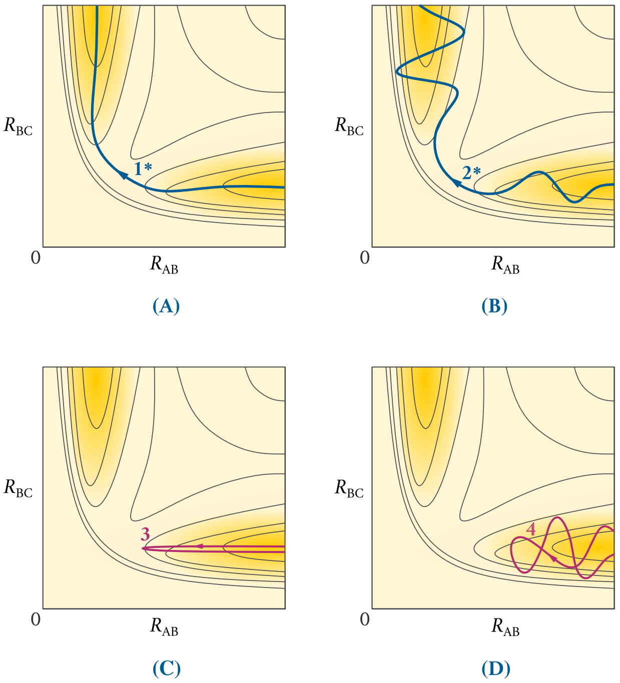

Figure 3.3.2.6: Four possible collision outcomes for the exchange reaction $H_A + H_BH_C \rightarrow H_AH_B + H_C$. 6A) The minimum energy pathway which leads to a successful exchange. 6B) The successful collision of a vibrating H_BH_C molecule with an H_A atom, resulting in the formation of a vibrating H_AH_B molecule. 6C) The approach of an H_A atom to a non-vibrating, slow-moving H_BH_C molecule that has insufficient kinetic energy to escape the potential energy well, leading to an unsuccessful exchange reaction. 6D) The approach of an H_A atom to a vibrating, slow-moving H_BH_C molecule that has insufficient kinetic energy to escape the potential energy well, leading to an unsuccessful exchange reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

3.3.2.3.3: The Exchange Reaction F + D_2 ⇒ DF + D

When modeling the potential energy for the reaction

$$\mathrm{F(g)} + \mathrm{D_2(g)} \longrightarrow \mathrm{DF(g)} + \mathrm{D(g)}$$

it is useful to differentiate between the two deuterium atoms, so we can designate them as D_A and D_B. Doing so allows us to determine how the potential energy of the pre-reaction system is affected by the F to D_A distance $R_{\mathrm{D}_A\mathrm{F}}$ and the D_A to D_B distance $R_{\mathrm{D}_A\mathrm{D}_B}$ (figure 3.3.2.7).

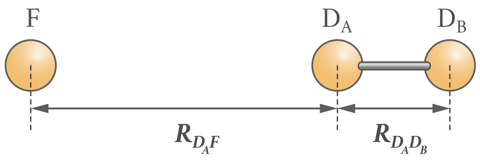

Figure 3.3.2.7: Defining the distances $R_{\mathrm{D}_A\mathrm{F}}$ and $R_{\mathrm{D}_A\mathrm{D}_B}$ (CC BY-NC; Ümit Kaya via LibreTexts)

As the F atom more closely approaches the $\mathrm{D_2}$ molecule, the interactions between these particles begin to affect the potential energy of the system. There are many possible potential energy pathways that the reaction could follow. Figure 3.3.2.8 shows the energy contour map for three possible reaction pathways:

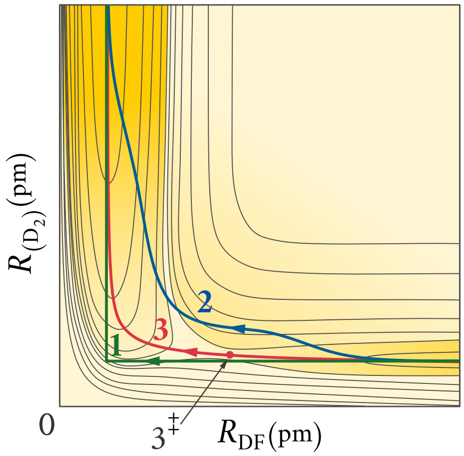

Figure 3.3.2.8: Three possible reaction pathways for the $F(g) + D_2(g) \longrightarrow DF(g) + D$ reaction. (CC BY-NC; Ümit Kaya via LibreTexts)

In pathway 1, the D_2 bond length $R_{D_AD_B}$ is held constant as the distance R_{D_AF} decreases. This type of interaction would lead to a continually increasing potential energy for the system as the F atom moves closer and closer to the D_2 molecule. Eventually, the new D_AF molecule would form, and the D_B atom would break off and would move farther and farther away.

Pathway 2 shows a second possible reaction pathway in which the D_2 bond length $R_{D_AD_B}$ increases even though the F atom is still relatively far away. This pathway is unlikely because it requires a great deal of potential energy to stretch the D_2 bond before the attractive force from the F atom influences this bond lengthening.

As the particles travel along Pathway 3, the reactants still must pass through a potential energy maximum at the saddle point, but this local maximum is the lowest energy barrier separating reactants from products. As noted above, this saddle point is called the transition state structure (designated by the red dot in pathway 3, labeled as $3^\ddagger$). This is the structure that is equally poised to return to the reactants or move forward to form products. Pathway 3 is the minimum energy pathway, and thus the one most likely to be followed during a successful reaction.

If we were to plot the potential energy curve for the reaction pathway along the minimum energy pathway, we would get the familiar potential energy curve of a reaction similar to that shown in Figure 3.3.2.9

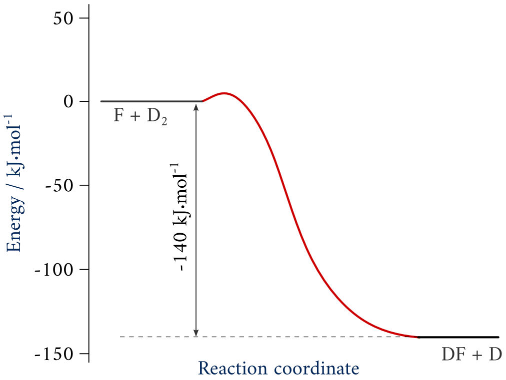

Figure 3.3.2.9: This graph shows the potential energy relationships for the reaction $F + D_2 \longrightarrow DF + D$. The activation energy for the forward reaction is about 6 kJ/mol. The difference in potential energy between the reactants and the products is $D_e(D_2) - D_e(DF)$. The curve's peak represents the transition state. (CC BY-NC; Ümit Kaya via LibreTexts)

Contributors and Attributions

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- Tom Neils, Grand Rapids Community College

3.3.3: The Hammond Postulate

Objective

After completing this section, you should be able to use the Hammond postulate to explain the formation of the most stable carbocation during the addition of a protic acid, HX, to an alkene.

Key Terms

Make certain that you can define, and use in context, the key term below.

- Hammond postulate

So far in this chapter the following points have been made about the electrophilic addition of HX to a double bond.

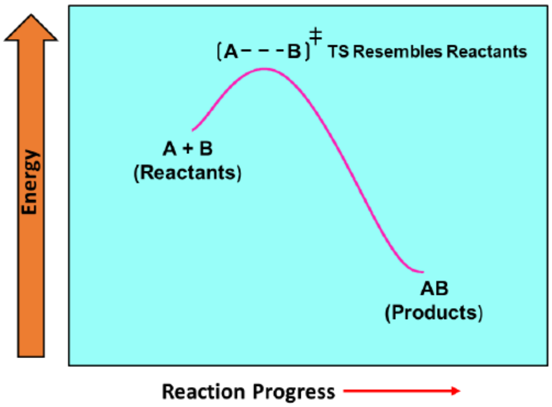
- The reaction takes place through a two step mechanism which forms a carbocation intermediate.
- During electrophilic addition the carbocation intermediate, and the subsequent H-X bond, forms on the double bond carbon with the most alkyl stubstituents *(***Markovnikov's rule)**
- Carbocations become more stable as the number of alkyl substituents increases.

It appears that the stability of the carbocation reactive intermediate has a direct effect on the products of a reaction. However, it is the activation energy required to reach the transition state of the reaction's rate determine step which determines which determines which product is produced. This implies that there is a relationship between the transition state and the carbocation reactive intermediate in the mechanism of electrophilic addition.

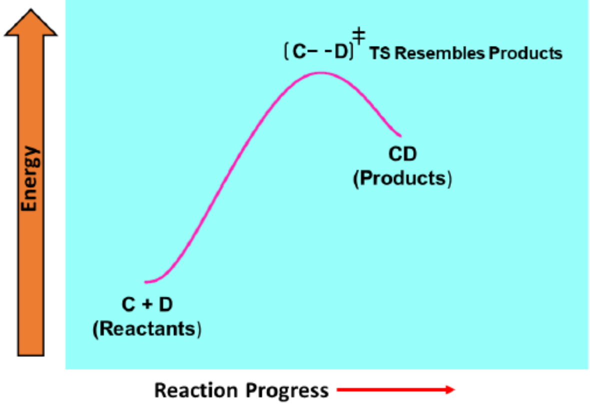
The Hammond Postulate

Chemists are often very interested in the structures of the transition states in a reaction's mechanism. In particular, the transition state for a mechanism's rate determining step directly determines the energy of activation barrier and thereby the rate for the overall reaction. Understanding the structure of a transition state allows chemists to consider structural features which might stabilize or destabilize the transition state causing a corresponding change in the rate of reaction. However, transition state structures cannot be directly observed because they are highly unstable activated complexes which instantly convert to a more stable species. In order to gain some insight into the structure of particular transition state, chemists often invoke the **Hammond postulate**, which states that *a transition state resembles the structure of the nearest stable species* (reactant, intermediate or product).

For an exergonic reaction, the transition state is closer in energy to the reactants. Therefore, the structure of the transition state can assumed to resemble the reactants more than the products. Shown below is a hypothetical exergonic reaction between reactant compounds A and B to form the product AB. The Hammond postulate would theorize that the distance between A and B in the transition state would be relatively large thus resembling the reactants where A and B are two isolated species.

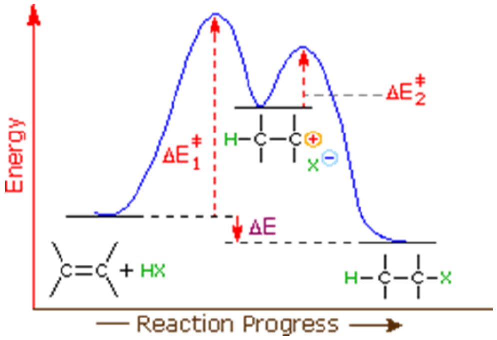


For an endergonic reaction, the transition state is closer in energy to the product. Therefore, the structure of the transition state can assumed to resemble the products more than the reactants. In the hypothetical endergonic reaction shown below, reactant compounds C and D react to form the product CD. The Hammond postulate would predict that the distance between C and D in the transition state would be relatively small thus resembling the products where C and D are bonded together as a single product CD.

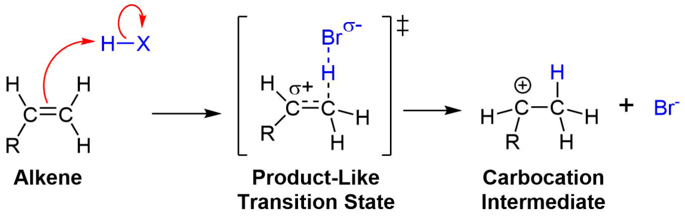


The Hammond Postulate and Electrophilic Addition

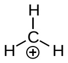
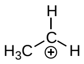
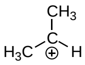
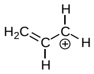
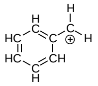
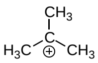
By applying the Hammond postulate and other ideas cultivated in this chapter the reason why electrophilic additions tend to follow Markovnikov's rule. When the energy diagram of an electrophilic addition was discussed in **Section 7.2**, it was noted the first step of the mechanism was the rate determining step. The first step of the mechanism also is endergonic and results in the formation of a carbocation intermediate.

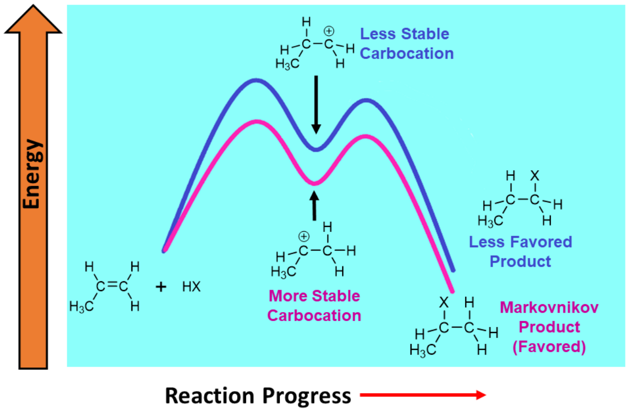


The Hammond postulate suggests that the transition state structure for the first step of the mechanism resembles that of the carbocation intermediate because they are the closest in energy. A transitions state, seen below, is typically drawn as a theoretical structure part way between the reactants and the product. For this transition state the pi bonds and the H-Br bond are in the process of being broken and are represented with a dashed line. The C-H bond is in the process of being formed so it also represented with a dashed line. The bromine is shown with a partial negative charge (sigma-) because it is becoming a bromide ion (Br$^-$) which has a full negative charge. Most importantly, the carbon is in the process of becoming a carbocation so it is shown to have a partial positive change (sigma+).



Because the Hammond postulate predicts this transitions state closely resembles the carbocation intermediate, the partial positive charge can said to closely resemble the full positive charge of the carbocation. Consequently, any structural feature that stabilized the carbocation intermediate will also stabilize the transition state. The partial positive charge of the transition state is stabilized by adjacent alkyl groups thorough inductive effects and hyperconjugation much like the carbocation intermediate. Adding more alkyl substituents to the partially positive charged carbon stabilizes the transition state, causing it to become lower in energy. This in turn, decreases the energy of activation and increases the rate of the reaction. In short, during an electrophilic addition, the double bond carbon with the most alkyl substituents will for a carbocation intermediate and therefore its C-X bond faster than the double bond carbon with fewer alkyl substituents. These effects cause electrophillic additions to follow Markovnikov's rule and place the halogen (X) group on the more substituted carbon of asymmetrically alkyl substituted double bond.

Carbocation Stability		<<		<</td>		≈		<</td>		≈	

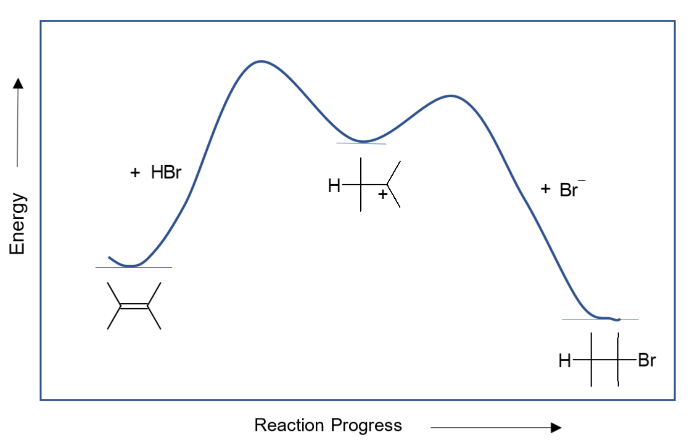


Exercise 3.3.3.1

Consider the second step in the electrophilic addition of HBr to an alkene. Is this step exergonic or endergonic and does the transition state represent the product or the reactant (cation)? Draw out an energy diagram of this step reaction.

Answer

Exergonic and the transition state (second step) represents the reactant (cation). As shown to go from intermediate cation to final product the step is exergonic.

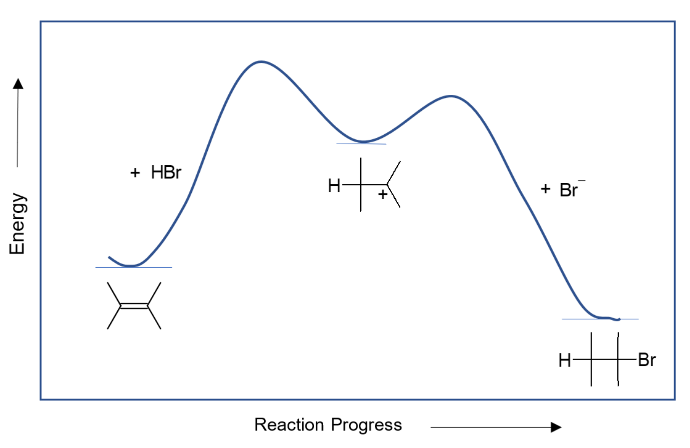


Exercise 3.3.3.2

Consider the second step in the electrophilic addition of HBr to an alkene. Is this step exergonic or endergonic and does the transition state represent the product or the reactant (cation)? Draw out an energy diagram of this step reaction.

Answer

Exergonic and the transition state (second step) represents the reactant (cation). As shown to go from intermediate cation to final product the step is exergonic.



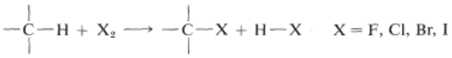
3.4: Reactivity and Selectivity

Comparing Reactivity

Given the knowledge that a particular reaction will proceed at a suitable rate, a host of practical considerations are necessary for satisfactory operation. These considerations include interference by possible side reactions that give products other than those desired, the ease of separation of the desired product from the reaction mixture, and costs of materials, apparatus, and labor. We shall consider these problems in connection with the important synthetic reactions discussed in this book.

The chlorination of saturated hydrocarbons can be induced by light, but also can be carried out at temperatures of about 300° in the dark. Under such circumstances the mechanism is similar to that of light-induced chlorination, except that the chlorine atoms are formed by thermal dissociation of chlorine molecules. Solid carbon surfaces catalyze thermal chlorination, possibly by aiding in the cleavage of the chlorine molecules.

Direct monohalogenation of saturated hydrocarbons works satisfactorily only with chlorine and bromine. For the general reaction



$$-\underset{|}{\overset{|}{C}}-H + X_2 \longrightarrow -\underset{|}{\overset{|}{C}}-X + H-X \qquad X = F, Cl, Br, I$$

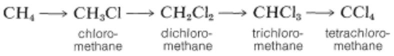
the calculated ΔH^0 value is negative and very large for fluorine, negative and moderate for chlorine and bromine, and positive for iodine (see Table 4-7). With fluorine, the reaction evolves so much heat that it may be difficult to control, and products from cleavage of carbon-carbon as well as of carbon-hydrogen bonds may be obtained. The only successful, direct fluorination procedure for hydrocarbons involves diffusion of minute amounts of fluorine mixed with helium into liquid or solid hydrocarbons at low temperatures, typically -78^{o} (Dry Ice temperature). As fluorination proceeds, the concentration of fluorine can be increased. The process is best suited for preparation of completely fluorinated compounds, and it has been possible to obtain in this way amounts of $(CF_3)_4C$ and $(CF_3)_3C-C(CF_3)_3$ from 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane corresponding to 10-15$\%$ yields based on the fluorine used.

Bromine generally is much less reactive toward hydrocarbons than chlorine is, both at high temperatures and with activation by light. Nonetheless, it usually is possible to brominate saturated hydrocarbons successfully. Iodine is unreactive.

***Table:** Calculated Heat of Reaction for Halogenation fo Hydrocarbons*

Halogen (X)	**ΔH^o (kcal/mole)[a]**
F	-116
Cl	-27
Br	-10
I	13
[a]Calculated from the bond energies of Table 4-3.	

The chlorination of methane does not have to stop with the formation of chloromethane (methyl chloride). It is usual when chlorinating methane to obtain some of the higher chlorination products: dichloromethane (methylene chloride), trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride):

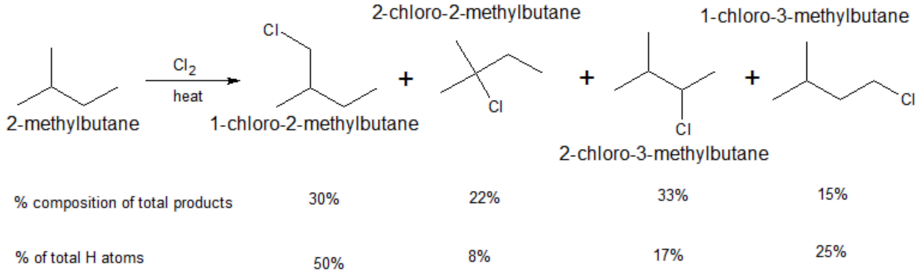


$$CH_4 \longrightarrow \underset{\text{chloro-methane}}{CH_3Cl} \longrightarrow \underset{\text{dichloro-methane}}{CH_2Cl_2} \longrightarrow \underset{\text{trichloro-methane}}{CHCl_3} \longrightarrow \underset{\text{tetrachloro-methane}}{CCl_4}$$

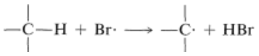
In practice, one can control the degree of substitution to a considerable extent by controlling the methane-chlorine ratio. For example, for monochlorination to predominate, a high methane-chlorine ratio is necessary such that the chlorine atoms react with CH_4 and not with CH_3Cl.

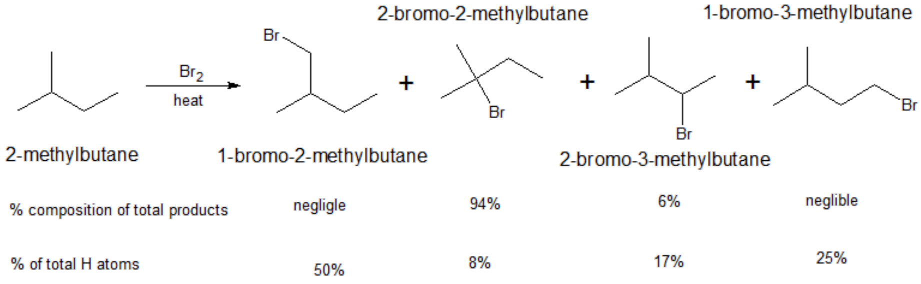
Selectivity in Alkane Halogenation

For propane and higher hydrocarbons for which more than one monosubstitution product is generally possible, difficult separation problems bay arise when a particular product is desired. For example, the chlorination of 2-methylbutane 3 at 300^{o} gives all four possible monosubstitution products. On a purely statistical basis, we may expect the ratio of products from 2-methylbutane to correlate with the number of available hydrogens at the various positions of substitution in the ratio 6:1:2:3 (50%:8%:17%:25%:). However, as can be seen from the strengths of bonds between hydrogen and primary, secondary, and tertiary carbons are not the same and we would expect the weaker $C-H$ bonds to preferentially react with $Cl\cdot$. As such, the proportion of the tertiary halide is about three times that expected on a statistical basis which is in accord with our expectation that the tertiary $C-H$ bond of 2-methylbutane should be the weakest of the $C-H$ bonds.



	1-chloro-2-methylbutane	2-chloro-2-methylbutane	2-chloro-3-methylbutane	1-chloro-3-methylbutane
% composition of total products	30%	22%	33%	15%
% of total H atoms	50%	8%	17%	25%

Bromine atoms are far more selective than chlorine atoms. This is not unexpected because  $-\overset{|}{\underset{|}{C}}-H + Br\cdot \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HBr$ is endothermic, whereas corresponding reactions with a chlorine atoms usually are exothermic (data from Table 4-6). Bromine removes only those hydrogens that are relatively weakly bonded to a carbon atom. As predicted, attack of $Br\cdot$ on 2-methylbutane leads mostly to 2-bromo-2-methylbutane, some secondary bromide, and essentially no primary bromides:

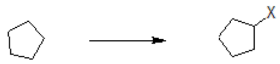


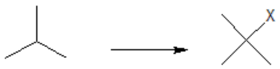
	1-bromo-2-methylbutane	2-bromo-2-methylbutane	2-bromo-3-methylbutane	1-bromo-3-methylbutane
% composition of total products	negligle	94%	6%	neglible
% of total H atoms	50%	8%	17%	25%

When the structure of the alkane is symmetrical, then the fast reactivity of chlorination can be used for efficiency. When the structure of the alkane can produce a range of monohalogenated products, then the selectivity of bromination can be used to produce the most stable product in the greatest percentage.

Exercises

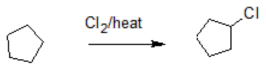
1. Specify the optimum halogenation conditions (Cl_2/heat or Br_2/heat) to produce the indicated major product.

a) 

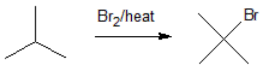
b) 

Solution

1.

a) 

All carbons are equivalent,
so use higher reactivity of Cl_2.

b) 

Higher selectivity of Br_2 will produce a greater percentage of the tertiary haldie.

Contributors and Attributions

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

3.5: The Principle of Microscopic Reversibility

The equilibrium constant expression is an important and fundamental relationship that relates the concentrations of reactants and products at equilibrium. We deduce it above from a simple model for the concentration dependence of elementary-reaction rates. In doing so, we use the criterion that the time rate of change of any concentration must be zero at equilibrium. Clearly, this is a necessary condition; if any concentration is changing with time, the reaction is not at equilibrium. However, our deduction uses another assumption that we have not yet emphasized. We assume that ***the forward and reverse rates of each elementary step are equal when the overall reaction is at equilibrium***. This is a special case of the ***principle of microscopic reversibility***

Definition: Principle of Microscopic Reversibility

Any molecular process and its reverse occur with equal rates at equilibrium

The principle of microscopic reversibility applies to any molecular process; it is inferred from the fact that such processes can be described by their equations of motion if the initial state of the constituent particles can be specified. The equations of motion can be either classical mechanical or quantum mechanical. We consider the implications of the principle for molecular processes that constitute elementary reactions. However, the principle also applies to equilibria in other molecular processes, notably the absorption and emission of radiation.

When we apply it to elementary reactions, we see that the principle of microscopic reversibility provides a necessary and sufficient condition for equilibrium from a reaction-mechanism perspective. The principle also imposes several significant conditions on the sequences of elementary processes that constitute a mechanism and on their relative rates.

In the previous section, we see that microscopic reversibility provides a ***sufficient*** basis for deducing the relationship relating reactant and product concentrations at equilibrium—the equilibrium constant expression—from our rate equations for elementary reactions. We now want to see that the principle of microscopic reversibility is indeed ***necessary***. That is, **setting $dn_x/dt=0$ for all species, X, involved in the reaction is not in itself *sufficient* to assure that the system is at equilibrium.**

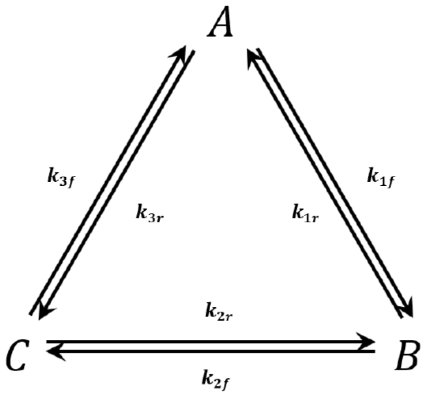


Figure 3. Cyclic equilibrium

We consider the triangular network of elementary reactions[3,4] shown in Figure 3. This network gives rise to the following reaction-rate equations:

$$V^{-1}\frac{dn_A}{dt}=-k_{1f}\left[A\right]+k_{1r}\left[B\right]+k_{3f}\left[C\right]-k_{3r}\left[A\right]$$

$$V^{-1}\frac{dn_B}{dt}=+k_{1f}\left[A\right]-k_{1r}\left[B\right]+k_{2r}\left[C\right]-k_{2f}\left[B\right]$$

$$V^{-1}\frac{dn_C}{dt}=+k_{2f}\left[B\right]-k_{2r}\left[C\right]+k_{3r}\left[A\right]-k_{3f}\left[C\right]$$

At equilibrium each of these equations must equal zero. Since we have three equations in three unknowns, it might at first appear that we can solve for the three unknowns $[A]$, $[B]$, and $[C]$. We can see, however, either from the equations themselves or by considering the physical situation that they represent, that only two of these equations are independent. That is, we have

$$\frac{dn_A}{dt}+\frac{dn_B}{dt}+\frac{dn_C}{dt}=0$$

While we cannot solve for $[A]$, $[B]$, and $[C]$ independently, we can solve for their ratios, which are

$$\frac{[B]}{[A]}=\frac{k_{1f}k_{2r}+k_{2r}k_{3r}+k_{1f}k_{3f}}{k_{2f}k_{3f}+k_{1f}k_{3f}+k_{1r}k_{2r}}$$

$$\frac{[C]}{[B]}=\frac{k_{1f}k_{2f}+k_{1r}k_{3r}+k_{2f}k_{3r}}{k_{1f}k_{2r}+k_{2r}k_{3r}+k_{1f}k_{3f}}$$

$$\frac{[A]}{[C]}=\frac{k_{2f}k_{3f}+k_{1r}k_{3f}+k_{1r}k_{2r}}{k_{1f}k_{2f}+k_{1r}k_{3r}+k_{2f}k_{3r}}$$

Since we deduce these equations from the condition that all the time derivatives are zero, it might seem that they should represent the criteria for the system of reactions to be at equilibrium. Purely as a name for easy reference, let us call these equations the *cyclic equilibrium set*.

When we consider the reactions one at a time, we deduce the following equilibrium relationships:

$$\frac{[B]}{[A]}=\frac{k_{1f}}{k_{1r}} \qquad \frac{[C]}{[B]}=\frac{k_{2f}}{k_{2r}} \qquad \frac{[A]}{[C]}=\frac{k_{3f}}{k_{3r}}$$

For easy reference, let us call these equations the *one-at-a-time set*.

Now, it cannot be true that both sets of relationships specify a sufficient condition for the system to be at equilibrium. To see this, let us first suppose that the principle of microscopic reversibility is a sufficient condition for equilibrium. Then the one-at-a-time set of equations must be sufficient to uniquely specify the position of equilibrium. It is easy to show that a set of rate constants that satisfies the one-at-a-time set also satisfies the cyclic set. Therefore, if microscopic reversibility is a sufficient condition for equilibrium, the cyclic network rate equations are necessarily equal to zero at equilibrium. In short, if we assume that microscopic reversibility is a sufficient condition for equilibrium, we encounter no inconsistencies, because the cyclic set of equations is satisfied by the same equilibrium-concentration ratios.

On the other hand, if we suppose that setting $dn_x/dt=0$ for all species, X, is a sufficient condition for equilibrium, then the cyclic set of equations must be sufficient to uniquely specify the position of equilibrium. Let us consider a particular set of rate constants:

- $k_{1f}=k_{2f}=k_{3f}=1$ and
- $k_{1r}=k_{2r}=k_{3r}=2$.

This set of rate constants satisfies the cyclic set of equations and requires that each of the equilibrium-concentration ratios be equal to 1. In this case, the one-at-a-time set of equations implied by microscopic reversibility cannot be satisfied. (We have $[B]/[A]=1$ and $k_{1f}/k_{1r}=1/2$. Therefore, $[B]/[A]\neq k_{1f}/k_{1r}$.) That is, if we assume that setting $dn_x/dt=0$, for all species, X, is a sufficient condition for equilibrium, we must conclude that the principle of microscopic reversibility is false. Using the contrapositive: If the principle of microscopic reversibility is true, it is false that setting $dn_x/dt=0$ for all species, X, is a sufficient condition for equilibrium.

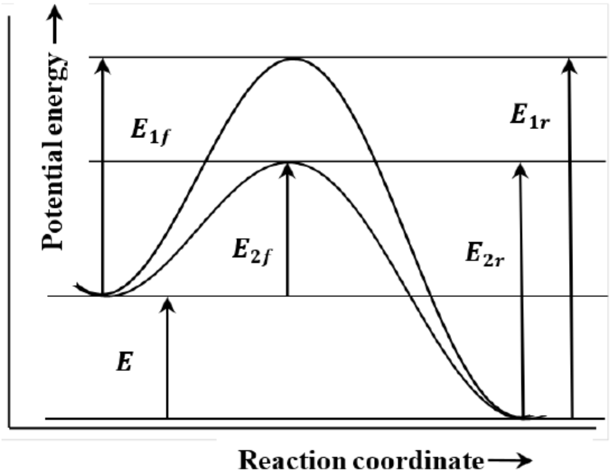


Figure 4. Potential energy versus reaction coordinate.

Setting the derivatives for the reaction network equal to zero is not sufficient to assure that the system is at equilibrium. It is merely necessary. To assure that the network is at equilibrium, we must apply the principle of microscopic reversibility and require that each elementary process in the network be at equilibrium.

The principle of microscopic reversibility requires that any **elementary process** occur via the same sequence of transitory molecular structures in both the forward and reverse directions. Consequently, if a sequence of elementary steps is a mechanism for a forward reaction, the same sequence of steps—traversed backwards—must be a mechanism for the reverse reaction. The principle does not exclude the possibility that a given reaction can occur simultaneously by two different mechanisms. However, it does mean that a given reaction cannot have one mechanism in the forward direction and a second, different mechanism in the reverse direction.

In describing reaction mechanisms, we assume that the energy of the reacting molecules depends on their progress along the path that they follow during the course of the reaction. We call this path the reaction coordinate. We suppose that we can plot the energy of the system as a function of the system's position on the path, or displacement along the reaction coordinate. In the context of such a graph, the principle of microscopic reversibility is essentially the observation that the path is the same irrespective of the direction in which it is traversed. Two such paths are sketched in Figure 4. In this sketch, E_{1f} and E_{2f} are the activation energies for the two forward reactions; E_{1r} and E_{2r} are the activation energies for the reverse reactions.

3.5.1: Microscopic Reversibility and the Second Law

The principle of microscopic reversibility requires that parallel mechanisms give rise to the same expression for the concentration-dependence of the equilibrium constant. That is, the ***function*** that characterizes the equilibrium composition must be the same for each mechanism. If, for the reaction $aA+bB\rightleftharpoons cC+dD$, the equilibrium composition for mechanism 1 is $[A]_1$, $[B]_1$, $[C]_1$, $[D]_1$, and that for mechanism 2 is $[A]_2$, $[B]_2$, $[C]_2$, $[D]_2$, microscopic reversibility asserts that

$$K_1=\frac{[C]^c_1[D]^d_1}{[A]^a_1[B]^b_1}$$

and

$$K_2=\frac{[C]^c_2[D]^d_2}{[A]^a_2[B]^b_2}$$

In and of itself, microscopic reversibility makes no assertion about the value of $[A]_1$ compared to that of $[A]_2$. While microscopic reversibility asserts that the same function characterizes the concentration relationships for parallel mechanisms, it does not assert that the numerical value of this function is necessarily the same for each of the mechanisms.

However, that these numerical values must be equal follows directly when we introduce another of our most basic observations. No matter how many mechanisms may be available to a reaction in a particular system, the concentration of any reagent can have only one value in an equilibrium state. At equilibrium, $[A]_1=[A]_2$, *etc.*; therefore, the numerical values of the equilibrium constants must be the same: $K_1=K_2$.

The uniqueness of the equilibrium composition is a fundamental feature of our ideas about what chemical equilibrium means. Nevertheless, it is of interest to show that we can arrive at this conclusion from a different perspective: We can use an idealized machine to show that the second law of thermodynamics requires that parallel mechanisms must produce the same the equilibrium composition. Our argument is a proof by contradiction.

Let us suppose that A, B, and C are gases. Suppose that the reaction $A\rightarrow B+C$ occurs in the absence of a catalyst, but that reaction occurs in the opposite direction, $C+B\rightarrow A$, when a catalyst is present. More precisely, we assume that the position of equilibrium $A\rightleftharpoons B+C$ lies to the right in the absence of the catalyst and to the left in its presence, while all other reaction conditions are maintained constant. These assumptions mean that the equilibrium composition for the catalyzed mechanism is different from that of the mechanism that does not involve the catalyst.

We can show that these assumptions imply that the second law of thermodynamics is false. If we accept the validity of the second law, this violation means that the assumptions cannot in fact describe any real system. (We are getting a bit ahead of ourselves here, inasmuch as our detailed consideration of the laws of thermodynamics begins in Chapter 6.)

Given our assumptions, we can build a machine consisting of a large cylinder, closed by a frictionless piston. The cylinder contains a mixture of A, B, and C, and a quantity of the catalyst. We provide a container for the catalyst, and construct the device so that the catalyst container can be opened and closed from outside the cylinder. Finally, we immerse the entire cylinder in a fluid, which we maintain at a constant temperature.

When the catalyst container is sealed, so that the gaseous contents of the cylinder are not in contact with the catalyst, reaction occurs according to $A\rightarrow B+C$, and the piston moves outward, doing work on the surroundings. When the catalyst container is open, reaction occurs according to $C+B\rightarrow A$, and the piston moves inward. Figure $3.5.1.1$ shows these changes schematically. At the end of a cycle, the machine is in exactly the same state as it was in the beginning, and the temperature of the reaction mixture is the same at the end of a cycle as it was at the beginning. By connecting the piston to a load, we can do net work on the load as the machine goes through a cycle. For example, if we connect the piston to a mechanical device that converts the reciprocating motion of the piston into rotary motion, we can wind a rope around an axle and thereby lift an attached weight.

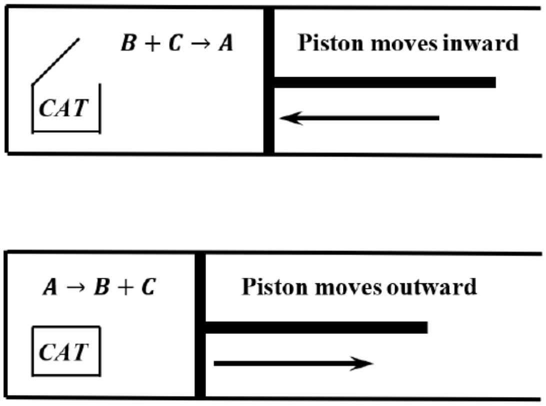


Figure 3.5.1.1: A machine that violates the second law.

We can operate this machine as an engine by alternately opening and closing the catalyst container. We can make the cylinder as large as we want, so the energy we expend in opening and closing the catalyst container can be made arbitrarily small compared to the amount of work we get out of the machine in a given cycle. All of this occurs with the machine maintained at a constant temperature. If energy is conserved, the machine must absorb heat from the bath during the cycle; otherwise, the machine would be doing work with no offsetting consumption of energy. This would be a violation of the first law of thermodynamics. (See Sections 5.7-5.11.)

From experience, we know that this machine cannot function in the manner we have described. This experience is embodied in the *second law of thermodynamics* we know that **it is impossible to construct a machine that operates in a cycle, exchanges heat with its surroundings at only one temperature, and produces work in the surroundings** (Section 9-1). Our argument assumes that two reaction mechanisms are available in a particular physical system, that they consume the same reactants, that they produce the same products, and that the equilibrium compositions are different. These assumptions imply that the second law is false. Since we are confident that it is possible for some system to satisfy the first three of these assumptions, the second law requires that the last one be false: the equilibrium compositions must be the same.

We see that there is a complementary relationship between microscopic reversibility and this statement of the second law. Microscopic reversibility asserts that a unique function of concentrations characterizes the equilibrium state for any reaction mechanism, but does not require that every mechanism reach the same state at equilibrium. This statement of the second law implies that a reaction's equilibrium composition unique, but it does not specify a law relating the equilibrium concentrations of the reacting species. (In Chapters 9 and 13, we see that, by augmenting this statement of the second law with some additional ideas, we are led to a more rigorous statement, from which we are eventually able to infer the same functional form for the equilibrium constant.)

> *Microscopic reversibility asserts that a unique function of concentrations characterizes the equilibrium state for any reaction mechanism, but does not require that every mechanism reach the same state at equilibrium.*

G. N. Lewis gave an early statement of the principle of microscopic reversibility. He called it "the law of entire equilibrium," and observed that it is "a law which in its general form is not deducible from thermodynamics, but proves to be compatible with the laws of thermodynamics in all cases where a comparison is possible."

It is worth noting that we have not shown that the existence of a unique equilibrium state implies either microscopic reversibility or the second law. Also, even though the principle of microscopic reversibility is inferred from the laws of mechanics, our development of the equilibrium constant relationship—which we do view as a law of thermodynamics—depends on our equations for the rates of elementary reactions. Our rate equations are not logical consequences of the laws of motion. Rather, they follow from assumptions we make about the average behavior of systems that contain many molecules. Consequently, we should not suppose that we have deduced a thermodynamic result (the condition for chemical equilibrium) solely from the laws of mechanics. In Section 12-2, we give brief additional consideration to the relationship between the theories of mechanics and thermodynamics. Beginning in Chapter 20, we develop thermodynamic equations by applying statistical models to the distribution of molecular energy levels.

3.6: Sterics and Conformation

CHAPTER OVERVIEW

4: Reagents and Reaction Mechanisms

4.1: Polar Reactions

Objectives

After completing this section, you should be able to

- identify the positive and negative ends of the bonds present in the common functional groups.
- explain how bond polarity can be enhanced by the interaction of a functional group with a solvent, metal cation or acid.
- explain how the polarizability of an atom can be an important factor in determining the reactivity of a bond.
- describe the heterolytic bond-breaking process.
- use curved (curly) arrows to indicate the movement of electron pairs during bond breakage and bond formation.
- predict whether a given species (compound or ion) is likely to behave as a nucleophile or as an electrophile.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- electrophile
- nucleophile
- polar reaction
- polarizability

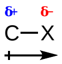
Study Notes

You may wish to review Section 2.1 before you begin this section. The relative electronegativities of the elements shown in the periodic table should already be familiar. Remember that it is the relative electronegativities that are important, not the actual numerical values.

Make sure that you understand the polarity patterns of the common functional groups. Do not try to memorize these polarities; rather, concentrate on why they arise. You will encounter these group polarities so frequently that they will soon become "second nature" to you.

Halogens and the Character of the Carbon-Halogen Bond

With respect to electronegativity, most halogens are more electronegative than carbon. This results in a carbon-halogen bond that is polarized. As shown in the image below, the carbon atom has a partial positive charge, while the halogen has a partial negative charge.



$$\overset{\delta+}{C}-\overset{\delta-}{X}$$

The following table shows the relationship between the halogens and electronegativity. Notice, as we move up the periodic table from iodine to fluorine, electronegativity increases.

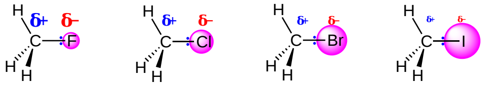
Electronegativity	I < Br < Cl < F

The following table shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C–F < C–Cl < C–Br < C–I
Bond strength	C–I < C–Br < C–Cl < C–F
Molecular size	F < Cl < Br < I

The influence of bond polarity

Of the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. Looking at the methyl halides as simple examples:



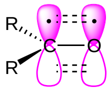
The electronegativities of carbon and iodine are not very different, and so there will be little separation of charge on the bond. One of the important set of reactions of alkyl halides involves replacing the halogen by something else - substitution reactions. These reactions can involve the carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged. Alternatively, something either fully or negatively charged is attracted to the slightly positive carbon atom and pushes off the halogen atom.

You might have thought that either of these would be more effective in the case of the carbon-fluorine bond with the quite large amounts of positive and negative charge already present. But that's not so - quite the opposite is true! The thing that governs the reactivity is the strength of the bonds which have to be broken. It is difficult to break a carbon-fluorine bond, but easy to break a carbon-iodine one.

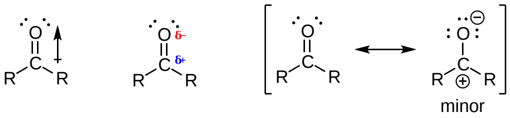
The Carbonyl Group

C=O is prone to additions and nucleophillic attack because or carbon's positive charge and oxygen's negative charge. The resonance of the carbon partial positive charge allows the negative charge on the nucleophile to attack the Carbonyl group and become a part of the structure and a positive charge (usually a proton hydrogen) attacks the oxygen. Just a reminder, the nucleophile is a good acid therefore "likes protons" so it will attack the side with a positive charge.

Before we consider in detail the reactivity of aldehydes and ketones, we need to look back and remind ourselves of what the bonding picture looks like in a carbonyl. Carbonyl carbons are sp^2 hybridized, with the three sp^2 orbitals forming overlaps with orbitals on the oxygen and on the two carbon or hydrogen atoms. These three bonds adopt trigonal planar geometry. The remaining unhybridized 2p orbital on the central carbonyl carbon is perpendicular to this plane, and forms a ‘side-by-side’ pi bond with a 2p orbital on the oxygen.

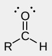
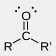
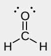
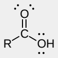
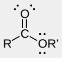
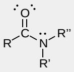
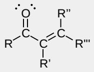
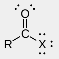
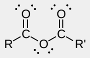


The carbon-oxygen double bond is polar: oxygen is more electronegative than carbon, so electron density is higher on the oxygen side of the bond and lower on the carbon side. Recall that bond polarity can be depicted with a dipole arrow, or by showing the oxygen as holding a partial negative charge and the carbonyl carbon a partial positive charge.



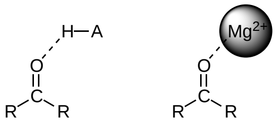
A third way to illustrate the carbon-oxygen dipole is to consider the two main resonance contributors of a carbonyl group: the major form, which is what you typically see drawn in Lewis structures, and a minor but very important contributor in which both electrons in the pbond are localized on the oxygen, giving it a full negative charge. The latter depiction shows the carbon with an empty 2p orbital and a full positive charge.

Some Carbonyl Compounds

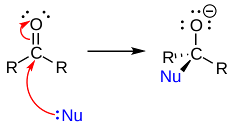
Compound	aldehyde	ketone	formaldehyde	carboxylic acid	ester	amide	enone	acyl halide	acid anhydride
Structure									
General Formula	RCHO	RCOR'	CH_2O	RCOOH	RCOOR'	RCONR'R''	RC(O)C(R')CR"R'''	RCOX	RCO_2COR'

Nucleophilic Addition to Aldehydes and Ketones

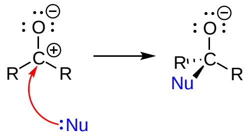
The result of carbonyl bond polarization, however it is depicted, is straightforward to predict. The carbon, because it is electron-poor, is an electrophile: it is a great target for attack by an electron-rich nucleophilic group. Because the oxygen end of the carbonyl double bond bears a partial negative charge, anything that can help to stabilize this charge by accepting some of the electron density will increase the bond's polarity and make the carbon more electrophilic. Very often a general acid group serves this purpose, donating a proton to the carbonyl oxygen.



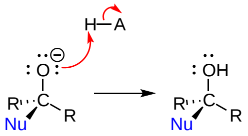
The same effect can also be achieved if a Lewis acid, such as a magnesium ion, is located near the carbonyl oxygen. Unlike the situation in a nucleophilic substitution reaction, when a nucleophile attacks an aldehyde or ketone carbon there is no leaving group – the incoming nucleophile simply 'pushes' the electrons in the pi bond up to the oxygen.



Alternatively, if you start with the minor resonance contributor, you can picture this as an attack by a nucleophile on a carbocation.



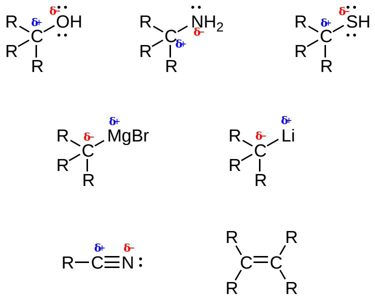
After the carbonyl is attacked by the nucleophile, the negatively charged oxygen has the capacity to act as a nucleophile. However, most commonly the oxygen acts instead as a base, abstracting a proton from a nearby acid group in the solvent or enzyme active site.



This very common type of reaction is called a **nucleophilic addition**. In many biologically relevant examples of nucleophilic addition to carbonyls, the nucleophile is an alcohol oxygen or an amine nitrogen, or occasionally a thiol sulfur. In one very important reaction type known as an aldol reaction, the nucleophile attacking the carbonyl is a resonance-stabilized carbanion. In this chapter, we will concentrate on reactions where the nucleophile is an oxygen or nitrogen.

1. Nucleophilic Addition to Aldehydes and Ketones
2. Nucleophilic Substitution of RCOZ (Z = Leaving Group)
3. General reaction
4. General mechanism

Polarity Patterns in Other Common Functional Groups



Nucleophile?

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? Enolate ions (section 7.5) are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Reactions with carbon nucleophiles will be dealt with in chapters 13 and 14, however - in this chapter and the next, we will concentrate on non-carbon nucleophiles.

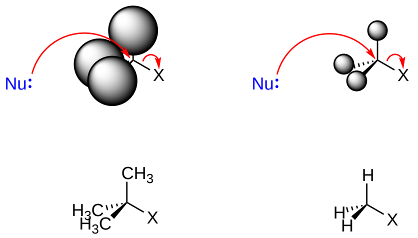
When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Neutral Nucleophiles	Charged Nucleophiles
H_2O, NH_3, RNH_2, R_2NH, R_3N, ROH, RCOOH, RSH, and PR_3	$^{\ominus}OH$, $^{\ominus}OR$, $^{\ominus}NH_2$, $^{\ominus}NHR$, $^{\ominus}NR_2$, $^{\ominus}SH$, $^{\ominus}SR$, $^{\ominus}SeR$, $^{\ominus}Cl$, $^{\ominus}Br$, $^{\ominus}I$, $^{\ominus}F$, $^{\ominus}CN$, $RCOO^{\ominus}$

Electrophiles

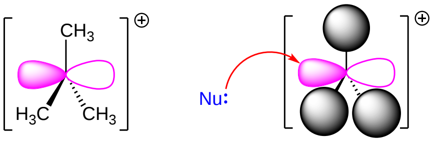
In the vast majority of the nucleophilic substitution reactions you will see in this and other organic chemistry texts, the electrophilic atom is a carbon which is bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom is an attractive target for something that is electron-rich, *i.e.* a nucleophile. However, we must also consider the effect of steric hindrance on electrophilicity. In addition, we must discuss how the nature of the electrophilic carbon, and more specifically the stability of a potential carbocationic intermediate, influences the S_N1 vs. S_N2 character of a nucleophilic substitution reaction.

Consider two hypothetical S_N2 reactions: one in which the electrophile is a methyl carbon and another in which it is tertiary carbon.



Because the three substituents on the methyl carbon electrophile are tiny hydrogens, the nucleophile has a relatively clear path for backside attack. However, backside attack on the tertiary carbon is blocked by the bulkier methyl groups. Once again, steric hindrance - this time caused by bulky groups attached to the electrophile rather than to the nucleophile - hinders the progress of an associative nucleophilic (S_N2) displacement.

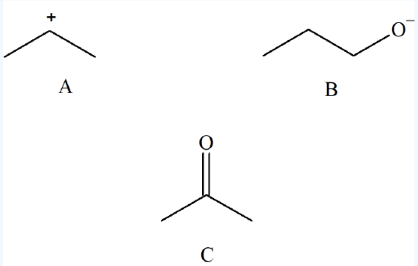
The factors discussed in the above paragraph, however, do not prevent a sterically-hindered carbon from being a good electrophile - they only make it less likely to be attacked in a *concerted S_N2 reaction*. Nucleophilic substitution reactions in which the electrophilic carbon is sterically hindered are more likely to occur by a two-step, dissociative (S_N1) mechanism. This makes perfect sense from a geometric point of view: the limitations imposed by sterics are significant mainly in an S_N2 displacement, when the electrophile being attacked is a sp^3-hybridized tetrahedral carbon with its relatively ‘tight’ angles of 109.4^o. Remember that in an S_N1 mechanism, the nucleophile attacks an sp^2-hybridized carbocation intermediate, which has trigonal planar geometry with ‘open’ 120 angles.



With this open geometry, the empty p orbital of the electrophilic carbocation is no longer significantly shielded from the approaching nucleophile by the bulky alkyl groups. A carbocation is a very potent electrophile, and the nucleophilic step occurs very rapidly compared to the first (ionization) step.

? Exercise 4.1.1

Label the following either an electrophile or a nucleophile.



Answer

A = Electrophile

B = Nucleophile

C = Both (carbonyl carbon is electrophile and oxygen is nucleophile)

4.1.1: Substitution Mechanisms

4.1.2: Elimination Mechanisms

4.2: Radical Reactions

Objectives

After completing this section, you should be able to

- give an example of a radical substitution reaction.
- identify the three steps (initiation, propagation and termination) that occur in a typical radical substitution reaction.
- write out the steps involved in a simple radical substitution reaction, such as the chlorination of methane.
- explain why the halogenation of an alkane is not a particularly useful method of preparing specific alkyl halides.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- chain reaction
- initiation step
- propagation step
- radical substitution
- termination step

Study Notes

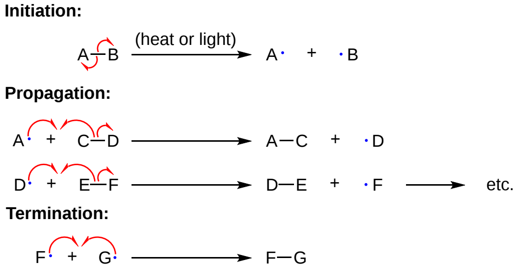
A *radical substitution reaction* is a reaction which occurs by a free radical mechanism and results in the substitution of one or more of the atoms or groups present in the substrate by different atoms or groups.

The *initiation step* in a radical chain reaction is the step in which a free radical is first produced. A *termination step* of a radical chain reaction is one in which two radicals react together in some way so that the chain can no longer be propagated.

While radical halogenation of very simple alkanes can be an effective synthetic strategy, it cannot be employed for larger more complex alkanes to yield specific alkyl halides, since the reactive nature of radicals always leads to mixtures of single- and multiple-halogenated products.

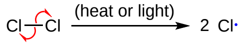
The Three Phases of Radical Chain Reactions

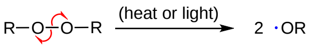
Because of their high reactivity, free radicals have the potential to be both extremely powerful chemical tools and extremely harmful contaminants. Much of the power of free radical species stems from the natural tendency of radical processes to occur in a chain reaction fashion. **Radical chain reactions** have three distinct phases: initiation, propagation, and termination.

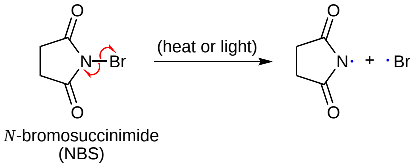


The **initiation phase** describes the step that initially creates a radical species. In most cases, this is a homolytic cleavage event, and takes place very rarely due to the high energy barriers involved. Often the influence of heat, UV radiation, or a metal-containing catalyst is necessary to overcome the energy barrier.

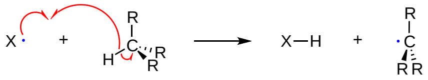
Molecular chlorine and bromine will both undergo homolytic cleavage to form radicals when subjected to heat or light. Other functional groups which also tend to form radicals when exposed to heat or light are chlorofluorocarbons, peroxides, and the halogenated amide N-bromosuccinimide (NBS).

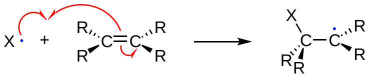




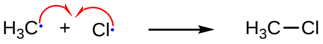


The **propagation phase** describes the 'chain' part of chain reactions. Once a reactive free radical is generated, it can react with stable molecules to form new free radicals. These new free radicals go on to generate yet more free radicals, and so on. Propagation steps often involve hydrogen abstraction or addition of the radical to double bonds.





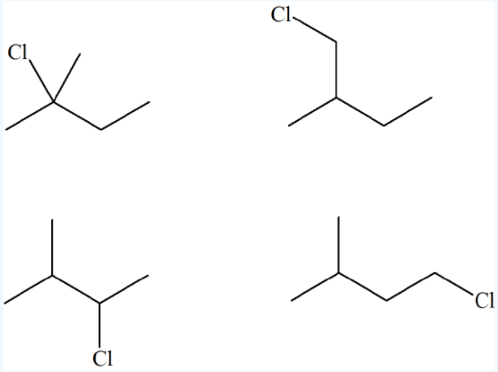
Chain termination occurs when two free radical species react with each other to form a stable, non-radical adduct. Although this is a very thermodynamically downhill event, it is also very rare due to the low concentration of radical species and the small likelihood of two radicals colliding with one another. In other words, the Gibbs free energy barrier is very high for this reaction, mostly due to entropic rather than enthalpic considerations. The active sites of enzymes, of course, can evolve to overcome this entropic barrier by positioning two radical intermediates adjacent to one another.



? Exercise 4.2.1

Radical chlorination of alkanes are not useful due to uncontrolled substitution. Draw the mono-substituted products of Cl_2 reacting with 2-methylbutane.

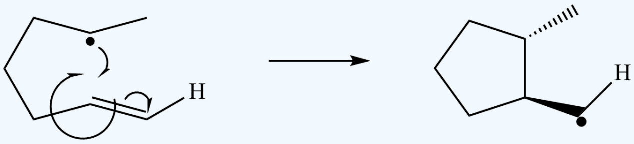
Answer



? Exercise 4.2.2

Propose a radical mechanism for the following reaction:

Answer



4.3: Reactive Species

4.3.1: Carbocation Structure and Stability

Objectives

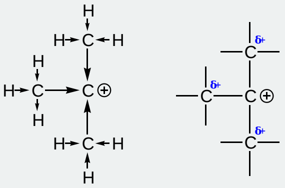
After completing this section, you should be able to

- describe the geometry of a given carbocation.
- arrange a given series of carbocations in order of increasing or decreasing stability.
- explain the relative stability of methyl, primary, secondary and tertiary carbocations in terms of hyperconjugation and inductive effects.

Study Notes

Although hyperconjugation can be used to explain the relative stabilities of carbocations, this explanation is certainly not the only one, and is by no means universally accepted. A more common explanation, involving the concept of an inductive effect, is given below.

It is a general principle in chemistry that the more a charge is dispersed, the more stable is the species carrying the charge. Put simply, a species in which a positive charge is shared between two atoms would be more stable than a similar species in which the charge is borne wholly by a single atom. In a tertiary carbocation, the positively charged carbon atom attracts the bonding electrons in the three carbon-carbon sigma (σ) bonds, and thus creates slight positive charges on the carbon atoms of the three surrounding alkyl groups (and, indeed, on the hydrogen atoms attached to them). Chemists sometimes use an arrow to represent this inductive release:



Note: These diagrams do not reflect the geometry of the carbocation. The overall charge on the carbocation remains unchanged, but some of the charge is now carried by the alkyl groups attached to the central carbon atom; that is, the charge has been dispersed.

In the tertiary carbocation shown above, the three alkyl groups help to stabilize the positive charge. In a secondary carbocation, only two alkyl groups would be available for this purpose, while a primary carbocation has only one alkyl group available. Thus the observed order of stability for carbocations is as follows:

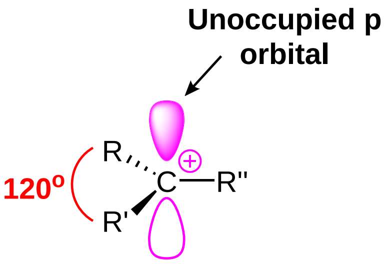
tertiary > secondary > primary > methyl.

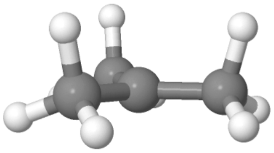
Stability of carbocation intermediates

The next step in understanding why Markovnikov's rule is often followed in electrophilic additions, involves understanding the structure and stability of the carboncation intermediate formed during the mechanism.

Carbocation Structure

Carbocations typically have three substituents which makes the carbon sp^2 hybridized and gives the overall molecule a trigonal planar geometry. The carbocation's substituents are all in the same plane and have a bond angle of 120º between them. The carbon atom in the carbocation is electron deficient; it only has six valence electrons which are used to form three sigma covalent bonds with the substituents. The carbocation carbon has an unoccupied p orbital which is perpendicular to the plane created by the substituents. The p orbital can easily accept electron pairs during reactions making carbocations excellent Lewis acids.

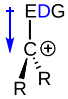
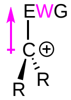




Stability of Carbocation Intermediates

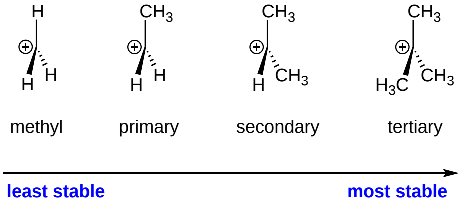
By being a reactive intermediate of the electrophilic addition mechanism, the stability of a carbocation has a direct effect on the reaction. The critical question now becomes, *what stabilizes a carbocation*?

A positively charged species such as a carbocation is very electron-poor, and thus anything which donates electron density will help to stabilize it. Conversely, a carbocation will be *destabilized* by an electron withdrawing group.

 electron donating group *stabilizes* a carbocation	 electron withdrawing group *destabilizes* a carbocation

Extensive experimental evidence has shown that a carbocation becomes more stable as the number of alkyl substituents increases. Carbocations can be given a designation based on the number of alkyl groups attached to the carbocation carbon. Three alkyl groups is called a tertiary (3°) carbocation, 2 alkyl groups is called secondary (2°), and 1 alkyl group is called primary (1°). No alkyl groups are attached (3 hydrogen substituents) is called a methyl carbocation.

The overall order of stability is as follows:

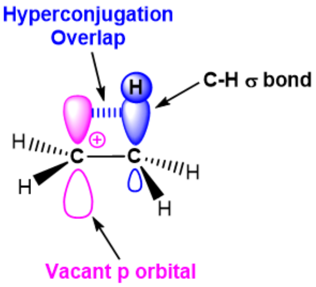


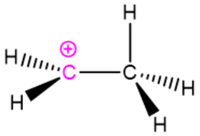
Alkyl groups stabilized carbocations for two reasons. The first is through inductive effects. As discussed in **Section 2-1**, inductive effects occur when the electrons in covalent bonds are shifted towards an nearby atom with a higher electronegativity. In this case, the positively charged carbocation draws in electron density from the surrounding substituents thereby gaining stabilization by slightly reducing its positive charge. Alkyl groups are more effective at inductively donating electron density than a hydrogen because they are larger, more polarizable, and contain more bonding electrons. As more alkyl groups are attached to the carbocation more inductive electron donation occurs and the carbocation becomes more stable.

The second reason alkyl groups stabilize carbocations is through hyperconjugation. As previously discussed in **Section 7.6**, hyperconjugation is an electron donation that occurs from the parallel overlap of p orbitals with adjacent hybridized orbitals participating in sigma bonds. This electron donation serves to stabilize the carbocation. As the number of alkyl substituents increases, the number of sigma bonds available for hyperconjugation increases, and the carbocation tends to become more stabilized.

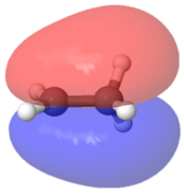
In the example of ethyl carbocation shown below, the p orbital from a sp^2 hybridized carbocation carbon involved interacts with a sp^3 hybridized orbital participating in an adjacent C-H sigma bond. Electron density from the C-H sigma bond is donated into carbocation's p orbital providing stabilization.

The molecular orbital of the ethyl carbocation shows the interaction of electrons in methyl group's C-H sigma bonds with the adjacent empty p orbital from the carbocation. The interaction creates a bonding molecular orbital which extends over the three atom chain (C-C-H) involved in hyperconjugation. The expanded molecular orbital helps to stabilize the carbocation.



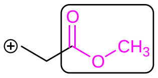


Ethyl carbocation

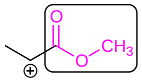


Extended Bonding MO created by hyperconjugation

It is not accurate to say, however, that carbocations with higher substitution are *always* more stable than those with less substitution. Just as electron-donating groups can stabilize a carbocation, electron-withdrawing groups act to destabilize carbocations. Carbonyl groups are electron-withdrawing by inductive effects, due to the polarity of the C=O double bond. It is possible to demonstrate in the laboratory that carbocation A below is more stable than carbocation B, even though A is a primary carbocation and B is secondary.



A: more stable

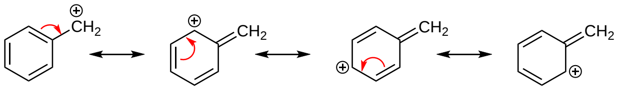


B: less stable

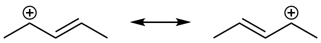
The difference in stability can be explained by considering the electron-withdrawing inductive effect of the ester carbonyl. Recall that inductive effects - whether electron-withdrawing or donating - are relayed through covalent bonds and that the strength of the effect decreases rapidly as the number of intermediary bonds increases. In other words, the effect decreases with distance. In species B the positive charge is closer to the carbonyl group, thus the destabilizing electron-withdrawing effect is stronger than it is in species A.

> In the next chapter we will see how the carbocation-destabilizing effect of electron-withdrawing fluorine substituents can be used in experiments designed to address the question of whether a biochemical nucleophilic substitution reaction is S_N1 or S_N2.

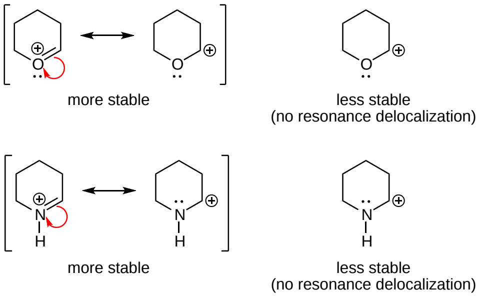
Stabilization of a carbocation can also occur through resonance effects, and as we have already discussed in the acid-base chapter, resonance effects as a rule are more powerful than inductive effects. Consider the simple case of a **benzylic** carbocation:



This carbocation is comparatively stable. In this case, electron donation is a resonance effect. Three additional resonance structures can be drawn for this carbocation in which the positive charge is located on one of three aromatic carbons. The positive charge is not isolated on the benzylic carbon, rather it is delocalized around the aromatic structure: this delocalization of charge results in significant stabilization. As a result, benzylic and **allylic** carbocations (where the positively charged carbon is conjugated to one or more non-aromatic double bonds) are significantly more stable than even tertiary alkyl carbocations.

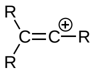


Because heteroatoms such as oxygen and nitrogen are more electronegative than carbon, you might expect that they would by definition be electron withdrawing groups that destabilize carbocations. In fact, the opposite is often true: if the oxygen or nitrogen atom is in the correct position, the overall effect is carbocation stabilization. This is due to the fact that although these heteroatoms are electron *withdrawing* groups by induction, they are electron *donating* groups by resonance, and it is this resonance effect which is more powerful. (We previously encountered this same idea when considering the relative acidity and basicity of phenols and aromatic amines in section 7.4). Consider the two pairs of carbocation species below:



In the more stable carbocations, the heteroatom acts as an electron donating group by resonance: in effect, the lone pair on the heteroatom is available to delocalize the positive charge. In the less stable carbocations the positively-charged carbon is more than one bond away from the heteroatom, and thus no resonance effects are possible. In fact, in these carbocation species the heteroatoms actually *destabilize* the positive charge, because they are electron withdrawing by induction.

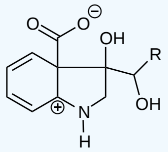
Finally, **vinylic** carbocations, in which the positive charge resides on a double-bonded carbon, are very unstable and thus unlikely to form as intermediates in any reaction.

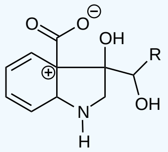


a vinylic carbocation (very unstable)

Example 4.3.1.1

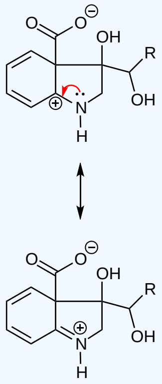
In which of the structures below is the carbocation expected to be more stable? Explain.

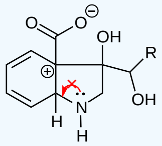




Answer

In the carbocation on the left, the positive charge is located in a position relative to the nitrogen such that the lone pair of electrons on the nitrogen can be donated to fill the empty orbital. This is not possible for the carbocation species on the right.

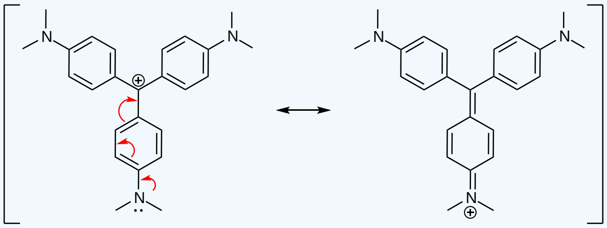




Example 4.3.1.2

Draw a resonance structure of the crystal violet cation in which the positive charge is delocalized to one of the nitrogen atoms.

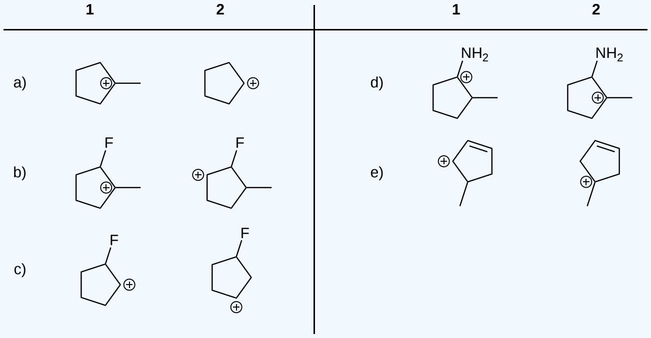
Answer



When considering the possibility that a nucleophilic substitution reaction proceeds *via* an S_N1 pathway, it is critical to evaluate the stability of the hypothetical carbocation intermediate. If this intermediate is not sufficiently stable, an S_N1 mechanism must be considered unlikely, and the reaction probably proceeds by an S_N2 mechanism. In the next chapter we will see several examples of biologically important S_N1 reactions in which the positively charged intermediate is stabilized by inductive and resonance effects inherent in its own molecular structure.

Example 4.3.1.3

State which carbocation in each pair below is more stable, or if they are expected to be approximately equal. Explain your reasoning.



Answer

a. 1 (tertiary vs. secondary carbocation)
b. 1 (tertiary vs. secondary carbocation)
c. 2 (positive charge is further from electron-withdrawing fluorine)
d. 1 (lone pair on nitrogen can donate electrons by resonance)
e. 1 (allylic carbocation – positive charge can be delocalized to a second carbon)

4.3.2: Carbanions II

A carbanion is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.[1] The carbanion exists in a trigonal pyramidal geometry. Formally, a carbanion is the conjugate base of a carbon acid.

$$R_3C{-}H + B^- \rightarrow R_3C^- + H{-}B \tag{4.3.2.1}$$

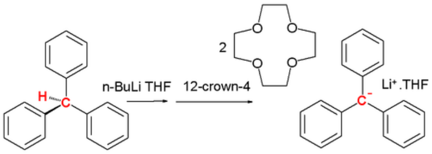
where B stands for the base. A carbanion is one of several reactive intermediates in organic chemistry.

Theory

A carbanion is a nucleophile, which stability and reactivity determined by several factors:

1. The inductive effect. Electronegative atoms adjacent to the charge will stabilize the charge;
2. Hybridization of the charge-bearing atom. The greater the s-character of the charge-bearing atom, the more stable the anion;
3. The extent of conjugation of the anion. Resonance effects can stabilize the anion. This is especially true when the anion is stabilized as a result of aromaticity.

A carbanion is a reactive intermediate and is encountered in organic chemistry for instance in the E1cB elimination reaction and in organometallic chemistry in for instance a Grignard reaction or in alkyl lithium chemistry. Stable carbanions do however exist. In 1984 Olmstead presented the lithium crown ether salt of the triphenylmethyl carbanion from triphenylmethane, n-butyllithium and 12-crown-4 at low temperatures:[2]

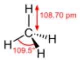
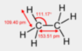
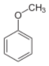
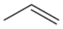
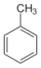
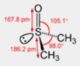
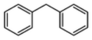
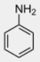
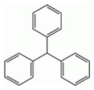
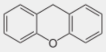


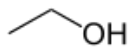
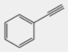
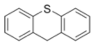
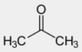
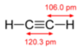
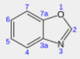
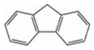
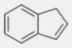
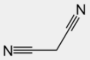
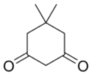
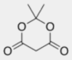
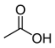
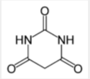
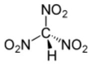
Adding n-butyllithium to triphenylmethane in THF at low temperatures followed by 12-crown-4 results in a red solution and the salt complex precipitates at −20 °C. The central C-C bond lengths are 145 pm with the phenyl ring propelled at an average angle of 31.2°. This propeller shape is less pronounced with a tetramethylammonium counterion.[3] One tool for the detection of carbanions in solution is proton NMR.[4] A spectrum of cyclopentadiene in DMSO shows four vinylic protons at 6.5 ppm and two methylene bridge protons at 3 ppm whereas the cyclopentadienyl anion has a single resonance at 5.50 ppm.

Carbon acids

Any molecule containing a C-H can lose a proton forming the carbanion. Hence any hydrocarbon containing C-H bonds can be considered an acid with a corresponding pKa value. Methane is certainly not an acid in its classical meaning yet its estimated pKa is 56. Compare this to acetic acid with pKa 4.76. The same factors that determine the stability of the carbanion also determine the order in pKa in carbon acids. These values are determined for the compounds either in water in order to compare them to ordinary acids, indimethyl sulfoxide in which the majority of carbon acids and their anions are soluble or in the gas phase. With DMSO the acidity window for solutes is limited to its own pKa of 35.5.

Table 1. Carbon acid acidities in pKa in DMSO [5]. Reference acids in bold.

name	formula	structural formula	pKa
Methane	$\mathbf{CH_4}$		**~ 56**
Ethane	C_2H_6		~ 50
Anisole	C_7H_8O		~ 49
Cyclopentane	C_5H_{10}		~ 45
Propene	C_3H_6		~ 44
Benzene	C_6H_6		~ 43
Toluene	$C_6H_5CH_3$		~ 43
Dimethyl sulfoxide	$(CH_3)_2SO$		35.5
Diphenylmethane	$C_{13}H_{12}$		32.3
Aniline	$\mathbf{C_6H_5NH_2}$		**30.6**
Triphenylmethane	$C_{19}H_{16}$		30.6
Xanthene	$C_{13}H_{10}O$		30

name	formula	structural formula	pKa
Ethanol	**C_2H_5OH**		**29.8**
Phenylacetylene	C_8H_6		28.8
Thioxanthene	$C_{13}H_{10}S$		28.6
Acetone	C_3H_6O		26.5
Acetylene	C_2H_2		25
Benzoxazole	C_7H_5NO		24.4
Fluorene	$C_{13}H_{10}$		22.6
Indene	C_9H_8		20.1
Cyclopentadiene	C_5H_6		18
Malononitrile	$C_3H_2N_2$		11.2
Hydrogen cyanide	HCN	$H-C\equiv N$	9.2
Acetylacetone	$C_5H_8O_2$		8.95
Dimedone	$C_8H_{12}O_2$		5.23
Meldrum's acid	$C_6H_8O_4$		4.97
Acetic acid	**CH_3COOH**		**4.76**
Barbituric acid	$C_4H_2O_3(NH)_2$		4.01
Trinitromethane	$HC(NO_2)_3$		0.17
Fulminic acid	HCNO		-1.07
Carborane superacid	$HCHB_{11}Cl_{11}$		-9

Note that the anions formed by ionization of acetic acid, ethanol or aniline are not carbanions.

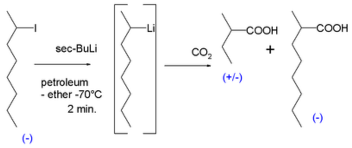
Starting from methane in Table 1, the acidity increases:

- when the anion is aromatic, either because the added electron causes the anion to become aromatic (as in indene and cyclopentadiene), or because the negative charge on carbon can be delocalized over several already-aromatic rings (as in triphenylmethane or the carborane superacid).
- when the carbanion is surrounded by strongly electronegative groups, through the partial neutralisation of the negative charge (as in malononitrile).
- when the carbanion is immediately next to a carbonyl group. The α-protons of carbonyl groups are acidic because the negative charge in the enolate can be partially distributed in the oxygen atom. Meldrum's acid and barbituric acid, historically named acids, are in fact a lactone and a lactam respectively, but their acidic carbon protons make them acidic. The acidity of carbonyl compounds is an important driving force in many organic reactions such as the aldol reaction.

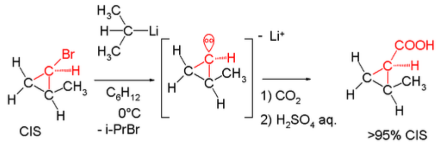
Chiral carbanions

With the molecular geometry for a carbanion described as a trigonal pyramid the question is whether or not carbanions can display chirality, because if the activation barrier for inversion of this geometry is too low any attempt at introducing chirality will end inracemization, similar to the nitrogen inversion. However, solid evidence exists that carbanions can indeed be chiral for example in research carried out with certain organolithium compounds.

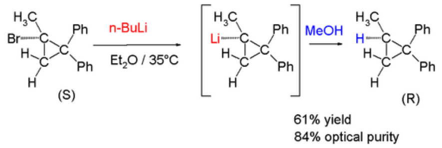
The first ever evidence for the existence of chiral organolithium compounds was obtained in 1950. Reaction of chiral 2-iodooctane with sec-butyllithium in petroleum ether at −70 °C followed by reaction with dry ice yielded mostly racemic 2-methylbutyric acid but also an amount of optically active 2-methyloctanoic acid which could only have formed from likewise optical active 2-methylheptyllithium with the carbon atom linked to lithium the carbanion:[6]



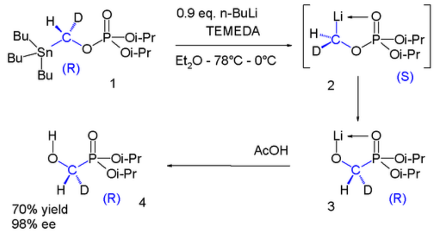
On heating the reaction to 0 °C the optical activity is lost. More evidence followed in the 1960s. A reaction of the cis isomer of 2-methylcyclopropyl bromide with sec-butyllithium again followed by carboxylation with dry ice yielded cis-2-methylcyclopropylcarboxylic acid. The formation of the trans isomer would have indicated that the intermediate carbanion was unstable.[7]



In the same manner the reaction of (+)-(S)-l-bromo-l-methyl-2,2-diphenylcyclopropane with n-butyllithium followed by quench with methanol resulted in product with retention of configuration:[8]



Of recent date are chiral methyllithium compounds:[9]



The phosphate **1** contains a chiral group with a hydrogen and a deuterium substituent. The stannyl group is replaced by lithium to intermediate **2** which undergoes a phosphate-phosphorane rearrangement to phosphorane **3** which on reaction with acetic acid givesalcohol **4**. Once again in the range of −78 °C to 0 °C the chirality is preserved in this reaction sequence.[10]

History

A carbanionic structure first made an appearance in the reaction mechanism for the benzoin condensation as correctly proposed by Clarke and Lapworth in 1907.[11] In 1904 Schlenk prepared Ph3C-NMe4+ in a quest for pentavalent nitrogen (fromTetramethylammonium chloride and Ph3CNa) [12] and in 1914 he demonstrated how triarylmethyl radicals could be reduced to carbonions by alkali metals.[13] The phrase carbanion was introduced by Wallis and Adams in 1933 as the negatively charged counterpart of the carbonium ion.[14][15]

External links

- Large database of Bordwell pKa values at www.chem.wisc.edu Link
- Large database of Bordwell pKa values at daecr1.harvard.edu Link

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4.3.3: Carbenes

A carbene is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons. The general formula is R-(C:)-R' or R=C:. The term "carbene" may also refer to the specific compound H2C:, also called methylene, the parent hydride from which all other carbene compounds are formally derived. Carbenes are classified as either singlets or triplets depending upon their electronic structure. Most carbenes are very short lived, although persistent carbenes are known. One well studied carbene is Cl2C:, or dichlorocarbene, which can be generated in situ from chloroform and a strong base.

Singlet and triplet carbenes

The two classes of carbenes are singlet and triplet carbenes. Singlet carbenes are spin-paired. In the language of valence bond theory, the molecule adopts an sp2 hybrid structure. Triplet carbenes have two unpaired electrons. They may be either linear or bent, i.e. sp or sp2 hybridized, respectively. Most carbenes have a nonlinear triplet ground state, except for those with nitrogen, oxygen, or sulfur atoms, and halides directly bonded to the divalent carbon.

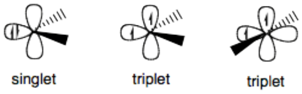
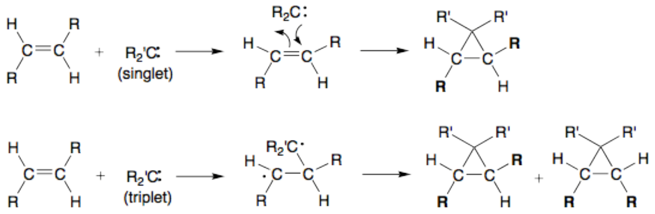


Figure 1: Image used with permission from Wikipedia

Carbenes are called singlet or triplet depending on the electronic spins they possess. Triplet carbenes are paramagnetic and may be observed by electron spin resonance spectroscopy if they persist long enough. The total spin of singlet carbenes is zero while that of triplet carbenes is one (in units of [\hbar]). Bond angles are 125-140° for triplet methylene and 102° for singlet methylene (as determined by EPR). Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media.

For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes (see also Hund's rule of maximum multiplicity), thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species.Substituents that can donate electron pairs may stabilize the singlet state by delocalizing the pair into an empty p-orbital. If the energy of the singlet state is sufficiently reduced it will actually become the ground state. No viable strategies exist for triplet stabilization. The carbene called 9-fluorenylidene has been shown to be a rapidly equilibrating mixture of singlet and triplet states with an approximately 1.1 kcal/mol (4.6 kJ/mol) energy difference.[3] It is, however, debatable whether diaryl carbenes such as the fluorene carbene are true carbenes because the electrons can delocalize to such an extent that they become in fact biradicals. In silico experiments suggest that triplet carbenes can be thermodynamically stabilized with electropositive heteroatoms such as in silyl and silyloxy carbenes, especially trifluorosilyl carbenes.[4]

Reactivity



Carbene addition to alkenes

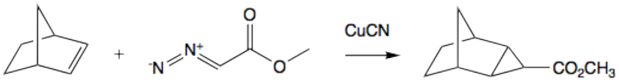
Singlet and triplet carbenes exhibit divergent reactivity. Singlet carbenes generally participate in cheletropic reactions as either electrophiles or nucleophiles. Singlet carbenes with unfilled p-orbital should be electrophilic. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions. Triplet carbenes have to go through an intermediate with two unpaired electrons whereas singlet carbene can react in a single concerted step.

Due to these two modes of reactivity, reactions of singlet methylene are stereospecific whereas those of triplet methylene are stereoselective. This difference can be used to probe the nature of a carbene. For example, the reaction of methylene generated from photolysis of diazomethane with *cis*-2-butene or with *trans*-2-butene each give a single diastereomer of the 1,2-dimethylcyclopropane product: *cis* from *cis* and *trans* from *trans*, which proves that the methylene is a singlet.[5] If the methylene were a triplet, one would not expect the product to depend upon the starting alkene geometry, but rather a nearly identical mixture in each case.

Reactivity of a particular carbene depends on the substituent groups. Their reactivity can be affected by metals. Some of the reactions carbenes can do are insertions into C-H bonds, skeletal rearrangements, and additions to double bonds. Carbenes can be classified as nucleophilic, electrophilic, or ambiphilic. For example, if a substituent is able to donate a pair of electrons, most likely carbene will not be electrophilic. Alkyl carbenes insert much more selectively than methylene, which does not differentiate between primary, secondary, and tertiary C-H bonds.

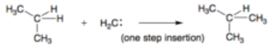
Cyclopropanation

Carbenes add to double bonds to form cyclopropanes. A concerted mechanism is available for singlet carbenes. Triplet carbenes do not retain stereochemistry in the product molecule. Addition reactions are commonly very fast and exothermic. The slow step in most instances is generation of carbene. A well-known reagent employed for alkene-to-cyclopropane reactions is Simmons-Smith reagent. This reagent is a system of copper, zinc, and iodine, where the active reagent is believed to be iodomethylzinc iodide. Reagent is complexed by hydroxy groups such that addition commonly happens syn to such group.



Carbene cyclopropanation

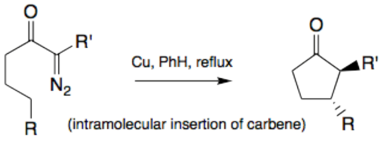
C—H insertion



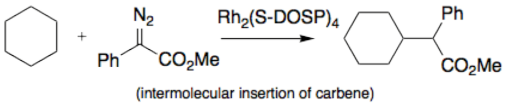
Carbene insertion

Insertions are another common type of carbene reactions. The carbene basically interposes itself into an existing bond. The order of preference is commonly: 1. X–H bonds where X is not carbon 2. C–H bond 3. C–C bond. Insertions may or may not occur in single step.

Intramolecular insertion reactions present new synthetic solutions. Generally, rigid structures favor such insertions to happen. When an intramolecular insertion is possible, no intermolecular insertions are seen. In flexible structures, five-membered ring formation is preferred to six-membered ring formation. Both inter- and intramolecular insertions are amendable to asymmetric induction by choosing chiral ligands on metal centers.

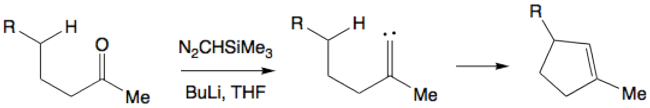


Carbene intramolecular reaction



Carbene intermolecular reaction

Alkylidene carbenes are alluring in that they offer formation of cyclopentene moieties. To generate an alkylidene carbene a ketone can be exposed to trimethylsilyl diazomethane.



Alkylidene carbene

Carbene dimerization

Carbenes and carbenoid precursors can undergo dimerization reactions to form alkenes. While this is often an unwanted side reaction, it can be employed as a synthetic tool and a direct metal carbene dimerization has been used in the synthesis of polyalkynylethenes. Persistent carbenes exist in equilibrium with their respective dimers. This is known as the Wanzlick equilibrium.

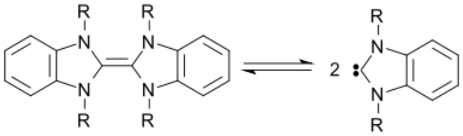


Figure : Wanzlick equilibrium

Carbene ligands in organometallic chemistry

In organometallic species, metal complexes with the formulae L_nMCRR' are often described as carbene complexes. Such species do not however react like free carbenes and are rarely generated from carbene precursors, except for the persistent carbenes. The transition metal carbene complexes can be classified according to their reactivity, with the first two classes being the most clearly defined:

- Fischer carbenes, in which the carbene is bonded to a metal that bears an electron-withdrawing group (usually a carbonyl). In such cases the carbenoid carbon is mildly electrophilic.
- Schrock carbenes, in which the carbene is bonded to a metal that bears an electron-donating group. In such cases the carbenoid carbon is nucleophilic and resembles Wittig reagent (which are not considered carbene derivatives).
- Persistent carbenes, also known as Arduengo or Wanzlick carbenes. These include the class of *N*-heterocyclic carbenes (NHCs) and are often are used as ancillary ligands in organometallic chemistry. Such carbenes are spectator ligands of low reactivity.

Generation of carbenes

- A method that is broadly applicable to organic synthesis is induced elimination of halides from gem-dihalides employing organolithium reagents. It remains uncertain if under these conditions free carbenes are formed or metal-carbene complex. Nevertheless, these metallocarbenes (or carbenoids) give the expected organic products.

  $R_2CBr_2 + BuLi \rightarrow R_2CLi(Br) +$

  BuBr

  R

  $_2CLi(Br) \rightarrow R_2C + LiBr$

- For cyclopropanations, zinc is employed in the Simmons–Smith reaction. In a specialized but instructive case, alpha-halomercury compounds can be isolated and separately thermolyzed. For example, the "Seyferth reagent" releases CCl_2 upon heating.

  $C_6H_5HgCCl_3 \rightarrow CCl_2 + C_6H_5HgCl$

- Most commonly, carbenes are generated from diazoalkanes, via photolytic, thermal, or transition metal-catalyzed routes. Catalysts typically feature rhodium and copper. The Bamford-Stevens reaction gives carbenes in aprotic solvents and carbenium ions in protic solvents.
- Base-induced elimination HX from haloforms (CHX_3) with under phase-transfer conditions.
- Photolysis of diazirines and epoxides can also be employed. Diazirines are cyclic forms of diazoalkanes. The strain of the small ring makes photoexcitation easy. Photolysis of epoxides gives carbonyl compounds as side products. With asymmetric epoxides, two different carbonyl compounds can potentially form. The nature of substituents usually favors formation of one over the other. One of the C-O bonds will have a greater double bond character and thus will be stronger and less likely to break. Resonance structures can be drawn to determine which part will contribute more to the formation of carbonyl. When one substituent is alkyl and another aryl, the aryl-substituted carbon is usually released as a carbene fragment.
- Carbenes are intermediates in the Wolff rearrangement

See also

- Transition metal carbene complexes, also known as carbenoids
- Atomic carbon a single carbon atom with the chemical formula :C:, in effect a twofold carbene. Also has been used to make "true carbenes" in situ.
- Foiled carbenes derive their stability from proximity of a double bond (i.e. their ability to form conjugated systems).
- Carbene analogs
- Carbenium ions, protonated carbenes
- Ring opening metathesis polymerization

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4.3.4: Free Radicals

In chemistry, a **radical** (more precisely, a **free radical**) is an atom, molecule, or ion that has unpaired valence electrons or an open electron shell, and therefore may be seen as having one or more "dangling" covalent bonds.

With some exceptions, these "dangling" bonds make free radicals highly chemically reactive towards other substances, or even towards themselves: their molecules will often spontaneously dimerize or polymerize if they come in contact with each other. Most radicals are reasonably stable only at very low concentrations in inert media or in a vacuum.

A notable example of a free radical is the hydroxyl radical (HO•), a molecule that is one hydrogen atom short of a water molecule and thus has one bond "dangling" from the oxygen. Two other examples are the carbene molecule (**:**CH2), which has two dangling bonds; and the superoxide anion (•O−2), the oxygen molecule O2 with one extra electron, which has one dangling bond. In contrast, the hydroxyl anion (HO−), the oxide anion (O2−) and thecarbenium cation (CH+3) are not radicals, since the bonds that may appear to be dangling are in fact resolved by the addition or removal of electrons.

Free radicals may be created in a number of ways, including synthesis with very dilute or rarefied reagents, reactions at very low temperatures, or breakup of larger molecules. The latter can be affected by any process that puts enough energy into the parent molecule, such as ionizing radiation, heat, electrical discharges, electrolysis, and chemical reactions. Indeed, radicals are intermediate stages in many chemical reactions.

Free radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes. In living organisms, the free radicals superoxide and nitric oxideand their reaction products regulate many processes, such as control of vascular tone and thus blood pressure. They also play a key role in the intermediary metabolism of various biological compounds. Such radicals can even be messengers in a process dubbed redox signaling. A radical may be trapped within a *solvent cage* or be otherwise bound.

Until late in the 20th century the word "radical" was used in chemistry to indicate any connected group of atoms, such as a methyl group or a carboxyl, whether it was part of a larger molecule or a molecule on its own. The qualifier "free" was then needed to specify the unbound case. Following recent nomenclature revisions, a part of a larger molecule is now called a functional group or substituent, and "radical" now implies "free". However, the old nomenclature may still occur in the literature.

History

The first organic free radical identified was triphenylmethyl radical. This species was discovered by Moses Gomberg in 1900 at the University of Michigan USA. Historically, the term *radical* in radical theory was also used for bound parts of the molecule, especially when they remain unchanged in reactions. These are now called functional groups. For example, methyl alcohol was described as consisting of a methyl "radical" and a hydroxyl "radical". Neither are radicals in the modern chemical sense, as they are permanently bound to each other, and have no unpaired, reactive electrons; however, they can be observed as radicals in mass spectrometry when broken apart by irradiation with energetic electrons.

Depiction in chemical reactions

In chemical equations, free radicals are frequently denoted by a dot placed immediately to the right of the atomic symbol or molecular formula as follows:

$$\mathrm{Cl}_2 \xrightarrow{UV} \mathrm{Cl}\cdot + \mathrm{Cl}\cdot$$

Chlorine gas can be broken down by ultraviolet light to form atomic chlorine radicals.

Radical reaction mechanisms use single-headed arrows to depict the movement of single electrons:

The homolytic cleavage of the breaking bond is drawn with a 'fish-hook' arrow to distinguish from the usual movement of two electrons depicted by a standard curly arrow. It should be noted that the second electron of the breaking bond also moves to pair up with the attacking radical electron; this is not explicitly indicated in this case.

Free radicals also take part in radical addition and radical substitution as reactive intermediates. Chain reactions involving free radicals can usually be divided into three distinct processes. These are *initiation*, *propagation*, and *termination*.

- **Initiation** reactions are those that result in a net increase in the number of free radicals. They may involve the formation of free radicals from stable species as in Reaction 1 above or they may involve reactions of free radicals with stable species to form more free radicals.
- **Propagation** reactions are those reactions involving free radicals in which the total number of free radicals remains the same.
- **Termination** reactions are those reactions resulting in a net decrease in the number of free radicals. Typically two free radicals combine to form a more stable species, for example: $2\mathrm{Cl}\cdot \rightarrow \mathrm{Cl}_2$

Formation

The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy. For example, splitting H_2 into 2H• has a $\Delta H°$ of +435 kJ/mol, and Cl_2 into 2Cl• has a $\Delta H°$ of +243 kJ/mol. This is known as the homolytic bond dissociation energy, and is usually abbreviated as the symbol $\Delta H°$. The bond energy between two covalently bonded atoms is affected by the structure of the molecule as a whole, not just the identity of the two atoms. Likewise, radicals requiring more energy to form are less stable than those requiring less energy. Homolytic bond cleavage most often happens between two atoms of similar electronegativity. In organic chemistry this is often the O-O bond in peroxide species or O-N bonds. Sometimes radical formation is spin-forbidden, presenting an additional barrier. However, propagation is a very exothermic reaction. Likewise, although radical ions do exist, most species are electrically neutral. Radicals may also be formed by single electron oxidation or reduction of an atom or molecule. An example is the production of superoxide by the electron transport chain. Early studies of organometallic chemistry, especially tetra-alkyl lead species by F.A. Paneth and K. Hahnfeld in the 1930s supported heterolytic fission of bonds and a radical based mechanism.

Persistence and stability

The radical derived from *α-tocopherol*

Although radicals are generally short-lived due to their reactivity, there are long-lived radicals. These are categorized as follows:

Stable radicals

The prime example of a stable radical is molecular dioxygen (O_2). Another common example is nitric oxide (NO). Organic radicals can be long lived if they occur in a conjugated π system, such as the radical derived from α-tocopherol (vitamin E). There are also hundreds of examples of thiazyl radicals, which show low reactivity and remarkable thermodynamic stability with only a very limited extent of π resonance stabilization.[1][2]

Persistent radicals

Persistent radical compounds are those whose longevity is due to steric crowding around the radical center, which makes it physically difficult for the radical to react with another molecule.[3] Examples of these include Gomberg's triphenylmethyl radical, Fremy's salt(Potassium nitrosodisulfonate, $(KSO_3)_2NO·$), nitroxides, (general formula $R_2NO·$) such as TEMPO, TEMPOL, nitronyl nitroxides, and azephenylenyls and radicals derived from PTM (perchlorophenylmethyl radical) and TTM (tris(2,4,6-trichlorophenyl)methyl radical). Persistent radicals are generated in great quantity during combustion, and "may be responsible for the oxidative stress resulting in cardiopulmonary disease and probably cancer that has been attributed to exposure to airborne fine particles."[4]

Diradicals

Diradicals are molecules containing two radical centers. Multiple radical centers can exist in a molecule. Atmospheric oxygen naturally exists as a diradical in its ground state as triplet oxygen. The low reactivity of atmospheric oxygen is due to its diradical state. Non-radical states of dioxygen are actually less stable than the diradical. The relative stability of the oxygen diradical is primarily due to the spin-forbidden nature of the triplet-singlet transition required for it to grab electrons, i.e., "oxidize". The diradical state of oxygen also results in its paramagnetic character, which is demonstrated by its attraction to an external magnet.[5]

Reactivity

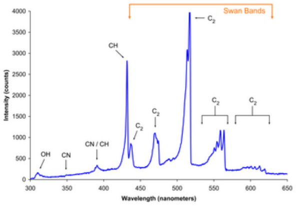
Radical alkyl intermediates are stabilized by similar physical processes to carbocations: as a general rule, the more substituted the radical center is, the more stable it is. This directs their reactions. Thus, formation of a tertiary radical ($R_3C·$) is favored over secondary ($R_2HC·$), which is favored over primary ($RH_2C·$). Likewise, radicals next to functional groups such as carbonyl, nitrile, and ether are more stable than tertiary alkyl radicals.

Radicals attack double bonds. However, unlike similar ions, such radical reactions are not as much directed by electrostatic interactions. For example, the reactivity of nucleophilic ions with α,β-unsaturated compounds (C=C–C=O) is directed by the electron-withdrawing effect of the oxygen, resulting in a partial positive charge on the carbonyl carbon. There are two reactions that are observed in the ionic case: the carbonyl is attacked in a direct addition to carbonyl, or the vinyl is attacked in conjugate addition, and in either case, the charge on the nucleophile is taken by the oxygen. Radicals add rapidly to the double bond, and the resulting α-radical carbonyl is relatively stable; it can couple with another molecule or be oxidized. Nonetheless, the electrophilic/neutrophilic character of radicals has been shown in a variety of instances. One example is the alternating tendency of the copolymerization of maleic anhydride (electrophilic) and styrene (slightly nucleophilic).

In intramolecular reactions, precise control can be achieved despite the extreme reactivity of radicals. In general, radicals attack the closest reactive site the most readily. Therefore, when there is a choice, a preference for five-membered rings is observed: four-membered rings are too strained, and collisions with carbons six or more atoms away in the chain are infrequent.

Carbenes and nitrenes, which are diradicals, have distinctive chemistry.

Combustion



Spectrum of the blue flame from a butane torch showing excited molecular radical band emission and Swan bands

A familiar free-radical reaction is combustion. The oxygen molecule is a stable diradical, best represented by ·O-O·. Because spins of the electrons are parallel, this molecule is stable. While the ground stateof oxygen is this unreactive spin-unpaired (triplet) diradical, an extremely reactive spin-paired (singlet) state is available. For combustion to occur, the energy barrier between these must be overcome. This barrier can be overcome by heat, requiring high temperatures. The triplet-singlet transition is also "forbidden". This presents an additional barrier to the reaction. It also means molecular oxygen is relatively unreactive at room temperature except in the presence of a catalytic heavy atom such as iron or copper.

Combustion consists of various radical chain reactions that the singlet radical can initiate. The flammability of a given material strongly depends on the concentration of free radicals that must be obtained before initiation and propagation reactions dominate leading to combustion of the material. Once the combustible material has been consumed, termination reactions again dominate and the flame dies out. As indicated, promotion of propagation or termination reactions alters flammability. For example, because lead itself deactivates free radicals in the gasoline-air mixture, tetraethyl lead was once commonly added to gasoline. This prevents the combustion from initiating in an uncontrolled manner or in unburnt residues (engine knocking) or premature ignition (preignition).

When a hydrocarbon is burned, a large number of different oxygen radicals are involved. Initially, hydroperoxyl radical (HOO·) are formed. These then react further to give organic hydroperoxides that break up into hydroxyl radicals (HO·).

Polymerization

In addition to combustion, many polymerization reactions involve free radicals. As a result many plastics, enamels, and other polymers are formed through radical polymerization. For instance, drying oils and alkyd paints harden due to radical crosslinking by oxygen from the atmosphere.

Recent advances in radical polymerization methods, known as living radical polymerization, include:

- Reversible addition-fragmentation chain transfer (RAFT)
- Atom transfer radical polymerization (ATRP)
- Nitroxide mediated polymerization (NMP)

These methods produce polymers with a much narrower distribution of molecular weights.

Atmospheric radicals

The most common radical in the lower atmosphere is molecular dioxygen. Photodissociation of source molecules produces other free radicals. In the lower atmosphere, the most important examples of free radical production are the photodissociation of nitrogen dioxide to give an oxygen atom and nitric oxide (see eq. 1 below), which plays a key role in smog formation—and the photodissociation of ozone to give the excited oxygen atom O(1D) (see eq. 2 below). The net and return reactions are also shown (eq. 3 and 4, respectively).

1. $NO_2 \xrightarrow{h\nu} NO + O$
2. $O + O_2 \rightarrow O_3$

3. $NO_2 + O_2 \xrightarrow{h\nu} NO + O_3$
4. $NO + O_3 \rightarrow NO_2 + O_2$

In the upper atmosphere, a particularly important source of radicals is the photodissociation of normally unreactive chlorofluorocarbons (CFCs) by solar ultraviolet radiation, or by reactions with other stratospheric constituents (see eq. 1 below). These reactions give off the chlorine radical, Cl•, which reacts with ozone in a catalytic chain reaction ending in Ozone depletion and regeneration of the chlorine radical, allowing it to reparticipate in the reaction (see eq. 2–4 below). Such reactions are believed to be the primary cause of depletion of the ozone layer (the net result is shown in eq. 5 below), and this is why the use of chlorofluorocarbons as refrigerants has been restricted.

1. $CFCS \xrightarrow{h\nu} Cl\cdot$
2. $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$
3. $O_3 \xrightarrow{h\nu} O + O_2$
4. $O + ClO\cdot \rightarrow Cl\cdot + O_2$
5. $2O_3 \xrightarrow{h\nu} 3O_2$

In biology

Free radicals play an important role in a number of biological processes. Many of these are necessary for life, such as the intracellular killing of bacteria by phagocytic cells such as granulocytes and macrophages. Researchers have also implicated free radicals in certain cell signalling processes,[6] known as redox signaling.

The two most important oxygen-centered free radicals are superoxide and hydroxyl radical. They derive from molecular oxygen under reducing conditions. However, because of their reactivity, these same free radicals can participate in unwanted side reactions resulting in cell damage. Excessive amounts of these free radicals can lead to cell injury and death, which may contribute to many diseases such as cancer, stroke, myocardial infarction, diabetes and major disorders.[7] Many forms of cancer are thought to be the result of reactions between free radicals and DNA, potentially resulting in mutations that can adversely affect the cell cycle and potentially lead to malignancy.[8] Some of the symptoms of aging such as atherosclerosis are also attributed to free-radical induced oxidation of cholesterol to 7-ketocholesterol.[9] In addition free radicals contribute to alcohol-induced liver damage, perhaps more than alcohol itself. Free radicals produced by cigarette smoke are implicated in inactivation of alpha 1-antitrypsin in the lung. This process promotes the development of emphysema.

Free radicals may also be involved in Parkinson's disease, senile and drug-induced deafness, schizophrenia, and Alzheimer's.[10] The classic free-radical syndrome, the iron-storage disease hemochromatosis, is typically associated with a constellation of free-radical-related symptoms including movement disorder, psychosis, skin pigmentary melanin abnormalities, deafness, arthritis, and diabetes mellitus. The free-radical theory of aging proposes that free radicals underlie the aging process itself. Similarly, the process of mitohormesis suggests that repeated exposure to free radicals may extend life span.

Because free radicals are necessary for life, the body has a number of mechanisms to minimize free-radical-induced damage and to repair damage that occurs, such as the enzymes superoxide dismutase, catalase, glutathione peroxidase and glutathione reductase. In addition, antioxidants play a key role in these defense mechanisms. These are often the three vitamins, vitamin A, vitamin C and vitamin E and polyphenol antioxidants. Furthermore, there is good evidence indicating that bilirubin and uric acid can act as antioxidants to help neutralize certain free radicals. Bilirubin comes from the breakdown of red blood cells' contents, while uric acid is a breakdown product of purines. Too much bilirubin, though, can lead to jaundice, which could eventually damage the central nervous system, while too much uric acid causes gout.[11]

Reactive oxygen species

Reactive oxygen species or ROS are species such as superoxide, hydrogen peroxide, and hydroxyl radical and are associated with cell damage. ROS form as a natural by-product of the normal metabolism of oxygen and have important roles in cell signaling.

Oxybenzone has been found to form free radicals in sunlight, and therefore may be associated with cell damage as well. This only occurred when it was combined with other ingredients commonly found in sunscreens, like titanium oxide and octyl methoxycinnamate.[12]

Loose definition of radicals

In most fields of chemistry, the historical definition of radicals contends that the molecules have nonzero spin. However in fields including spectroscopy, chemical reaction, and astrochemistry, the definition is slightly different. Gerhard Herzberg, who won the Nobel prize for his research into the electron structure and geometry of radicals, suggested a looser definition of free radicals: "any transient (chemically unstable) species (atom, molecule, or ion)".[13] The main point of his suggestion is that there are many chemically unstable molecules that have zero spin, such as C_2, C_3, CH_2 and so on. This definition is more convenient for discussions of transient chemical processes and astrochemistry; therefore researchers in these fields prefer to use this loose definition.[14]

Diagnostics

Free radical diagnostic techniques include:

- Electron spin resonance

  A widely used technique for studying free radicals, and other paramagnetic species, is electron spin resonance spectroscopy (ESR). This is alternately referred to as "electron paramagnetic resonance" (EPR) spectroscopy. It is conceptually related to nuclear magnetic resonance, though electrons resonate with higher-frequency fields at a given fixed magnetic field than do most nuclei.

- Nuclear magnetic resonance using a phenomenon called CIDNP
- Chemical labelling

  Chemical labelling by quenching with free radicals, e.g. with nitric oxide (NO) or DPPH (2,2-diphenyl-1-picrylhydrazyl), followed by spectroscopic methods like X-ray photoelectron spectroscopy (XPS) or absorption spectroscopy, respectively.

- Use of free radical markers

  Stable, specific or non-specific derivates of physiological substances can be measured e.g. lipid peroxidation products (isoprostanes, TBARS), amino acid oxidation products (meta-tyrosine, ortho-tyrosine, hydroxy-Leu, dityrosine etc.), peptide oxidation products (oxidized glutathione – GSSG)
  2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) is a chemical compound used to study the chemistry of the oxidation of drugs.[15] It is a free radical-generating azo compound. It is gaining prominence as a model oxidant in small molecule and proteintherapeutics for its ability to initiate oxidation reactions via both nucleophilic and free radical mechanisms.[16]

- Indirect method

Measurement of the decrease in the amount of antioxidants (e.g. TAS, reduced glutathione – GSH)

- Trapping agents

Using a chemical species that reacts with free radicals to form a stable product that can then be readily measured (Hydroxyl radical and salicylic acid)

See also

- -yl
- Electron pair
- Globally Harmonized System of Classification and Labelling of Chemicals
- Hofmann–Löffler reaction

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4.3.5: Nucleophiles

What is a nucleophile?

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? Enolate ions (section 7.5) are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Reactions with carbon nucleophiles will be dealt with in chapters 13 and 14, however - in this chapter and the next, we will concentrate on non-carbon nucleophiles.

When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

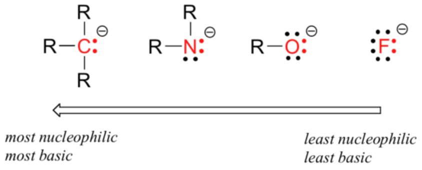
Now, lets discuss some of the major factors that affect nucleophilicity.

Protonation states and nucleophilicity

The protonation state of a nucleophilic atom has a very large effect on its nucleophilicity. This is an idea that makes intuitive sense: a hydroxide ion is much more nucleophilic (and basic) than a water molecule, because the negatively charged oxygen on the hydroxide ion carries greater electron density than the oxygen atom of a neutral water molecule. In practical terms, this means that a hydroxide nucleophile will react in an S_N2 reaction with methyl bromide much faster (about 10,000 times faster) than a water nucleophile.

Periodic trends and solvent effects in nucleophilicity

There are predictable periodic trends in nucleophilicity. Moving horizontally across the second row of the table, the trend in nucleophilicity parallels the trend in basicity:

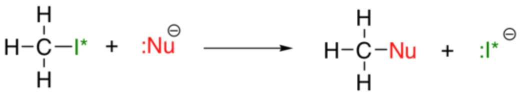


The reasoning behind the horizontal nucleophilicity trend is the same as the reasoning behind the basicity trend: more electronegative elements hold their electrons more tightly, and are less able to donate them to form a new bond.

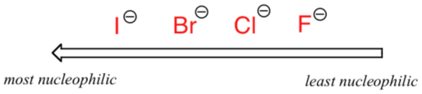
This horizontal trends also tells us that amines are more nucleophilic than alcohols, although both groups commonly act as nucleophiles in both laboratory and biochemical reactions.

Recall that the basicity of atoms decreases as we move vertically down a column on the periodic table: thiolate ions are less basic than alkoxide ions, for example, and bromide ion is less basic than chloride ion, which in turn is less basic than fluoride ion. Recall also that this trend can be explained by considering the increasing size of the 'electron cloud' around the larger ions: the electron density inherent in the negative charge is spread around a larger area, which tends to increase stability (and thus reduce basicity).

The vertical periodic trend for nucleophilicity is somewhat more complicated that that for basicity: depending on the solvent that the reaction is taking place in, the nucleophilicity trend can go in either direction. Let's take the simple example of the SN2 reaction below:



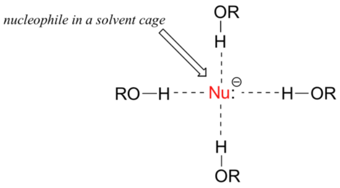
. . .where Nu$^-$ is one of the halide ions: fluoride, chloride, bromide, or iodide, and the leaving group I* is a radioactive isotope of iodine (which allows us to distinguish the leaving group from the nucleophile in that case where both are iodide). If this reaction is occurring in a **protic solvent** (that is, a solvent that has a hydrogen bonded to an oxygen or nitrogen - water, methanol and ethanol are the most important examples), then the reaction will go fastest when iodide is the nucleophile, and slowest when fluoride is the nucleophile, reflecting the relative strength of the nucleophile.



Relative nucleophilicity in a protic solvent

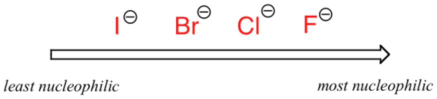
This of course, is opposite that of the vertical periodic trend for basicity, where iodide is the *least* basic. What is going on here? Shouldn't the stronger base, with its more reactive unbonded valence electrons, also be the stronger nucleophile?

As mentioned above, it all has to do with the solvent. Remember, we are talking now about the reaction running in a *protic* solvent like ethanol. Protic solvent molecules form very strong ion-dipole interactions with the negatively-charged nucleophile, essentially creating a 'solvent cage' around the nucleophile:



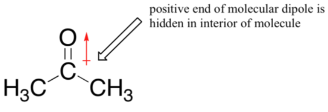
In order for the nucleophile to attack the electrophile, it must break free, at least in part, from its solvent cage. The lone pair electrons on the larger, less basic iodide ion interact less tightly with the protons on the protic solvent molecules - thus the iodide nucleophile is better able to break free from its solvent cage compared the smaller, more basic fluoride ion, whose lone pair electrons are bound more tightly to the protons of the cage.

The picture changes if we switch to a **polar aprotic solvent**, such as acetone, in which there is a molecular dipole but *no hydrogens bound to oxygen or nitrogen*. Now, fluoride is the best nucleophile, and iodide the weakest.



Relative nucleophilicity in a polar aprotic solvent

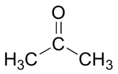
The reason for the reversal is that, with an aprotic solvent, the ion-dipole interactions between solvent and nucleophile are much weaker: the positive end of the solvent's dipole is hidden in the interior of the molecule, and thus it is shielded from the negative charge of the nucleophile.



acetone

A weaker solvent-nucleophile interaction means a weaker solvent cage for the nucleophile to break through, so the solvent effect is much less important, and the more basic fluoride ion is also the better nucleophile.

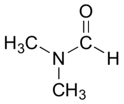
Why not use a completely nonpolar solvent, such as hexane, for this reaction, so that the solvent cage is eliminated completely? The answer to this is simple - the nucleophile needs to be in solution in order to react at an appreciable rate with the electrophile, and a solvent such as hexane will not solvate an a charged (or highly polar) nucleophile at all. That is why chemists use polar aprotic solvents for nucleophilic substitution reactions in the laboratory: they are polar enough to solvate the nucleophile, but not so polar as to lock it away in an impenetrable solvent cage. In addition to acetone, three other commonly used polar aprotic solvents are acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).



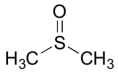
acetone

$N\equiv C-CH_3$

acetonitrile



dimethylformamide
(DMF)

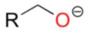


dimethylsulfoxide
(DMSO)

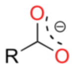
In biological chemistry, where the solvent is protic (water), the most important implication of the periodic trends in nucleophilicity is that thiols are more powerful nucleophiles than alcohols. The thiol group in a cysteine amino acid, for example, is a powerful nucleophile and often acts as a nucleophile in enzymatic reactions, and of course negatively-charged thiolates (RS^-) are even more nucleophilic. This is not to say that the hydroxyl groups on serine, threonine, and tyrosine do not also act as nucleophiles - they do.

Resonance effects on nucleophilicity

Resonance effects also come into play when comparing the inherent nucleophilicity of different molecules. The reasoning involved is the same as that which we used to understand resonance effects on basicity. If the electron lone pair on a heteroatom is delocalized by resonance, it is inherently less reactive - meaning less nucleophilic, and also less basic. An alkoxide ion, for example, is more nucleophilic and more basic than a carboxylate group, even though in both cases the nucleophilic atom is a negatively charged oxygen. In the alkoxide, the negative charge is localized on a single oxygen, while in the carboxylate the charge is delocalized over two oxygen atoms by resonance.

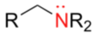


alkoxide ion:
charge is localized
more nucleophilic

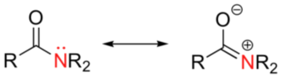


carboxylate ion:
charge is spread over both oxygens
less nucleophilic

The nitrogen atom on an amide is less nucleophilic than the nitrogen of an amine, due to the resonance stabilization of the nitrogen lone pair provided by the amide carbonyl group.



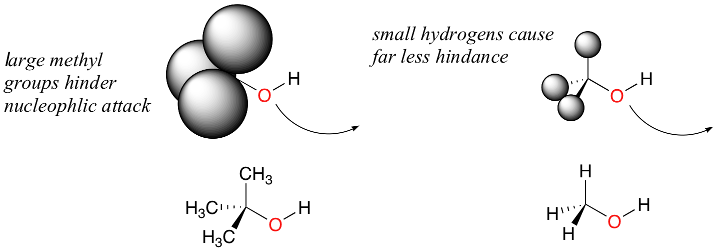
amine
more nucleophilic



amide
less nucleophilic

Steric effects on nucleophilicity

Steric hindrance is an important consideration when evaluating nucleophility. For example, *tert*-butanol is less potent as a nucleophile than methanol. This is because the comparatively bulky methyl groups on the tertiary alcohol effectively block the route of attack by the nucleophilic oxygen, slowing the reaction down considerably (imagine trying to walk through a narrow doorway while carrying three large suitcases!).



It is not surprising that it is more common to observe serines acting as nucleophiles in enzymatic reactions compared to threonines - the former is a primary alcohol, while the latter is a secondary alcohol.

Example

Which is the better nucleophile - a cysteine side chain or a methionine side chain? Explain.

Example

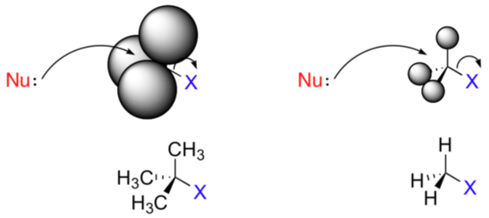
In each of the following pairs of molecules/ions, which is the better nucleophile in a reaction with CH_3Br in acetone solvent? Explain your choice.

a. phenolate ion (deprotonated phenol) or benzoate ion (deprotonated benzoic acid)
b. water and hydronium ion
c. trimethylamine and triethylamine
d. chloride anion and iodide anion
e. CH_3NH^- and CH_3CH_2NH

4.3.6: Electrophiles

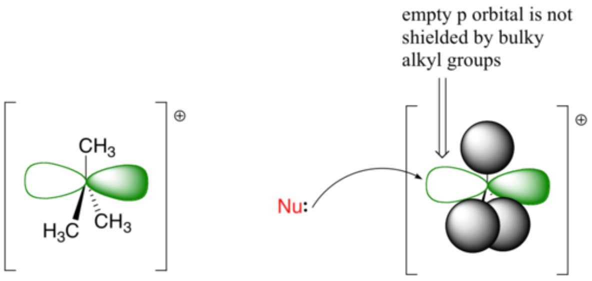
In the vast majority of the nucleophilic substitution reactions you will see in this and other organic chemistry texts, the electrophilic atom is a carbon which is bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom is an attractive target for something that is electron-rich, *i.e.* a nucleophile. However, we must also consider the effect of steric hindrance on electrophilicity. In addition, we must discuss how the nature of the electrophilic carbon, and more specifically the stability of a potential carbocationic intermediate, influences the S_N1 vs. S_N2 character of a nucleophilic substitution reaction.

Consider two hypothetical S_N2 reactions: one in which the electrophile is a methyl carbon and another in which it is tertiary carbon.



Because the three substituents on the methyl carbon electrophile are tiny hydrogens, the nucleophile has a relatively clear path for backside attack. However, backside attack on the tertiary carbon is blocked by the bulkier methyl groups. Once again, steric hindrance - this time caused by bulky groups attached to the electrophile rather than to the nucleophile - hinders the progress of an associative nucleophilic (S_N2) displacement.

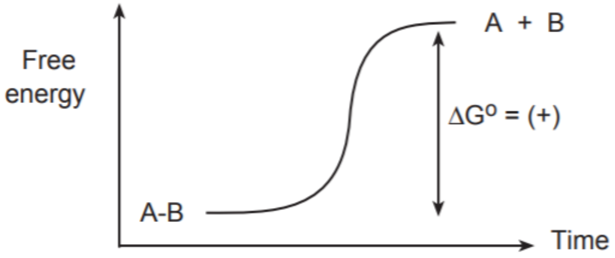
The factors discussed in the above paragraph, however, do not prevent a sterically-hindered carbon from being a good electrophile - they only make it less likely to be attacked in a *concerted* S_N2 *reaction*. Nucleophilic substitution reactions in which the electrophilic carbon is sterically hindered are more likely to occur by a two-step, dissociative (S_N1) mechanism. This makes perfect sense from a geometric point of view: the limitations imposed by sterics are significant mainly in an S_N2 displacement, when the electrophile being attacked is a sp^3-hybridized tetrahedral carbon with its relatively ‘tight’ angles of 109.4^o. Remember that in an S_N1 mechanism, the nucleophile attacks an sp^2-hybridized carbocation intermediate, which has trigonal planar geometry with ‘open’ 120 angles.



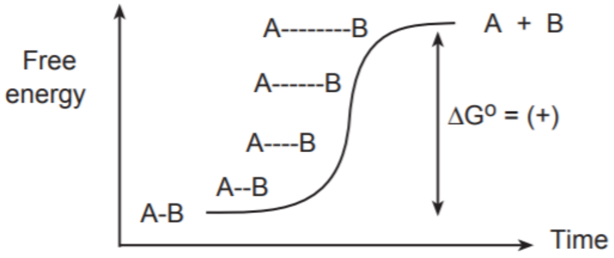
With this open geometry, the empty p orbital of the electrophilic carbocation is no longer significantly shielded from the approaching nucleophile by the bulky alkyl groups. A carbocation is a very potent electrophile, and the nucleophilic step occurs very rapidly compared to the first (ionization) step.

4.4: Bond Breaking and Bond Formation

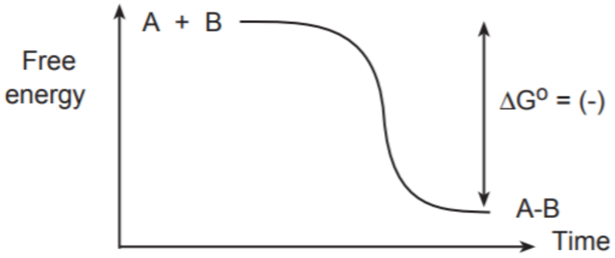
The simplest and first process that takes place during a chemical transformation is the breaking of a bond. The following discussion is confined to covalent bonds because they are the most prevalent in organic molecules. ***Breaking bonds always requires an energy input***. A free energy diagram for the breaking of a covalent bond between atoms A and B would have the following appearance.



If we were to visualize the breaking of this bond "frame by frame," we would see the bond stretching gradually until it snapped. At the same time we would see a gradual increase of the free energy of the system.



The process of **bond formation,** being the opposite of bond breaking, **always releases energy.** That is, lowers the energy of the system.



NOTE: This discussion assumes that the reader is familiar with basic thermodynamic concepts such as free energy, enthalpy, entropy, etc. Refer to the appropriate sections in your textbook for detailed explanations (Sections 4-4 and 4-5 in the Wade textbook, 4th and 5th editions)

4.4.1: Transition States

4.4.2: Reactive Intermediates

CHAPTER OVERVIEW

5: Structure Reactivity Relationships

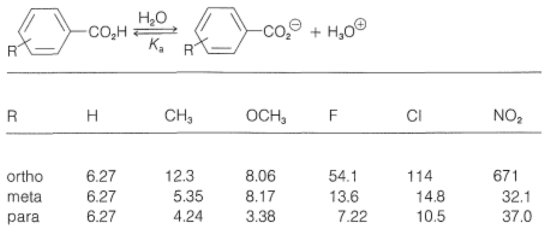
5.1: Correlations of Structure with Reactivity of Aromatic Compounds

This section is concerned with the quantitative correlation of reaction rates and equilibria of organic reactions with the structure of the reactants. We will restrict the discussion to benzene derivatives. The focus is on a remarkably simple treatment developed by L. P. Hammett in 1935, which has been tremendously influential. Hammett's correlation covers chemical reactivity, spectroscopy and other physical properties, and even the biological activity of drugs. Virtually all quantitative treatments of reactivity of organic compounds in solution start with the kinds of correlations that are discussed in this section.

5.1.1: The Hammett Equation

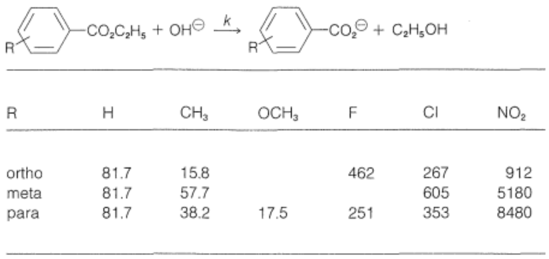
If we compare the acid strengths (K_a) of a series of substituted benzoic acids with the strength of benzoic acid itself (Table 26-4), we see that there are considerable variations with the nature of the substituent and its ring position, ortho, meta, or para. Thus all three nitrobenzoic acids are appreciably stronger than benzoic acid in the order ortho $\gg$ para $>$ meta. A methoxy substituent in the ortho or meta position has a smaller acid-strengthening effect, and in the para position decreases the acid strength relative to benzoic acid. Rate effects also are produced by different substituents, as is evident from the data in Table 26-5 for basic hydrolysis of some substituted ethyl benzoates. A nitro substituent increases the rate, whereas methyl and methoxy substituents decrease the rate relative to that of the unsubstituted ester.

Table 26-4: *Dissociation Constants* $(10^{-5} \times K_a)$ *of Some Substituted Benzoic Acids in Water at* 25^{o}



R	H	CH_3	OCH_3	F	Cl	NO_2
ortho	6.27	12.3	8.06	54.1	114	671
meta	6.27	5.35	8.17	13.6	14.8	32.1
para	6.27	4.24	3.38	7.22	10.5	37.0

Table 26-5: *Specific Rate Constants*^{a} *for Alkaline Hydrolysis of Some Substituted Ethyl Benzoates in* 85% *Ethanol-Water Solution at* 30^{o}



R	H	CH_3	OCH_3	F	Cl	NO_2
ortho	81.7	15.8		462	267	912
meta	81.7	57.7			605	5180
para	81.7	38.2	17.5	251	353	8480

$^{a}10^{5}k$, liter mole^{-1} sec^{-1}.

Figure 26-3). The linear correlation for meta and para substituents is observed for the rates or equilibrium constants for many other reactions. For example, straight lines are obtained on plotting log K for the dissociation of phenylethanoic acids (meta- and para-$RC_6H_4CH_2CO_2H$) against log K' for the dissociation of phenylammonium ions (meta- and *para*-$RC_6H_4\overset{\oplus}{N}H_3$), or against log k for the rate of hydrolysis of phenylmethyl halides (*meta*- and *para*-$RC_6H_4CH_2X$).

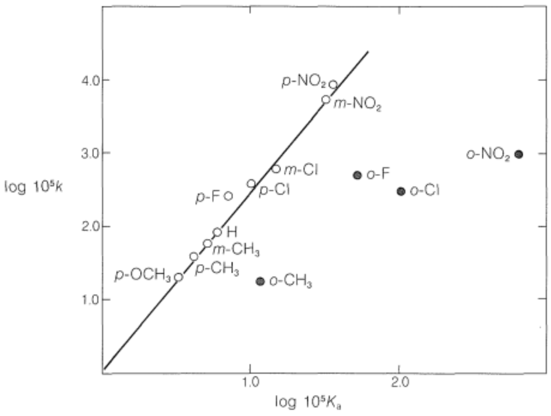


Figure 26-3: Plot of log 10^5 K_a for the dissociation of substituted benzoic acids in water at 25^o against log 10^5 k for the rates of alkaline hydrolysis of substituted ethyl benzoates in 85% ethanol-water at 30^o.

The straight line in Figure 26-3 can be expressed conveniently by Equation 26-3, in which the two variables are log k and log K, the slope of the line is ρ, and the intercept is C:

$$\log k = \rho \log K + C \tag{26-3}$$

For the particular case for which the ring substituent is hydrogen (R=H), Equation 26-3 becomes

$$\log k_0 = \rho \log K_0 + C \tag{26-4}$$

in which K_0 is the dissociation constant of benzoic acid and k_0 is the rate of hydrolysis of ethyl benzoate. Subtracting Equation 26-4 from Equation 26-3 we obtain

$$\log \frac{k}{k_0} = \rho \log \frac{K}{K_0} \tag{26-5}$$

This equation could be tested on the ratios of any rates or equilibrium constants, but it is convenient to reserve log (K/K_0) for the dissociation of benzoic acids in water at 25^o (Table 26-4) and correlate the rate or equilibrium constants for all other processes with log (K/K_0). The common procedure is to rewrite Equation 26-5 as Equation 26-6:

$$\log \frac{k}{k_0} = \rho\sigma \tag{26-6}$$

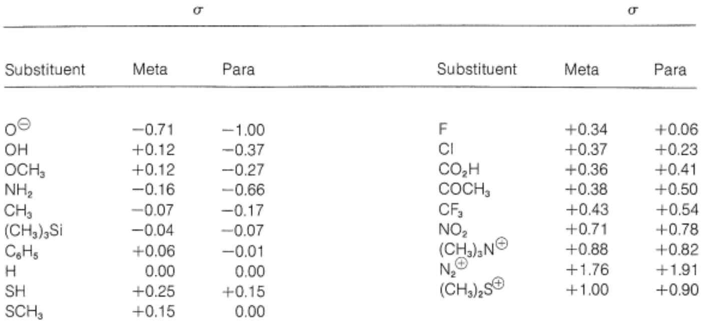
in which σ is defined as:

$$\sigma = \log \frac{K}{K_0} \tag{26-7}$$

Equation 26-6 is known as the **Hammett equation**, but before we discuss its general applications, it will be helpful to say more about the σ term in Equation 26-7.

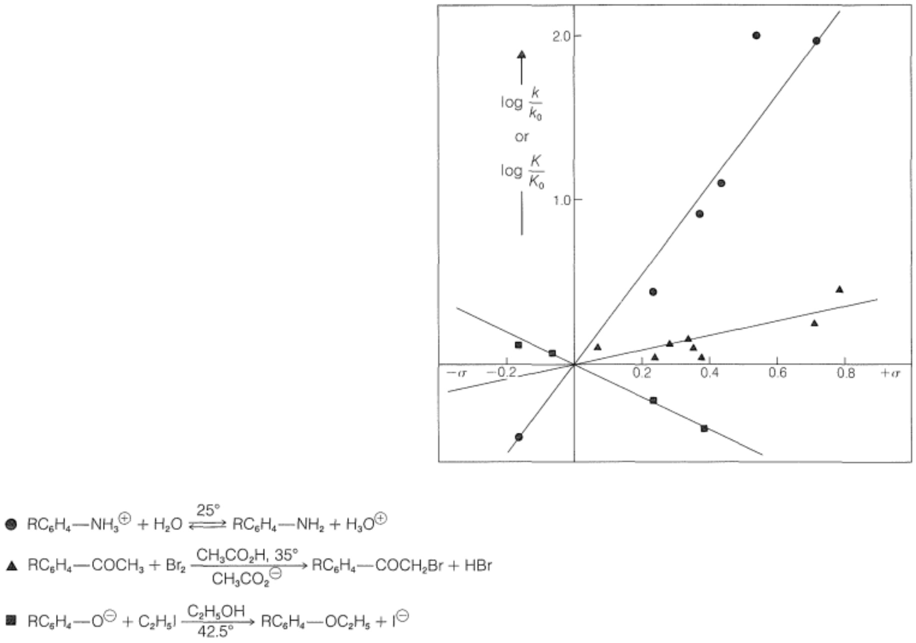
The *relative strength* of a substituted benzoic acid and hence the value of σ depends on the *nature* and *position* of the substituent in the ring. For this reason, σ is called the **substituent constant**. Table 26-6 lists several substituent constants and these will be seen to correspond to the polar character of the respective substituents. Thus the more electron-attracting a substituent is, by either resonance or induction, the more acid-strengthening it is, and the more *positive* is its σ value (relative to H as 0.000). Conversely, the more strongly a substituent donates electrons by resonance or induction, the more *negative* is its σ value. We expect that among the more electron-attracting and electron-donating substituents will be those with electric charges, positive and negative respectively. Indeed, a diazonium group $\left(-\text{N}_2^+\right)$ in the para position has a very large σ value of +1.91, whereas a para $-\text{O}^\ominus$ group has a σ value of -1.00. In general, meta σ constants correspond to the inductive effect of the substituent while the para σ constants represent the *net* influence of inductive and resonance effects. If there is a substantial resonance effect, and it and the inductive effect operate in the same direction, σ_para will have a considerably greater magnitude than σ_meta. The converse will be true if the resonance and inductive effects operate in opposite directions.

Table 26-6: *Hammett Substituent Constants*



	σ			σ	
Substituent	Meta	Para	Substituent	Meta	Para
$O^{\ominus}$	−0.71	−1.00	F	+0.34	+0.06
OH	+0.12	−0.37	Cl	+0.37	+0.23
OCH_3	+0.12	−0.27	CO_2H	+0.36	+0.41
NH_2	−0.16	−0.66	$COCH_3$	+0.38	+0.50
CH_3	−0.07	−0.17	CF_3	+0.43	+0.54
$(CH_3)_3Si$	−0.04	−0.07	NO_2	+0.71	+0.78
C_6H_5	+0.06	−0.01	$(CH_3)_3N^{\oplus}$	+0.88	+0.82
H	0.00	0.00	$N_2^{\oplus}$	+1.76	+1.91
SH	+0.25	+0.15	$(CH_3)_2S^{\oplus}$	+1.00	+0.90
SCH_3	+0.15	0.00			

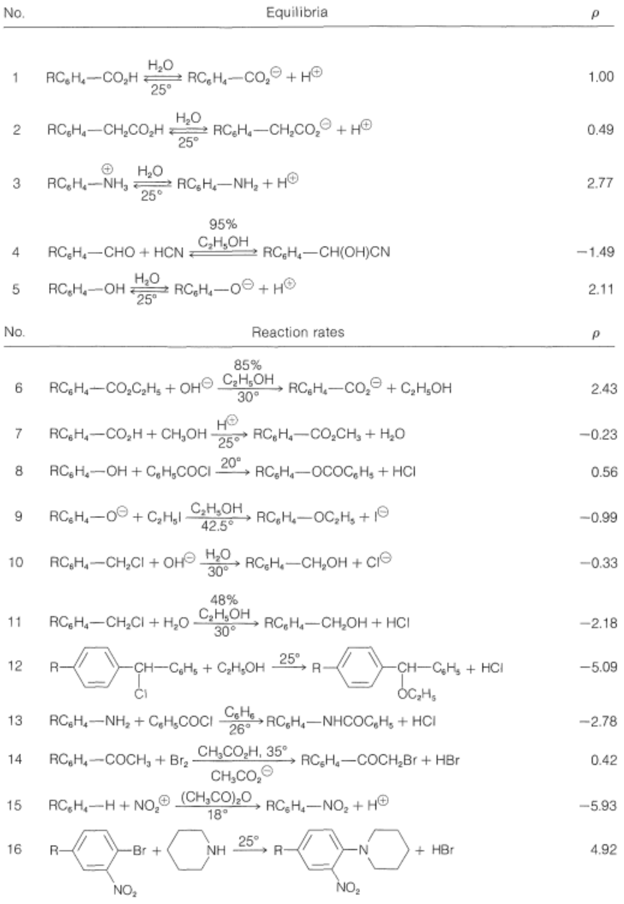
Figure 26-4, which shows plots of log (k/k_0) or of log (K/K_0) against σ for several different reactions. For the examples given, the fit to the Hammett equation is fair. A number of ρ values (slopes) are listed separately in Table 26-7. It can be seen that ρ values vary with the type of reaction and are appropriately called reaction constants. However, the real significance of ρ is that it measures the sensitivity of the reaction to the electrical effects of substituents in meta and para positions. A large ρ constant, positive or negative, means a high sensitivity to substituent influences. Reactions that are assisted by high electron density at the reaction site characteristically have negative ρ values (e.g., Reaction 15, Table 26-7), whereas reactions that are favored by withdrawal of electrons from the reaction site have positive ρ values (e.g., Reaction 16, Table 26-7).



● $RC_6H_4{-}NH_3^{\oplus} + H_2O \xrightleftharpoons{25^\circ} RC_6H_4{-}NH_2 + H_3O^{\oplus}$

▲ $RC_6H_4{-}COCH_3 + Br_2 \xrightarrow[CH_3CO_2^{\ominus}]{CH_3CO_2H,\ 35^\circ} RC_6H_4{-}COCH_2Br + HBr$

■ $RC_6H_4{-}O^{\ominus} + C_2H_5I \xrightarrow[42.5^\circ]{C_2H_5OH} RC_6H_4{-}OC_2H_5 + I^{\ominus}$



No.	Equilibria	ρ
1	$RC_6H_4-CO_2H \overset{H_2O}{\underset{25°}{\rightleftharpoons}} RC_6H_4-CO_2^{\ominus} + H^{\oplus}$	1.00
2	$RC_6H_4-CH_2CO_2H \overset{H_2O}{\underset{25°}{\rightleftharpoons}} RC_6H_4-CH_2CO_2^{\ominus} + H^{\oplus}$	0.49
3	$RC_6H_4-\overset{\oplus}{N}H_3 \overset{H_2O}{\underset{25°}{\rightleftharpoons}} RC_6H_4-NH_2 + H^{\oplus}$	2.77
4	$RC_6H_4-CHO + HCN \overset{95\%}{\underset{}{\overset{C_2H_5OH}{\rightleftharpoons}}} RC_6H_4-CH(OH)CN$	−1.49
5	$RC_6H_4-OH \overset{H_2O}{\underset{25°}{\rightleftharpoons}} RC_6H_4-O^{\ominus} + H^{\oplus}$	2.11

No.	Reaction rates	ρ
6	$RC_6H_4-CO_2C_2H_5 + OH^{\ominus} \xrightarrow[30°]{85\%\ C_2H_5OH} RC_6H_4-CO_2^{\ominus} + C_2H_5OH$	2.43
7	$RC_6H_4-CO_2H + CH_3OH \xrightarrow[25°]{H^{\oplus}} RC_6H_4-CO_2CH_3 + H_2O$	−0.23
8	$RC_6H_4-OH + C_6H_5COCl \xrightarrow{20°} RC_6H_4-OCOC_6H_5 + HCl$	0.56
9	$RC_6H_4-O^{\ominus} + C_2H_5I \xrightarrow[42.5°]{C_2H_5OH} RC_6H_4-OC_2H_5 + I^{\ominus}$	−0.99
10	$RC_6H_4-CH_2Cl + OH^{\ominus} \xrightarrow[30°]{H_2O} RC_6H_4-CH_2OH + Cl^{\ominus}$	−0.33
11	$RC_6H_4-CH_2Cl + H_2O \xrightarrow[30°]{48\%\ C_2H_5OH} RC_6H_4-CH_2OH + HCl$	−2.18
12	$R-C_6H_4-CH(Cl)-C_6H_5 + C_2H_5OH \xrightarrow{25°} R-C_6H_4-CH(OC_2H_5)-C_6H_5 + HCl$	−5.09
13	$RC_6H_4-NH_2 + C_6H_5COCl \xrightarrow[26°]{C_6H_6} RC_6H_4-NHCOC_6H_5 + HCl$	−2.78
14	$RC_6H_4-COCH_3 + Br_2 \xrightarrow[CH_3CO_2^{\ominus}]{CH_3CO_2H,\ 35°} RC_6H_4-COCH_2Br + HBr$	0.42
15	$RC_6H_4-H + NO_2^{\oplus} \xrightarrow[18°]{(CH_3CO)_2O} RC_6H_4-NO_2 + H^{\oplus}$	−5.93
16	$R-C_6H_3(NO_2)-Br + C_5H_{10}NH \xrightarrow{25°} R-C_6H_3(NO_2)-NC_5H_{10} + HBr$	4.92

Usually, ρ for a given reaction is influenced by conditions such as the temperature and composition of the solvent. However, the changes normally are not large unless an actual change in mechanism occurs with a change in the reaction conditions.

5.1.2: Scope of the Hammett Equation

The Hammett treatment provides a correlation of much experimental data. Tables 26-6 and 26-7 contain 38 substituent constants and 16 reaction constants. This means that we can calculate relative k or K values for 608 individual reactions. To illustrate, let us suppose that we need to estimate the relative rates of Reaction 16 of Table 2-7 for the para-substituents $\mathrm{R}=\mathrm{OCH_3}$ and $\mathrm{R}=\mathrm{CF_3}$. According to the ρ value of 4.92 for this reaction and the σ values of p-$\mathrm{OCH_3}$ and p-$\mathrm{CF_3}$ in Table 26-6, we may write

$$\log \frac{k_{\text{p-OCH}_3}}{k_0} = 4.92 \times (-0.27)\,, \text{ and } \log \frac{k_{\text{p-CF}_3}}{k_0} = 4.92 \times (0.54) \tag{5.1.1}$$

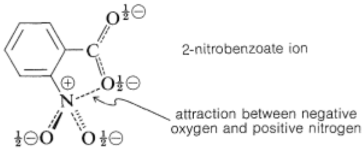
Subtracting these two equations gives the result:

This then is a rate ratio of 1/10,000. If we have a further table of the sixteen k_0 or K_0 values for the reactions listed in Table 26-7, we can calculate actual k or K values for 608 different reactions. It should be recognized that neither Table 26-6 nor Table 26-7 is a complete list; at least 80 substituent constants[1] and several hundred ρ constants are now available.

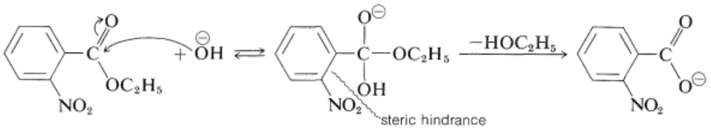
The Hammett relationship formalizes and puts into quantitative terms much of the qualitative reasoning we have used for reactions involving aliphatic, alicyclic, and aromatic compounds. Considerable effort has been made to extend the Hammett idea to cover reactions other than of meta- and para-substituted benzene derivatives, but these will not be discussed here.[1]

5.1.3: Limitations of the Hammett Equation

The effects of substituents in ortho positions on the reactivity of benzene derivatives do not correlate well with the Hammett equation, as can be seen in Figure 26-3. The problem is that ortho substituents are close enough to the reaction site to exert significant "proximity" effects, which may be polar as well as steric in origin. Thus the enhanced acid strength of 2-nitrobenzoic acid over the 3- and 4-isomers (see Table 26-4) may be due to a polar stabilization of the acid anion by the neighboring positive nitrogen, which of course is not possible with the 3- and 4-isomers:



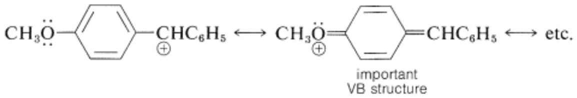
In contrast, the slower rate of alkaline hydrolysis of ethyl 2-nitrobenzoate than of its 3- and 4-isomers is more likely due to a steric hindrance effect of the 2-nitro group (see Table 26-5):



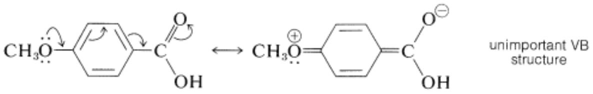
Because the effect of steric hindrance on different types of reactions is not expected to be the same, a given substituent is unlikely to exert the same relative steric effect in one reaction as in another. Consequently we cannot hope to find a very simple relationship such as the Hammett equation that will correlate structure and reactivity of ortho-substituted compounds.

The Hammett equation also fails for open-chain aliphatic derivatives. For example, there is no simple linear relationship between log K for a series of substituted ethanoic acids $(\mathrm{RCH_2CO_2H})$ and log k for the hydrolysis rates of similarly substituted ethyl ethanoates $(\mathrm{RCH_2CO_2C_2H_5})$. The freedom of motion available to a flexible open-chain compound permits a much wider range of variations in steric effects than for meta- and para-substituted aromatic compounds.

The Hammett equation sometimes fails for meta- and para-substituted aromatic compounds. This failure may be expected whenever the opportunity arises for strong electron delocalization between the substituent and the reaction site. Generally, reactions that are strongly assisted by donation of electrons to the reaction site, as in $S_\mathrm{N}1$ reactions and electrophilic aromatic substitution, will be facilitated by electron-delocalization effects of substituents with unshared electron pairs adjacent to the aromatic group (e.g., $-\mathrm{OCH_3}$, $-\mathrm{OH}$, $-\mathrm{O^{\ominus}}$, $-\mathrm{NH_2}$, and $-\mathrm{Cl}$). Such reactions generally give a poor Hammett correlation. Thus a diphenylmethyl chloride with one 4-methoxy group solvolyzes in ethanol at 25° at a rate much faster than predicted by the Hammett equation, because of the resonance stabilization provided by the substituent to the intermediate carbocation:



The same type of stabilization by a 4-methoxy group does not appear to be important in influencing the ionization of 4-methoxybenzoic acid.



Similarly, those reactions that are strongly assisted by *withdrawal of electrons* from the reaction site, such as nucleophilic aromatic substitution, give a poor fit to a Hammett plot for the substituents that are capable of withdrawing electrons by delocalization ($-\mathrm{NO_2}$, $-\mathrm{N_2^+}$, $-\mathrm{C\equiv N}$, and so on). An example is Reaction 16 in Table 26-7. To correlate reactivity data with structures where strong resonance effects operate, different sets of substituent constants are required.[1]

[1] J. Hine, *Structural Effects on Equilibria in Organic Chemistry*, Wiley-Interscience, New York, 1975, p. 65. This book offers a very broad coverage of quantitative correlations of substituent effects on processes as diverse as radical formation and rates of rotation around single $\mathrm{C-C}$ bonds.

5.1.4: Contributors and Attributions

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

5.2: Linear Free Energy Relationships

The Linear Free Energy Relation (LFER) is a tool that can indicate the importance of bond breakage or bond formation in the rate-determining step. In the case of a dissociative mechanism, for example, bond breaking is critical for reaction progress. Therefore, the strength of the M-X bond influences not only the extent to which the reaction will happen, but also the rate. Although thermodynamic stability of a complex does not necessarily indicate the kinetic rate at which it will react, there is a relationship between bond stability and the rate of reaction *if the breaking or formation of that bond is involved in the rate-determining step*. The relationship can be stated as follows:

$$ln\ k = ln\ K + c$$

And this relationship can be justified using the Arrhenius equation and equation for the temperature-dependence of the equilibrium constant.

$$\ln k = \ln A - \frac{E_A}{RT} \quad \text{and} \quad \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

In an experiment designed to test the Linear Free Energy Relationship, several reactions would be conducted under nearly identical conditions, where only the identity of the leaving group, X, is varied. In these experiment, the temperature would be constant and the same in each case. If we assume that the pre-exponential factor, A is the same for each reaction condition (and it should be at identical temperatures for analogous reactions), then the $\ln K$ term of the Arrhenius equation becomes proportional to the activation energy, E_a (and proportional to Gibb's energy of activation, $\Delta G^\ddagger$, and Gibb's energy ΔG). And since the Gibb's energy is related to the equilibrium constant, K, by $\Delta G = RT \ln K$, the value of K and k should be correlated. Likewise, if T is constant over the reaction conditions and ΔS° is similar across the analogous reactions (which it should be), then $\ln K$ becomes proportional to enthalpy, ΔH°, which is proportional to Gibb's free energy of reaction ΔG°.

If a Linear Free Energy Relation plot of $\ln K$ vs $\ln k$ is linear, but with a slope less than one, it indicates a dissociative mechanism with some degree of associative character (for example, an I_d mechanism or a mechanism involving the formation of preassociation complex). If the plot of $\log K$ vs $\log k$ for the reactions is linear, this is evidence that the reaction is dissociative. An example for a linear free energy plot is shown in Figure $5.2.1$ for the hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{X}]_2^+$ (this is the substitution of X^- with H_2O).

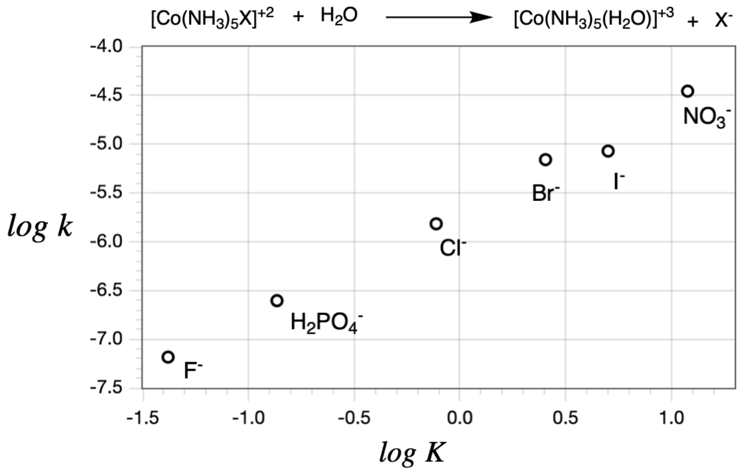


Figure 5.2.1: Linear Free Energy relationship lot for $[\text{Co}(\text{NH}_3)_5\text{X}]_2^+$ where $\text{X}^-{=}\text{F}-, \text{H}_2\text{PO}_4-, \text{Cl}-, \text{Br}-, \text{I}-, \text{NO}_3^-$. This is summarized in Cooper H. Langford, *Inorganic Chemistry* **1965** *4* (2), 265-266, DOI: 10.1021/ic50024a041. (CC-BY-SA; Kathryn Haas)

When the slope is approximately 1, as it is in the case of $[\text{Co}(\text{NH}_3)_5\text{X}]_2^+$ in Figure $5.2.1$, it indicates that the variation of the X^- leaving group has a similar effect on the magnitude of both ΔG (thermodynamic, related to K) and $\Delta G^\ddagger$ (kintetic, related to k). In other words, a slope close to 1 indicates a purely dissociative pathway (D). This data shown in Figure $5.2.1$, for example, is evidence of a dissociative mechanism for $[\text{Co}(\text{NH}_3)_5\text{X}]_2^+$.

The argument that a reaction is dissociative can also be supported by evidence showing little effect of the incoming ligand on reaction rate. For example, data supporting the argument that $[\mathrm{Co(NH_3)_5H_2O}]_3^+$ reacts by a dissociative pathway is shown below. The data show that variation of the identity of the incoming ligand, $\mathrm{Y^-}$, has little effect on the rate constant (they are approximately within one order of magnitude).

$$\text{For the reaction: } [\mathrm{Co(NH_3)_5H_2O}]^{3+} + \mathrm{Y^{m-}} \rightleftharpoons [\mathrm{Co(NH_3)_5Y}]^{(3-m)^+} + \mathrm{H_2O}$$

Table 5.2.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo cobalt(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry, 5th edition*, pg 448.

Entering Ligand, $\mathrm{Y^-}$	Rate Constant, k_1 $(10^{-6}s^{-1})$ (pseudo-first order with excess $[\mathrm{Y^-}]$)
$\mathrm{H_2O}$	100
$\mathrm{N_3^-}$	100
$\mathrm{SO_4^{2-}}$	24
$\mathrm{Cl^-}$	21
$\mathrm{NCS^-}$	16

CHAPTER OVERVIEW

6: Acidity and Basicity

6.1: New Page

CHAPTER OVERVIEW

7: Kinetic Isotope Effects

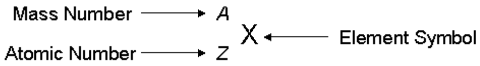
7.1: Kinetic Isotope Effects

The **kinetic isotope effect** (KIE) is a phenomenon associated with isotopically substituted molecules exhibiting different reaction rates. Isotope effects such as KIEs are invaluable tools in both physical and biological sciences and are used to aid in the understanding of reaction kinetics, mechanisms, and solvent effects.

Introduction

Research was first introduced on this topic over 50 years ago and has grown into an enormous field. The scientists behind much of the understanding and development of kinetic isotope effects were Jacob Bigeleisen and Maria Goeppert Mayer who published the first paper on isotope effects [J. Chem. Phys., 15, 261 (1947)]. Kinetic isotope effects specifically explore the change in rate of a reaction due to isotopic substitution.

An element is identified by its symbol, mass number, and atomic number. The atomic number is the number of protons in the nucleus while the mass number is the total number of protons and neutrons in the nucleus. Isotopes are two atoms of the same element that have the same number of protons but different numbers of neutrons. Isotopes are specified by the mass number.



As an example consider the two isotopes of chlorine, you can see that their mass numbers vary, with ^{35}Cl being the most abundant isotope, while their atomic numbers remain the same at 17.

$$^{35}Cl \text{ and } ^{37}Cl \tag{7.1.1}$$

The most common isotope used in light atom isotope effects is hydrogen (^1H) commonly replaced by its isotope deuterium (^2H). Note: Hydrogen also has a third isotope, tritium (^2H). Isotopes commonly used in heavy atom isotope effects include carbon (^{12}C, ^{13}C, nitrogen (^{14}N, ^{15}N), oxygen, sulfur, and bromine. Not all elements exhibit reasonably stable isotopes (i.e. Fluorine, ^{19}F), but those that due serve as powerful tools in isotope effects.

Potential Energy Surfaces

Understanding potential energy surfaces is important in order to be able to understand why and how isotope effects occur as they do. The harmonic oscillator approximation is used to explain the vibrations of a diatomic molecule. The energies resulting from the quantum mechanic solution for the harmonic oscillator help to define the internuclear potential energy of a diatomic molecule and are

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{7.1.2}$$

where

- n is a positive integer (n=1,2,3...),
- h is Planck's constant and
- ν is the frequency of vibration.

The Morse potential is an analytic expression that is used as an approximation to the intermolecular potential energy curves:

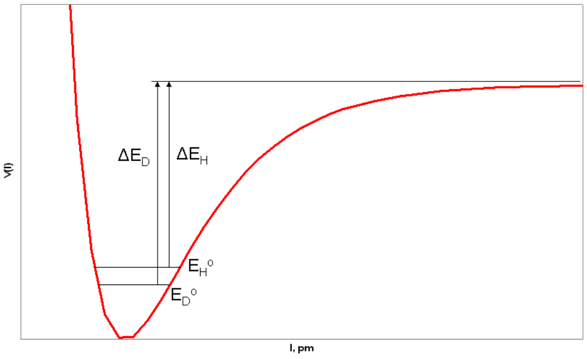
$$V(l) = D_e \left(1 - e^{-\beta(l - l_o)}\right)^2 \tag{7.1.3}$$

where

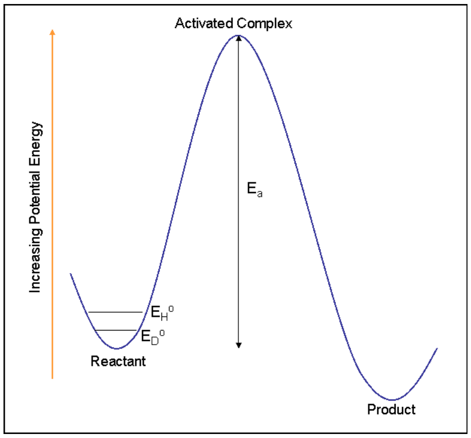
- $V(l)$ is the potential energy,
- D_e is the dissociation energy of the molecule,
- β is the measure of the curvature of the potential at its minimum,
- l is displacement, and
- l_o is the equilibrium bond length.

The D_e, β, and l_o variables can be looked up in a textbook or CRC handbook.

Below is an example of a Morse potential curve with the zero point vibrational energies of two isotopic molecules (for example R-H and R-D where R is a group/atom that is much heavier than H or D). The y-axis is potential energy and the x axis is internuclear distance. In this figure E_D^o and E_H^o correspond to the zero point energies of deuterium and hydrogen. The zero point energy is the lowest possible energy of a system and equates to the ground state energy. Zero point energy is dependent upon the reduced mass of the molecule as will be shown in the next section. The heavier the molecule or atom, the lower the frequency of vibration and the smaller the zero point energy. Lighter molecules or atoms have a greater frequency of vibration and a higher zero point energy. We see this is the figure below where deuterium is heavier than hydrogen and therefore has the lower zero point energy.



This results in different bond dissociation energies for R-D and R-H. The bond dissociation energy for R-D (E_D) is greater than the bond dissociation energy of R-H (E_H). This difference in energy due to isotopic replacement results in differing rates of reaction, the effect that is measured in kinetic isotope effects. The reaction rate for the conversion of R-D is slower than the reaction rate for the conversion of R-H.



It is important to note that isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions the molecule may undergo. Only the rate of the reaction is affected.

Activation Energies

The energy of the vibrational levels of a vibration (i.e., a bond) in a molecule is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{7.1.4}$$

where we assume that the molecule is in its ground state and we can compare zero-point vibrational energies,

$$E_o = \left(\frac{1}{2}\right) hv \tag{7.1.5}$$

Using the harmonic oscillator approximation the fundamental vibrational frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{7.1.6}$$

where

- k is the force constant of the bond and
- μ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7.1.7}$$

The Arrhenius equation is used to determine reaction rates and activation energies and since we are interested in the change in rate of reactions with different isotopes, this equation is very important,

$$k = Ae^{-\frac{E_a}{kT}} \tag{7.1.8}$$

where

- k is the reaction rate,
- E_a is the activation energy, and
- A is the Arrhenius constant.

The Arrhenius equation can be used to compare the rates of a reaction with R-H and R-D,

$$k_H = A_H e^{-\frac{E_a^H}{kT}} \tag{7.1.9}$$

$$k_D = A_D e^{-\frac{E_a^D}{kT}} \tag{7.1.10}$$

where k_H and k_D are the rates of reaction associated with R-H and the isotope substituted R-D. We will then assume the Arrhenius constants are equal ($A_H = A_D$). The ratio of the rates of reaction gives an approximation for the isotope effect resulting in:

$$\frac{k_H}{k_D} = e^{-\frac{E_a^H - E_a^D}{kT}} \tag{7.1.11}$$

By using the relationship that for both R-H and R-D

$$E_o = \left(\frac{1}{2}\right) h\nu \tag{7.1.12}$$

a substitution can be made resulting in

$$\frac{k_H}{k_D} = e^{\frac{h(\nu_H - \nu_D)}{2kT}} \tag{7.1.13}$$

The vibrational frequency (Equation 5) can then be substituted for R-H and R-D and the value of the expected isotope effect can be calculated.

$$\frac{k_H}{k_D} = e^{\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}} \tag{7.1.14}$$

The same general procedure can be followed for any isotope substitution.

In summary, the greater the mass the more energy is needed to break bonds. A heavier isotope forms a stronger bond. The resulting molecule has less of a tendency to dissociate. The increase in energy needed to break the bond results in a slower reaction rate and the observed isotope effect.

Kinetic Isotope Effects

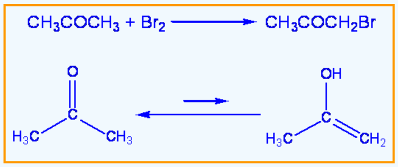
Kinetic Isotope Effects (KIEs) are used to determine reaction mechanisms by determining rate limiting steps and transition states and are commonly measured using NMR to detect isotope location or GC/MS to detect mass changes. In a KIE experiment an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio k_H/k_D (as explained above). Normal KIEs for the deuterium effect are around 1 to 7 or 8. Large effects are seen because the percentage mass change between hydrogen and deuterium is great. Heavy atom isotope effects involve the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The difference in KIE magnitude is directly related to the percentage change in mass. Large effects are seen when hydrogen is replaced with deuterium because the percentage mass change is very large (mass is being doubled) while smaller percent mass changes are present when an atom like sulfur is replaced with its isotope (increased by two mass units).

Primary KIEs

Primary kinetic isotope effects are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction.

✓ Example

Consider the bromination of acetone: kinetic studies have been performed that show the rate of this reaction is independent of the concentration of bromine. To determine the rate determining step and mechanism of this reaction the substitution of a deuterium for a hydrogen can be made.



When hydrogen was replaced with deuterium in this reaction a $\frac{k_H}{k_D}$ of 7 was found. Therefore the rate determining step is the tautomerization of acetone and involves the breaking of a C-H bond. Since the breaking of a C-H bond is involved, a substantial isotope effect is expected.

Heavy Atom Isotope Effects

A rule of thumb for heavy atom isotope effects is that the maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.

$$PhCH_2—CH_2S^+Me_2 \quad \overset{Base}{} \quad PhCH{=}CH_2 + SMe_2 + BH^+$$

- Expected:

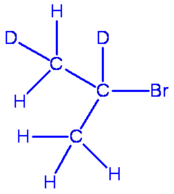
$$\frac{k_{32}}{k_{34}} = \sqrt{\frac{34}{32}} = 1.031 \tag{7.1.15}$$

- Experimental:

$$\frac{k_{32}}{k_{34}} = 1.072 \tag{7.1.16}$$

Secondary KIEs

Secondary kinetic isotope effects are rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction. These come in three forms: α, β, and γ effects.



β secondary isotope effects occur when the isotope is substituted at a position next to the bond being broken.

$$(\mathrm{CH_3})_2\mathrm{CHBr} + \mathrm{H_2O} \xrightarrow{k_H} (\mathrm{CH_3})_2\mathrm{CHOH} \tag{7.1.17}$$

$$(\mathrm{CD_3})_2\mathrm{CHBr} + \mathrm{H_2O} \xrightarrow{k_D} (\mathrm{CD_3})_2\mathrm{CHOH} \tag{7.1.18}$$

This is thought to be due to hyperconjugation in the transition state. Hyperconjugation involves a transfer of electron density from a sigma bond to an empty p orbital (for more on hyperconjugation see outside links).

Solvent Effects in Reactions

Reactions may be affected by the type of solvent used (for example H_2O to D_2O or ROH to ROD). There are three main ways solvents effect reactions:

1. The solvent can act as a reactant resulting in a primary isotope effect.
2. Rapid hydrogen exchange can occur between substrate molecules labeled with deuterium and hydrogen atoms in the solvent. Deuterium may change positions in the molecule resulting in a new molecule that is then reacted in the rate determining step of the reaction.
3. The nature of solvent and solute interactions may also change with differing solvents. This could change the energy of the transition state and result in a secondary isotope effects.

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Problems

1. Describe the difference between primary and secondary kinetic isotope effects.
2. Estimate the $k_{N\text{-}H}/k_{N\text{-}D}$ for a deuterium substitution on nitrogen given that v_H=9.3x1013 Hz and the activation energy is equal to 5.31 kJ/mol.
3. Using the 'rule of thumb' for heavy isotope effects, calculate the expected effect for a bromine isotope substitution, ^{79}Br and ^{81}Br.
4. Explain some of the main ways kinetic isotope effects are used.
5. As discussed, the rate-limiting step in the bromination of acetone is the breaking of a carbon-hydrogen bond. Estimate kC-H/KC-D for this reaction at 285 K. (Given: vtilde$_{C\text{-}H}$=3000 cm^{-1} and vtilde$_{C\text{-}D}$=2100 cm^{-1})

Solutions

1. Primary isotope effects involve isotopic substitution at the bond being broken in a reaction, while secondary isotope effects involve isotopic Substitution on bonds adjacent to the bond being broken.
2. 8.5
3. 1.0126
4. To determine reaction mechanisms, to determine rate limiting steps in reactions, to determine transition states in reactions.
5. 9.685

CHAPTER OVERVIEW

8: Catalysis

8.1: A. Methods of Catalysis

Learning Objectives

- define and give examples of general acid/base, electrostatic, nucleophilic (covalent), and intramolecular methods of catalysis of chemical reactions in the absence of enzymes;
- draw mechanisms showing transition states and intermediates in general acid/base and nucleophilic catalysis;
- explain the role of transition state stabilization and preferential binding of the transition state compared to the substrate for macromolecule-catalyzed chemical reactions

Catalysts, including enzymes, can employ at least five different ways to stabilize transition states. Reactions in solution that are not catalyzed are slow since charge development and separation occurs in the transition state. When bonds are made or broken, charged intermediates are often formed which are higher in energy than the reactants. Since the intermediate is higher in energy than the reactants, the transition state would be even higher in energy, and hence more closely resemble the charged intermediate. Anything that can stabilize the charges on the intermediate and hence the developing charges in the transition states will lower the energy of the transition state and catalyze the reaction.

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8.1.1: A1. General Acid and Base Catalysis

Reactions in solution that are not catalyzed are slow since charge development and separation occurs in the transition state. When bonds are made or broken, charged intermediates are often formed which are higher in energy than the reactants. Since the intermediate is higher in energy than the reactants, the transition state would be even higher in energy, and hence more closely resemble the charged intermediate. Anything that can stabilize the charges on the intermediate and hence the developing charges in the transition states will lower the energy of the transition state and catalyze the reaction. In this section we will investigate the mechanism underlying the catalysis by small molecules of chemical reactions. Presumably, biological macromolecular catalyst (like protein enzymes) will use similar mechanisms in their catalytic effects (which will be discussed in the next section).

Catalysts, including enzymes, can employ at least 5 different ways to stabilize transition states.

Charge development in the TS can be decreased by either donation of a proton from general acids (like acetic acid or a protonated indole ring) to an atom such as a carbonyl O which develops a partial negative charge in the TS when it is attached by a nucleophile. Proton donation decreases the developing negative in the TS. Alternatively, a nucleophile such as water which develops a partial positive charge in the TS as it begins to form a bond to an electrophilic C in a carbonyl can be stabilized by the presence of a general base (such as acetate or the deprotonated indole ring). Proton abstraction decreases the developing positive charge

Figure: CHARGE DEVELOPMENT IN THE TRANSITION STATE FOR ESTER HYDROLYSIS

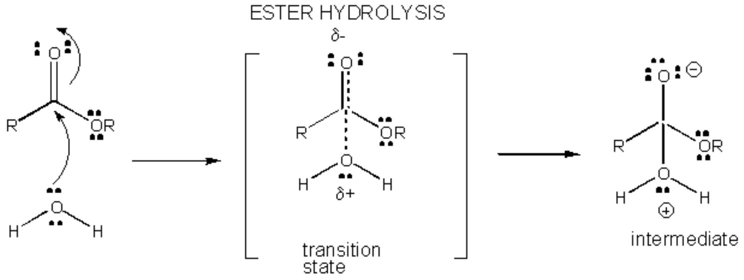


Figure: MECHANISM OF GENERAL ACID CATALYSIS

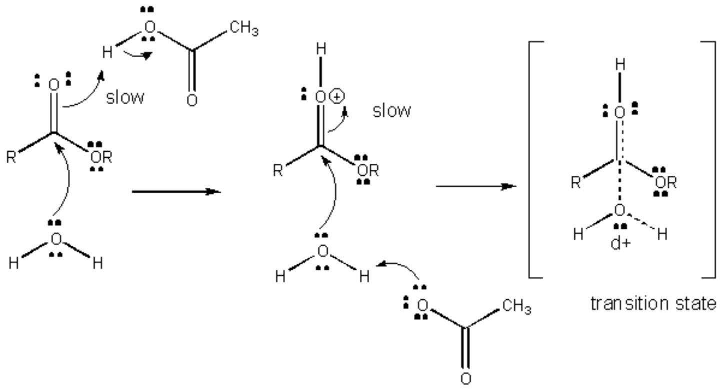
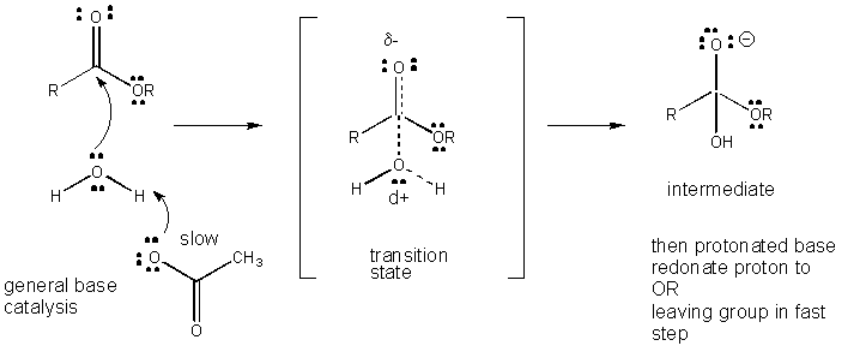


Figure: MECHANISM OF GENERAL BASE CATALYSIS



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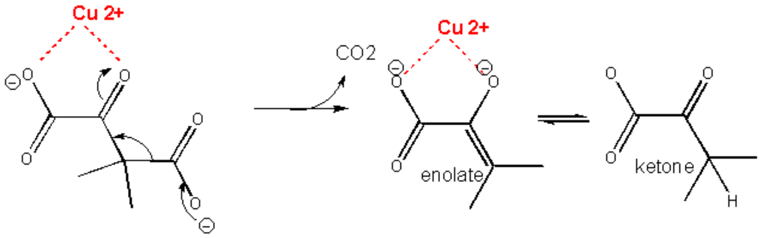
8.1.2: A2. Metal Ion or Electrostatic Catalysis

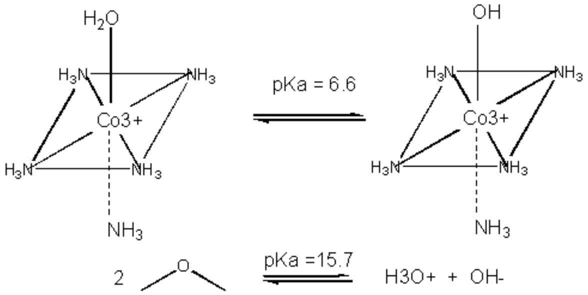
A metal such as Cu^{2+} or Zn^{2+} can also stabilize the TS. The metal must be able to be bound to the charged intermediate and hence the TS. The tetrahedral oxyanion intermediate of the reaction of an electrophilic carbonyl C can interact with a metal if there is an O on an adjacent atom which can help coordinate the metal ion. This charge stabilization of the developing negative in the TS and the full negative in the intermediate is often called electrostatic catalysis. This method is likely to be found in many enzymes since nearly 1/3 of all enzymes require metal ions. A classic example of an enzyme using metal ion catalysis is carboxypeptidase A.

Figure: METAL ION OR ELECTROSTATIC CATALYSIS - STABILIZATION OF TS CHARGE



Metals can also act in a different way. They may coordinate a water and by further polarizing the H-O bond increase the acidity of the bound water. For instance, the water molecule in the pentammineaquacobalt(III) ion has a pKa of 6.6, compared to pure water, with a pKa of 15.7. (To calculate the latter, write the equilibrium expression for water: H2O + H2O <==> $H3O^+$ + OH^- . Then write the Ka expression, as for a generic acid, which is [H3O+][OH-]/ [H2O] = 10^{-14}/55.5. The pKa is 15.7). The complexed hydroxide is a better nucleophile than bulk water. An example of an enzyme whose bound metal increases the nucleophilicity of water is carbonic anhydrase.

Figure: METAL ION CATALYSIS - DECREASING pKa OF WATER



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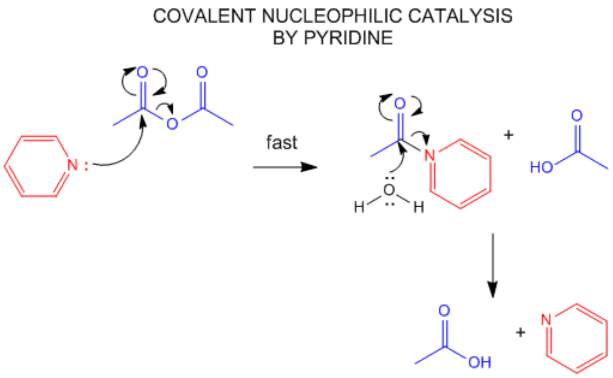
8.1.3: A3. Covalent or Nucleophilic Catalysis

One way to change the activation energy of the reaction is to change the reaction mechanism in ways which introduces new steps with lower activation energy. A typical way is to add a nucleophilic catalyst which forms a covalent intermediate with the reactant. The original nucleophile can then interact with the intermediate in a nucleophilic substitution reaction. If the nucleophilic catalyst is a better nucleophile than the original nucleophile (usually water) then the reaction is catalyzed. The nucleophilic catalyst and the original nucleophile usually interact with a carbonyl C in a substitution reaction, initially forming the tetrahedral oxyanion intermediate.

Figure: NUCLEOPHILIC COVALENT CATALYSIS BY PYRIDINE.



If an amine is used as the nucleophilic catalyst, then the initial addition product (a carbinolamine) can become dehydrated, since the free pair of electrons on the N are more likely to be shared with the carbon to form a double bond than electrons from the original carbonyl O, which is more electronegative than the N). An imine or Schiff Base forms, with a pKa of about 7.

Figure: MECHANISM OF SCHIFF BASE FORMATION

This is easily protonated to form a positively charged N at the former carbonyl O center. This serves as an excellent electron sink for decarboxylation reactions of beta-keto acids and illustrates an important point. Electrons in chemical reactions can be viewed as flowing from a source (such as a carboxyl group) to a sink (such as an nucleophilic carbonyl O or a positively charged N in a Schiff base).

Figure: MECHANISM OF NUCLEOPHILIC CATALYSIS BY AMINES - SCHIFF BASE FORMATION.

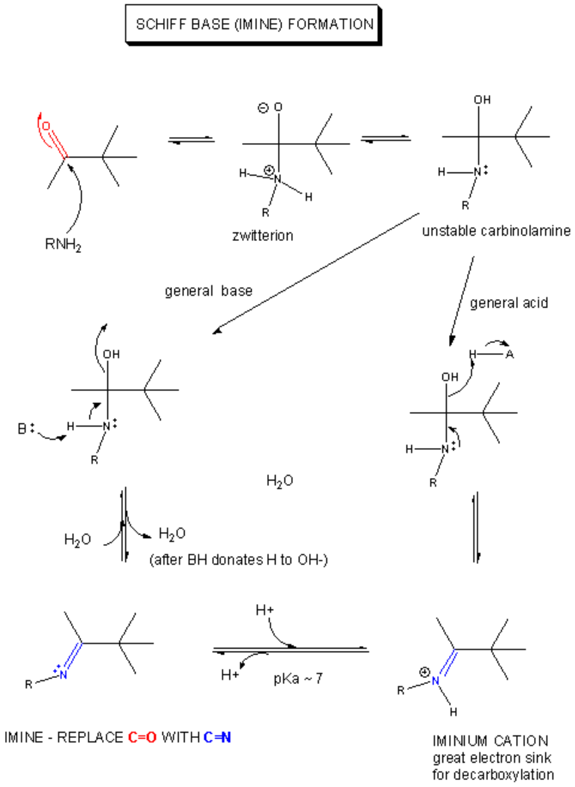
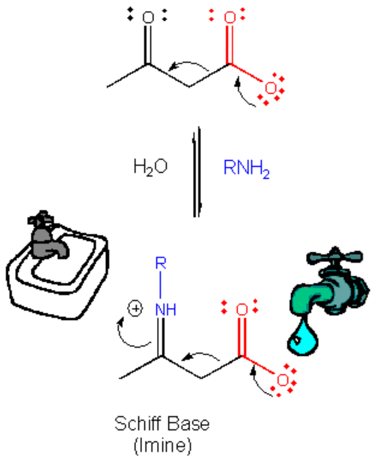
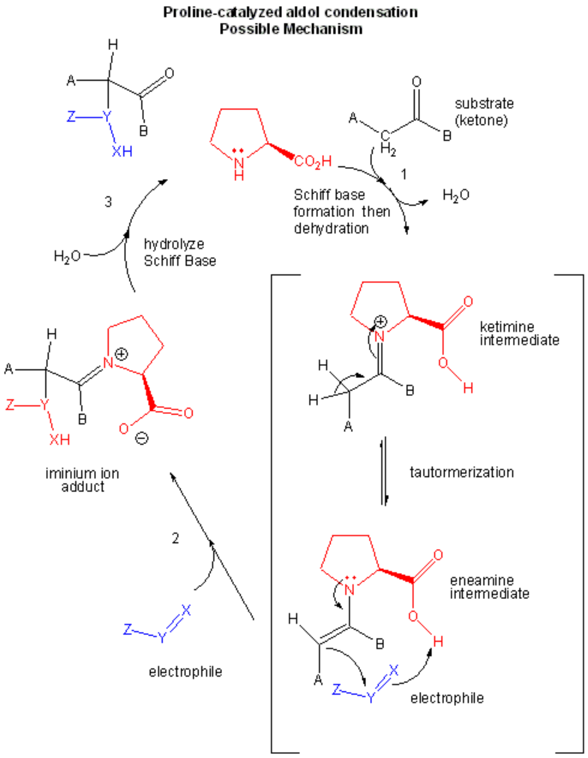


Figure: ELECTRON FLOW: SOURCE TO SINK



In a subsequent section, we will discuss how protein enzymes use these same catalytic strategies. An intriguing question arises: how much of the structure of a large protein is really needed for catalysis? Much work has been directed to the development of small molecule catalysis mimetics of large protein enzymes. Just how small can you go in reducing the size of a protein and still get catalysis. One important feature of enzyme catalysis is that they catalyze reactions in which only one enantiomer is produced. That is, the synthesis is assymertric. This is typically a consequence of the asymmetric enzyme (itself chiral) binding only one enantiomer as a reactant and/or the imposition of steric restrictions on the possible reactions of the bound substrate. Recently, it has been show that L-Pro alone can act as such an assymetric catalyst in an aldol condensation reaction.

Figure: L-PRO CATALYSIS OF AN ALDOL CONDENSATION: POSSIBLE MECHANISM



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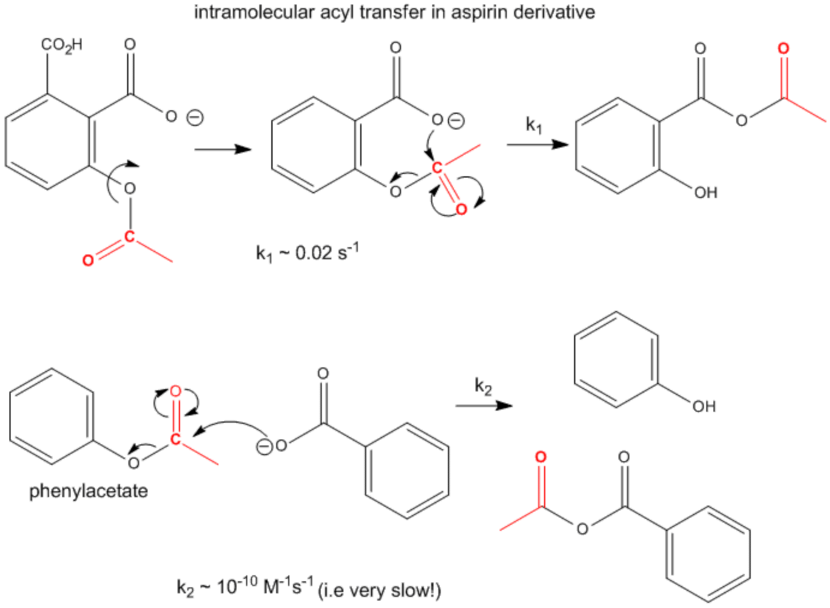
8.1.4: A4. Intramolecular Catalysis

Consider the hydrolysis of phenylacetate. This reaction, a nucleophilic subsitution reaction, could be catalyzed by the addition to solution of the general base acetate, as described above. Since this reaction would double with the doubling of the solution acetate, the reaction is bimolecular (first order in reactant and catalyst). Now consider the same reaction only when the the general base part of the catalyst, the carboxyl group, is part of the reactant phenylacetate. Such a case occurs in the acetylated form of salicylic acid - i.e. aspirin. When the carboxy group is ortho compared to the acetylated phenolic OH, it is in perfect position to accept a proton from water, decreasing the charge development on the O in the transition state. The general base does not have to diffuse to the appropriate site when it is intramolecular with respect to the carbonyl C of the ester link. The rate of this intramolecular base catalysis is about 100 fold greater than of an intermolecular base catalyst like acetate. It is as if the effective concentration of the intramolecular carboxyl base catalyst is much higher due to its proximity to the reaction site.

Another type of reactions involving a carboxyl group (in addition to simple proton transfer) is when the negatively charged carboxyl O acts as a nucleophile and attacks an electrophilic carbonyl carbon. When the carbonyl is part of an ester, the carboxyl group engages in a nucleophilic substitution reaction, expelling the alcohol part of the ester as a leaving group. The remaining examples below consider the nucleophilic (carboxyl) substitution on phenylesters, with phenolate as the leaving group. The reactions in effect transfer an acyl group to the carboxyl group to create an anhydride. These examples come from a great book by Abeles, Frey and Jencks (Biochemistry, Jones and Bartlett:Boston, 1992).

First consider acyl transfer with aspirin derivatives. Aspirin, as you know, contains a carboxyl group ortho to an ester substitutent. Hence the carboxyl group can act as a nucleophile and attack the carbonyl carbon of the ester in a nucleophilic substitution reaction. The net effect is to transfer the acetyl group from the phenolic OH to the carboxyl group converting it to an anhydride. This is an intramolecular reaction. Compare this reaction to a a comparable bimolecular reaction shown below.

Figure: ACYL TRANSFER IN ASPIRIN DERIVATIVES.

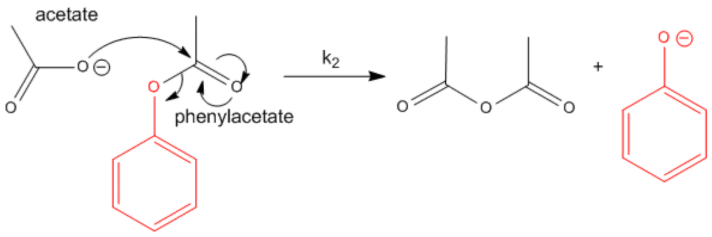


k_1/k_2 ~ 2 x 10^7 M
or it would take that concentration of phenyleacetate to react
with 1 M benzoate to give the same rate as the top reaction.

The first order rate constant of the intramolecular transfer of the acetyl group to the carboxyl group, k1 = 0.02 s^{-1}. The analogous bimolecular reaction rate constant k2~ 10^{-10} $M^{-1}s^{-1}$. Dividing k1/k2 gives the relative rate enhancement of the intramolecular over the intermolecular reaction. With units of molarity, this ratio can be interpreted as the relative effective concentration of the intramolecular nucleophile. This makes the effective concentration of the carboxylate in the aspirin derivative 2 x 10^7 M.

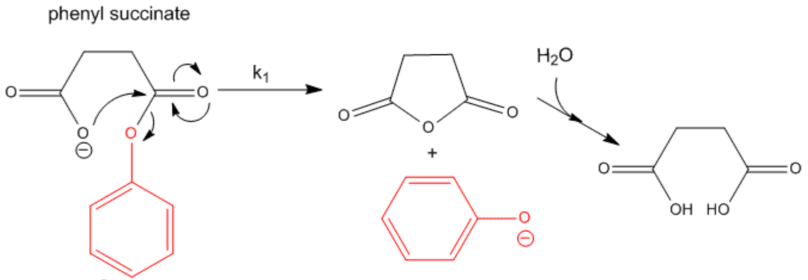
Now consider the cleavage of phenylacetate using acetate as the nucleophile. The products are acetic anhydride and phenolate. This is a bimolecular reaction (a slow one at that), with a bimolecular rate constant, k2 which I will arbitrarily set to 1 for comparison to some similar reactions.

Figure: REACTION OF ACETATE WITH PHENYLACETATE



Now consider a monoester derivatives of succinic acid - phenyl succinate - in which the free carboxyl group of the ester attacks the carbonyl carbon of the ester derivative.

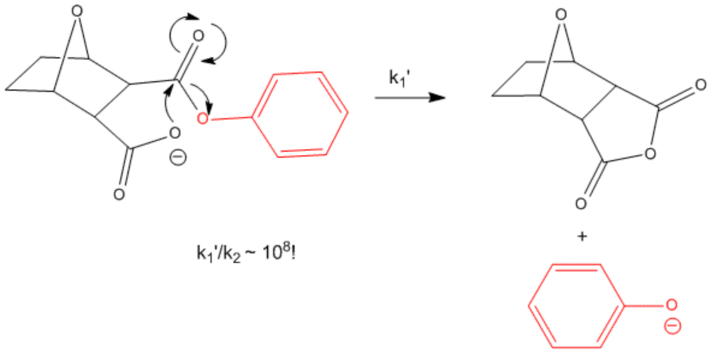
Figure: INTRAMOLECULAR REACTION OF PHENYLSUCCIATE



$k_1/k_2 = 10^5$ M = effective M (i.e. [acetate] take for rx with 1 M phenylacetate to go as quickly!

If you assign a second order rate constant k2 = 1 $M^{-1}s^{-1}$ to the analogous intermolecular reaction of acetate with phenylacetate (as described above), the first order rate constant for the intramolecular reaction of phenylsuccinate is 105 s^{-1}. The ratio of rate constants, k1/k2 = 105 M. That is it would take 10^5 M concentration of acetate reacting with 1 M phenylacetate in the first bimolecular reaction to get a reaction as fast as the intramolecular reaction of phenylsuccinate. An even more sterically restricated bicyclic phenylcarboxylate shows a k1/k2 = 10^8 M.

Figure: INTRAMOLECULAR REACTION OF BICYCLIC PHENYLCARBOXYLATE

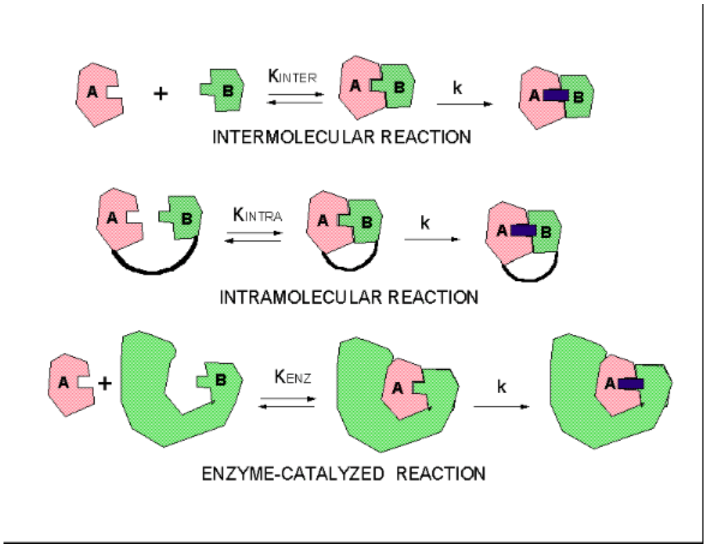


$k_1'/k_2 \sim 10^8$!

Another example is anhydride formation between two carboxyl groups. The ΔGo for such a reaction is positive, suggesting an unfavorable reaction. Consider two acetic acid molecules condensing to form acetic anhydride. For this intermolecular reaction, Keq = 3x10-12 M-1. Now consider the analogous intramolecular reaction of the dicarboxylic acid succinic acid. It condenses in an intramolecular reaction to form succinic anhydride with a Keq = $8x10^{-7}$ (no units). The ratio Keq-intra/Keq inter = 3 x 10^5 M. It is as if the effective concentration of the reacting groups. because they do not have to diffuse together to react, is 3 x 10^5 M.

How does this apply to enzyme catalyzed reaction? Enzymes bind substrates in physical steps which are typically fast. The slow step is chemical conversion of the bound substrate, which is effectively intramolecular. These three kinds of reactions, intermolecular, intramolecular, and enzyme-catalysed can be broken down into two hypothetical steps, a binding followed by catalysis.

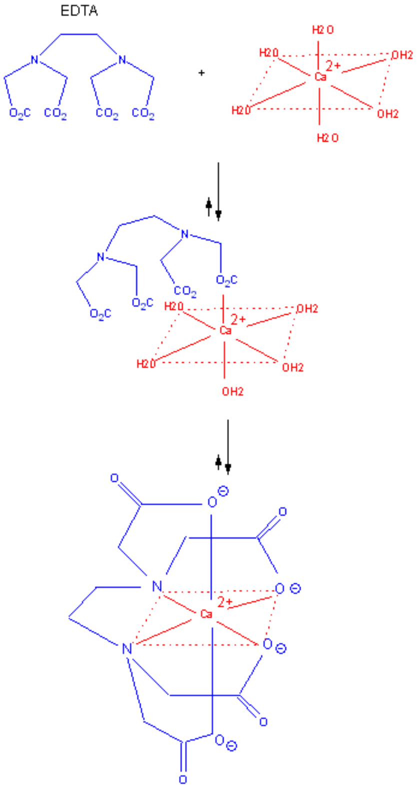
Figure: three kinds of reactions, intermolecular, intramolecular, and enzyme-catalysed



If the rate constants for the chemical steps are all identical, the advantage of the intramolecular and enzyme-catalyzed reaction over the intermolecular reaction is KINTRA/KINTER and KENZ/KINTER, respectively.

The advantage of intramolecular reactions can be seen by studying the Ca-EDTA complex. Calcium in solution exists as a octahedrally coordinated complex with water occupying all the coordination sites. EDTA, a multidentate ligand, first interacts through one of its potential six electron donors to Ca in a reaction which is entropically disfavored from the the Ca-EDTA perspective, although one water is released. Once this first intramolecular complex is formed, the rest of the ligands on the EDTA rapidly coordinate with the Ca and release bound water. The former is no longer entropically disfavored since it is now an intramolecular process while the later is favored through the release of the remaining five water molecules.

Figure: FIGURE: BINDING OF Ca2+ AND EDTA.



We modeled the catalytic advantage offered by intramolecular reaction in terms of a dramatic increase in the effective concentration of reactants, which sometimes reached levels of 108 M. Another way is to look at entropy changes associated with dimer formation. The table below shows that an intramolecular reaction is favored over an intermolecular reaction since in the latter, significant decreases in translational and rotation entropy result.

Translational, Rotational, and Internal Entropies for Dimer Formation: A + B <=> A-B (cal/K.mol)

System	A	B	A-B	ΔS
		Gas		
S trans	30	30	30	-30
S rot	20	20	20	-20
S int	5	5	20	+10
Gas -> Solution	-10	-10	-15	
S sol	45	46	55	-35 (Correspond to 108-109 M)

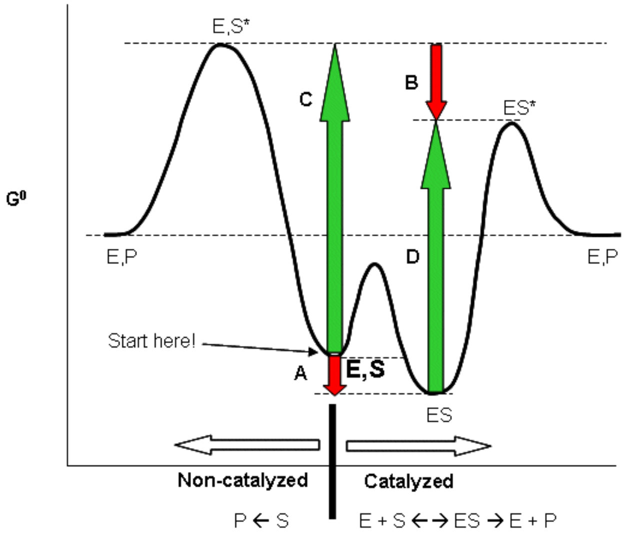
Contributors and Attributions

- Prof. Henry Jakubowski (College of St. Benedict/St. John's University)

8.1.5: A5. Transition State Stabilization

Linus Pauling postulated long ago that the only thing that a catalyst must do is bind the transition state more tightly than the substrate. That this must be the case can be seen from the diagram below, which shows how S and $S*$ (the transition state) can react with E to form a complex which then proceeds to product, or can go to product in the absence of E. From this diagram, it should be evident that $c-a=d-b$, where a is the ΔG^o for the binding of S to E, and b is the ΔG^o for the binding of S* to E. For an enzyme to be a catalyst the activation energy for the reaction in the presence of E, d, must be less than in the absence of enzyme, c. Therefore $c-d=a-b>0$. Since $\Delta G^o=-RT\ln K_{eq}$, K_{eq} for binding of $S*$ to E is greater than for S binding to E.

Figure: ENZYMES BIND THE TRANSITION STATE MORE TIGHTLY THAN THE SUBSTRATE



The stability of the transition state also affects the reaction kinetics (which makes sense given that the activation energy clearly affects the speed of a reaction). As you probably remember from organic chemistry, S_N2 reactions are slow when the central atom where the substitution will occur is surrounded by bulky substitutents (sterics once again). We discussed this in context to nucleophiliic substitution on a sp^2 hybridized carbonyl carbon in carboxylic acid derivatives versus on a sp^3 hybridized phosphorous in phosphoesters and diesters.; The explanation for this phenomena has usually been attributed to hindered access of the central atom caused by bulky substituents (intrinsic effects). Is this true?; Recent studies on S_N2 reactions of methylchloroacetonitrile and t-butylchloroacetonitrile (with the reagent labeled with ^{35}Cl) using $^{37}Cl^-$ as the incoming nucleophile in the gas phase shown that the more hindered t-butyl derivative's activation energy was only 1.6 kcal/mol higher than the methyl derivative, but in aqueous solution, the difference is much greater for comparable reactions. They attributed the differences to solvation effects of the transition state. The bulkier the substituents on the central atom, the more difficult it is to solvate the transition state since water can't reorient around it as well. In effect there is steric hindrance for both reactant and solvent.

Abyzmes - Antibody Catalysis

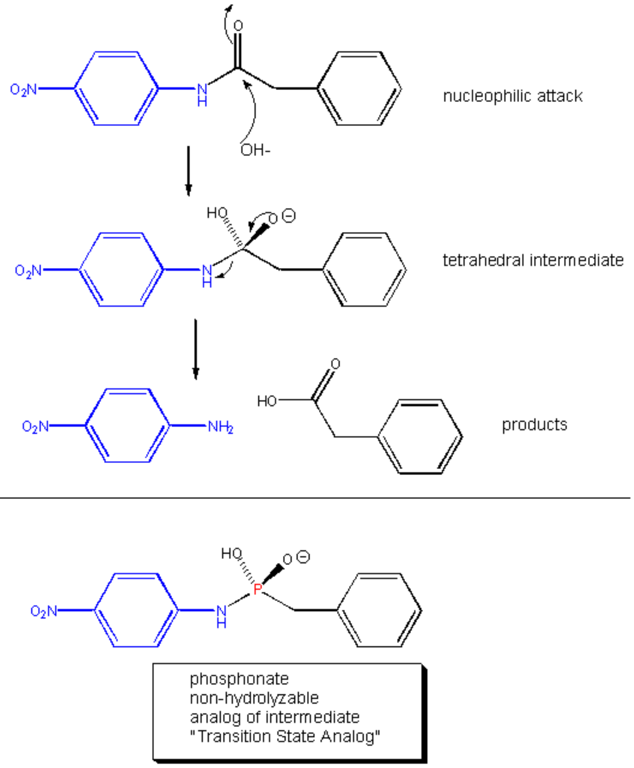
What does it take for a macromolecule (M) to be a catalyst - an enzyme. It seems the minimum criterion are:

- M binds a reactant
- M binds the transition state more tightly than the substrate

Anything above these is just "icing on the cake". If different functional group are present in the "active" site of the enzyme that would allow electrostatic, intramolecular, covalent, general acid and/or base catalysis, the better the catalyst.

Linus Pauling recognized the two key factors decades ago. He made the following hypothesis: Antibody molecules (immune system proteins that bind foreign molecules) that can be made to bind to transition state analogs of a substrate, should also presumably catalyze the conversion of substrate, through the transition state, to product. About a decade ago, his prediction was verified. Lerner et al. made a transition state analog of an ester. When an ester is hydrolyzed, the sp2 hybridized carbonyl carbon is converted to an sp3 hybridized center in the intermediate, with the carbonyl oxygen becoming an oxyanion. The transition state presumably looks more like this unstable intermediate (sp3, oxyanion). Lerner synthesized a phosphonate, an ester mimic with a sp3 hybridized phosphorous replacing the carbonyl C. It also has a negatively charged oxygen as does the intermediate for the ester. This phosphonate ester is very resistant to hydrolysis. When injected into a mouse (after first being covalently attached to a carrier protein so the small molecule becomes "immunogencic"), the mouse makes a protein antibody which binds to the phosphonate. When the corresponding carboxylic acid ester is added to the antibody, it is cleaved with nominal kcat and Km values. Site specific mutagenesis can then be done to make it an even better catalyst! The antibody enzymes have been called abzymes. The structure below shows how phosphonamides act as transition state analogs as well.

Figure: PHOSPHONAMIDES: TRANSITION STATE ANALOGS



phosphonate
non-hydrolyzable
analog of intermediate
"Transition State Analog"

Jmol: Updated Immunoglobulin 48G7 Germline Fab Antibody Complexed With Hapten 5-(Para-Nitrophenyl Phosphonate)-Pentanoic Acid Jmol14 (Java) | JSMol (HTML5)

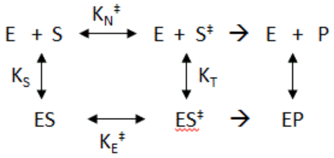
Transition state theory can be used to more clearly quantify the relationships described in the graphical analysis above. This analysis will use the equilibrium constant (in contrast to the last two chapters which used dissociation constants to characterize macromolecule, receptor, and enzyme binding to ligand). Let assume that a substrate S is in equilibrium with its transition state S‡. Hence Keq = [S‡]/[S]. The following reaction can be written: S --> S‡ --> P. Based on our previous kinetic analysis and experience in writing differential equations, dP/dt = k1[S‡]. By analogy, enzyme bound S (ES) can be converted to (ES‡) and then on to product as shown in the following chemical equation:

E + S <----> ES --> ES‡ --> E + P.

For the non-enzyme catalyzed reaction, transition state theory can be used to show that the first order rate constant k1= kT/h where k is the Boltzman's constant, T is the Kelvin temperature, and h is Planck's constant. Hence, using Keq = [S‡]/[S], equation 1 can be derived

1. $$\frac{dP}{dt} = \frac{kT}{h}[S^{\ddagger}] = \frac{kT}{h}K^{\ddagger}[S] = k_n[S]$$

where kn (hereafter written as kN) =(kT/h)K‡ is the effective first order rate for the non-catalyzed rate. Now lets create a more complicated linked equilibrium showing the same reaction in the presence of an enzyme.



Remember that the K values for this analysis are equilibrium constants not dissociation constants. Note two important equilibrium constants, KS, the equilibrium constant for the binding of free S to E, and KT, the equilibrium constant for the binding of free S‡ to E (assuming that free S‡ could bind to E before it converted to product). As we have seen for linked equilibrium before, since the Keq values are related to the standard free energy changes which are state functions, the sum of the standard free energies going from E + S to ES‡ (by either the top or bottom paths) are path independent so the products of the Keq for the top path are equal to those for the bottom paths. This gives the following equation:

$$\frac{K_T}{K_S}=\frac{K_{E‡}}{K_{N‡}}=\frac{k_E}{k_N}$$

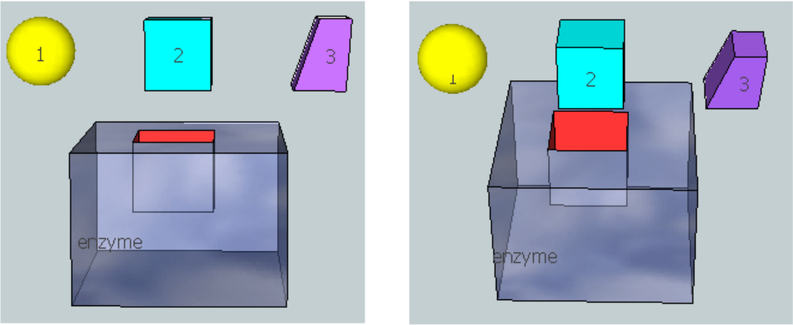
2.

The right hand side is the ratio of the effective first order rate constant for conversion or ES‡ --> E + P, kE dvided by the rate constant for the conversion of S‡ --> P for the noncatalyzed rate, kN. The final ratio of rate constants can be derived from the simple relationship that kx=(kT/h)K‡x where x is either N (non catalyzed) or E (enzyme catalyzed). Equation 2 states that the equilibrium constant for the binding of S‡ to E, KT, is greater than the equilibrium constant for the binding of S to E, KS (as kE > kN). KT/KR ranges from 108 - 1014. Given common values for the equilibrium constant for binding of S to E (103 - 105 M-1) which is equivalent to dissociation constant values Kd = 10 uM -1 mM, the calculated value of KT = 1015 M-1 which gives a dissociation constant for the enzyme and transition state of Kd = 10-15 M (1 femtomolar). This is as tight as one of the highest affinity binding interactions in the biological world, the binding of avidin and biotin. As we noted in Chapter 5A, assuming that the second order rate constant for avidin/biotin binding and as shown above for E/S‡ is diffusion controlled (about 108 M-1s-1), the off rate for the avidin-biotin or ES‡complex is 10-7 s-1, equivalent to a half life of the complex of 80 days. It doesn't get much tighter than that.

The figure below represent an image of an enzyme and three different molecules, 1-3, that could bind to it. Using the analysis above, which molecule do you think represents substrate? Transition state? Product?

Figure: 3D model for binding substrate, transition state, and product to an enzyme

Animated Version



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8.1.6: A6. Links and References

1. Movassaghi, M. & Jacobsen, E. The Simplest "Enzyme". Science, 298, pg 1904 (2002)
2. Regan, Craig, and Brauman. Nature 295, pg 2245 (2002)

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