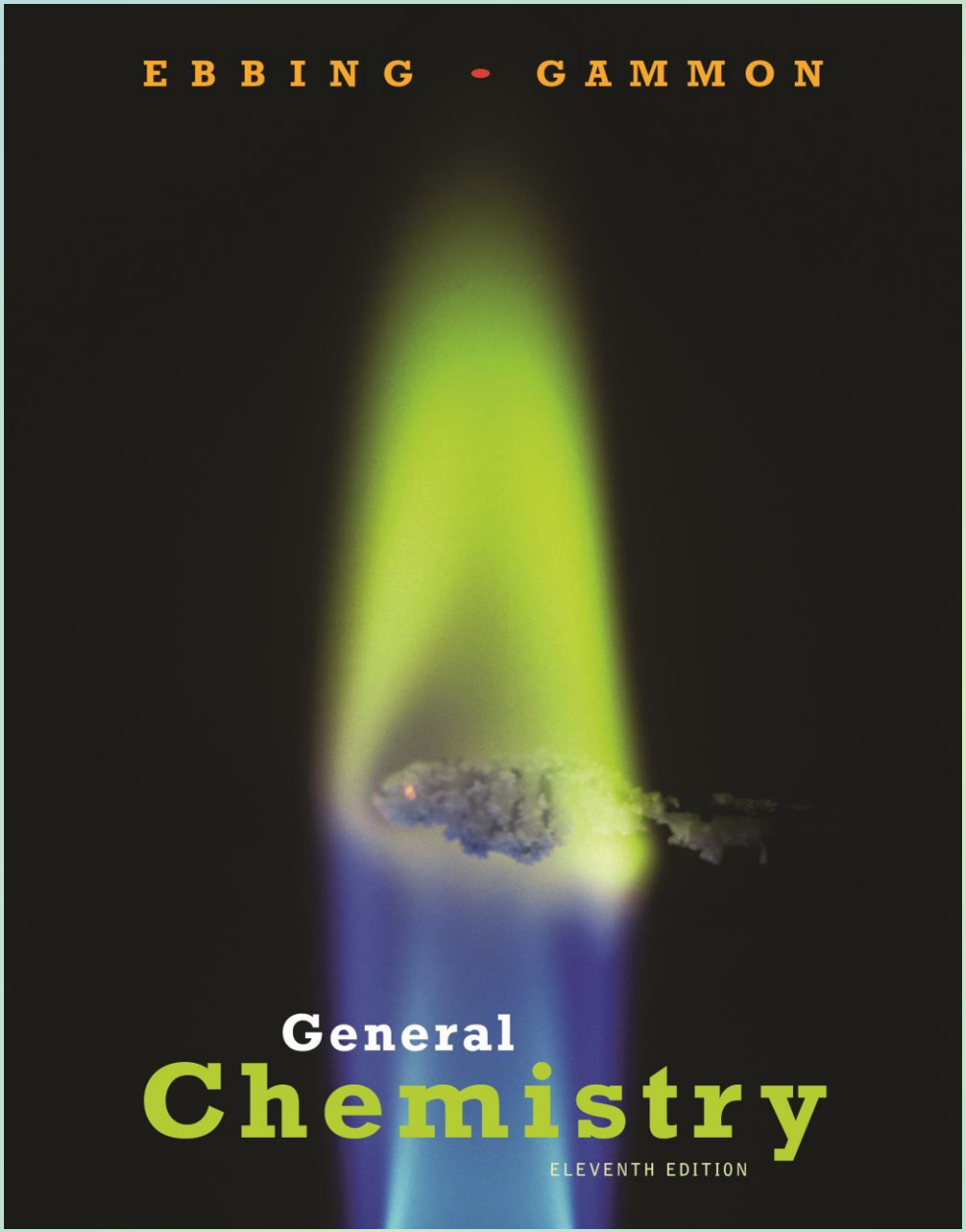


Chapter 2 Atoms, Molecules, and Ions

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Postulates of Dalton's Atomic Theory

An explanation of the structure of matter in terms of different combinations of very small particles

All matter is composed of indivisible atoms.

An **atom** is an extremely small particle of matter that retains its identity during chemical reactions.

An **element** is a type of matter composed of only one kind of atom.

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A **compound** is a type of matter composed of atoms of two or more elements chemically combined in fixed proportions.

A **chemical reaction** involves the rearrangement of the atoms present in the reacting substances to give new chemical combinations present in the substances formed by the reaction.

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Atomic Symbol

A one- or two-letter notation used to represent an atom corresponding to a particular element

Symbols are generally derived from the name of the element. Other names are derived from another language.

- The first letter is capitalized.
- The second letter, when present, is in lowercase.

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Law of Multiple Proportions

When two elements form more than one compound, the masses of one element in these compounds for a fixed mass of the other element are in ratios of small whole numbers.

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Consider a reaction between 1.000 gram of carbon and oxygen, forming two compounds.

The first compound contains 1.3321 grams of O_2 per 1.000 gram of carbon.

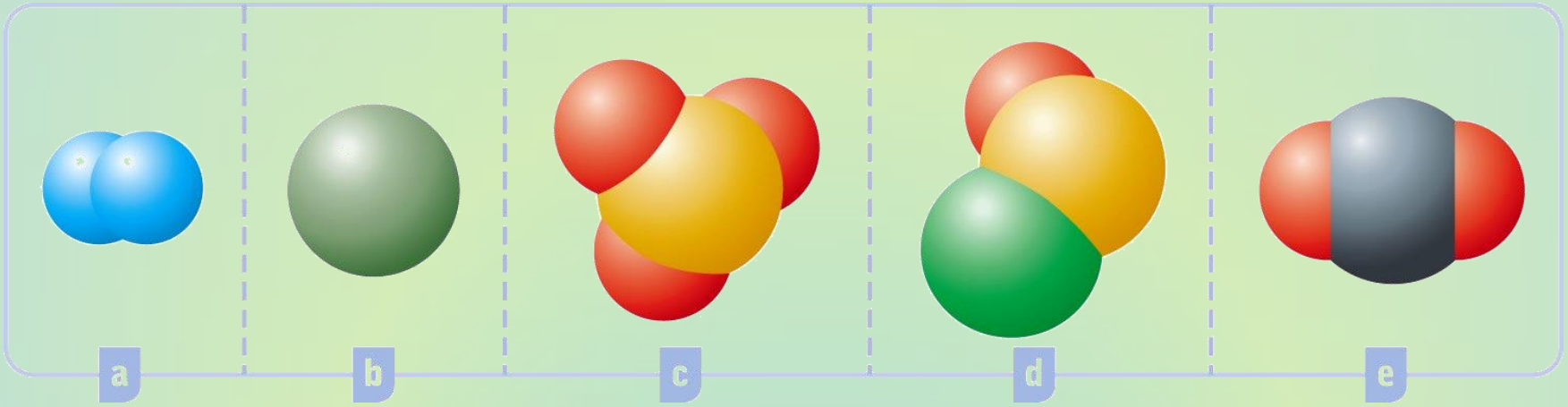
The second compound contains 2.6642 grams of O_2 per 1.000 gram of carbon.

The ratio of O_2 to C in both instances is 2 : 1, indicating that the second compound has twice the amount of O_2 than the first.

According to the atomic theory, if the first compound is represented as CO, then the second will be represented as CO_2.

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Like Dalton, today's chemists model atoms using spheres. Modern models are often drawn using computer programs and use different colors to represent atoms of different elements. Which of these models depicts CO_2?



(e) is CO_2

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Structure of the Atom

The atom is composed of two parts:

Nucleus

- Central core
- Positively charged
- Contains most of the atom's mass

Electrons

- Very light
- Negatively charged
- Exist in the region around the nucleus

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Discovery of the Electron

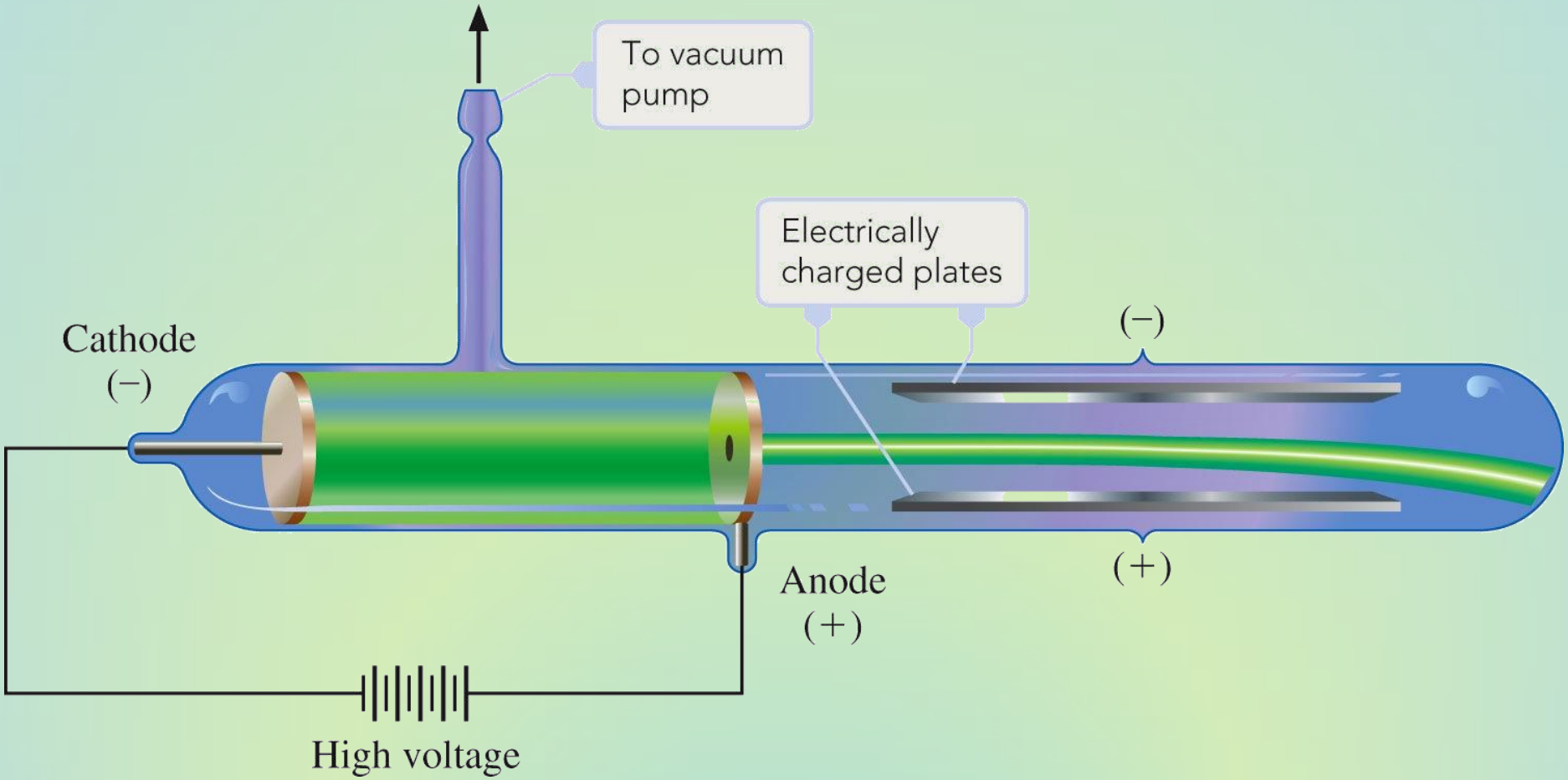
J. J. Thomson used a cathode-ray tube for a series of experiments, showing that atoms were not indivisible particles.

He concluded that a cathode ray comprises a beam of negatively charged particles and that all matter contained electrons.

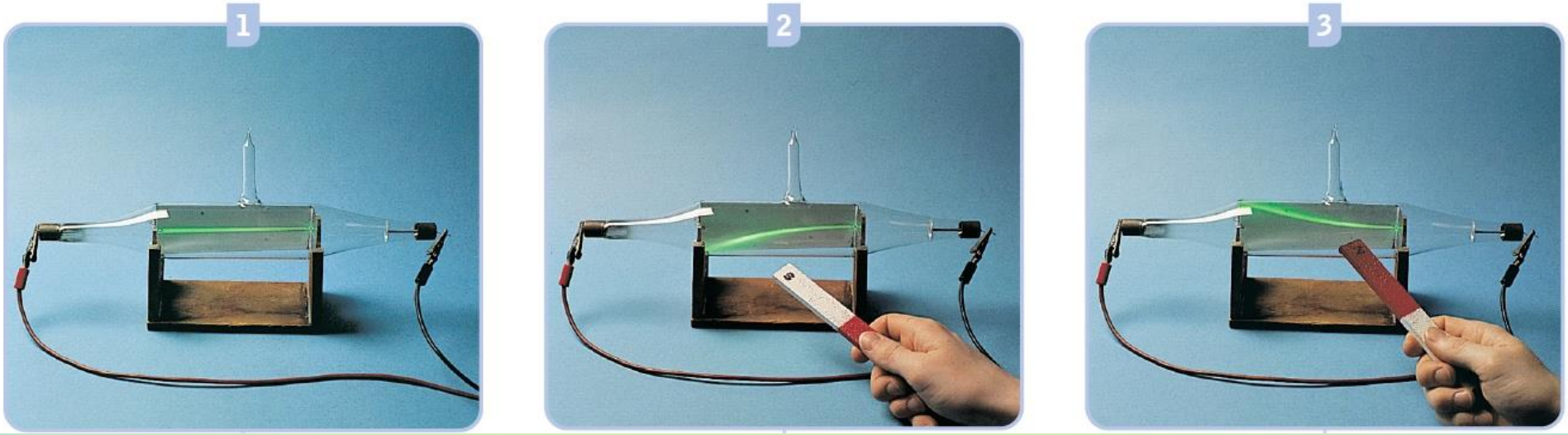
He was also able to calculate the ratio of the electron's mass, m_e, to its electric charge, e.

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Cathode-Ray Tube



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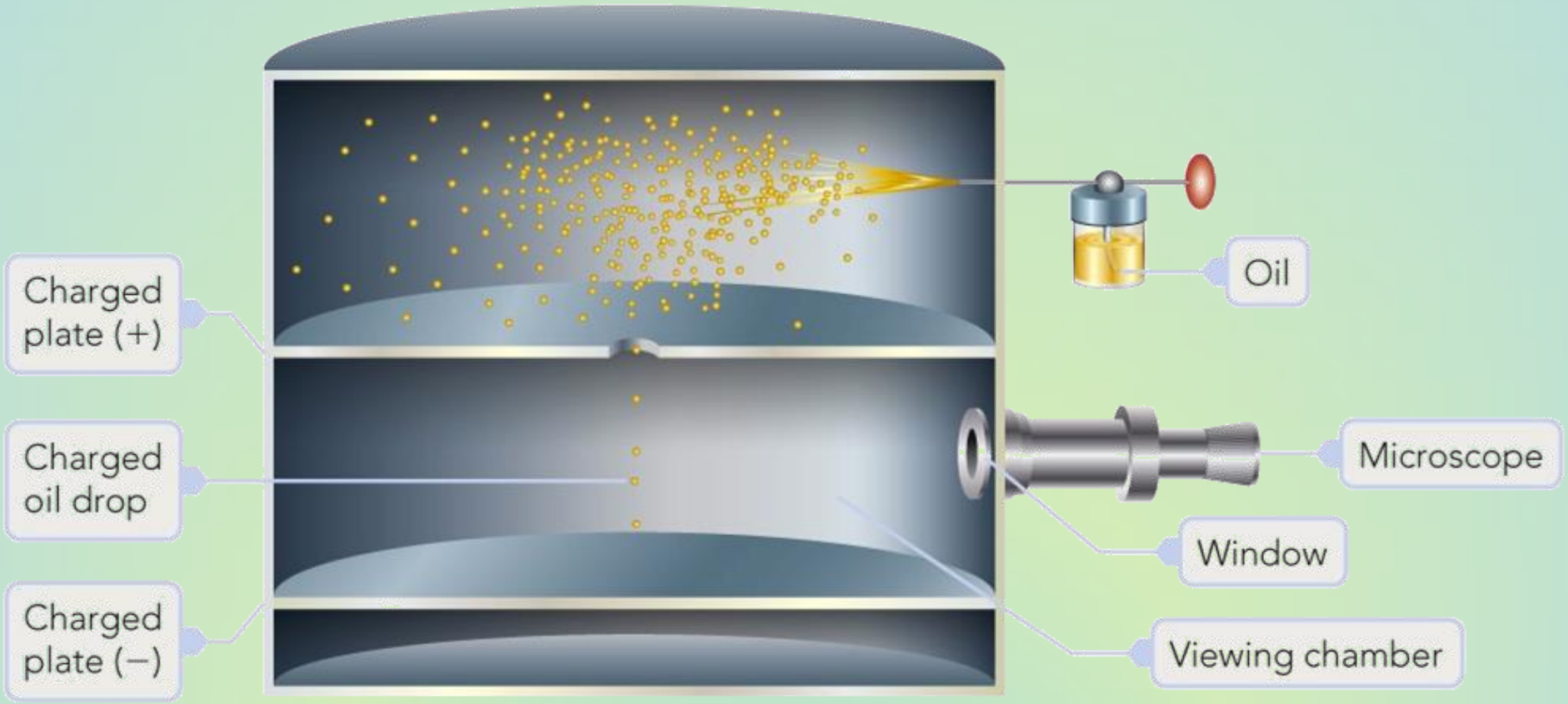
Cathode rays are attracted to the positive end of the magnet and repelled by the negative end.

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Robert Millikan determined the charge of an electron by observing a charged oil drop falling in the presence and absence of an electric field.

The charge of an electron is 1.602×10^{-19} coulombs.

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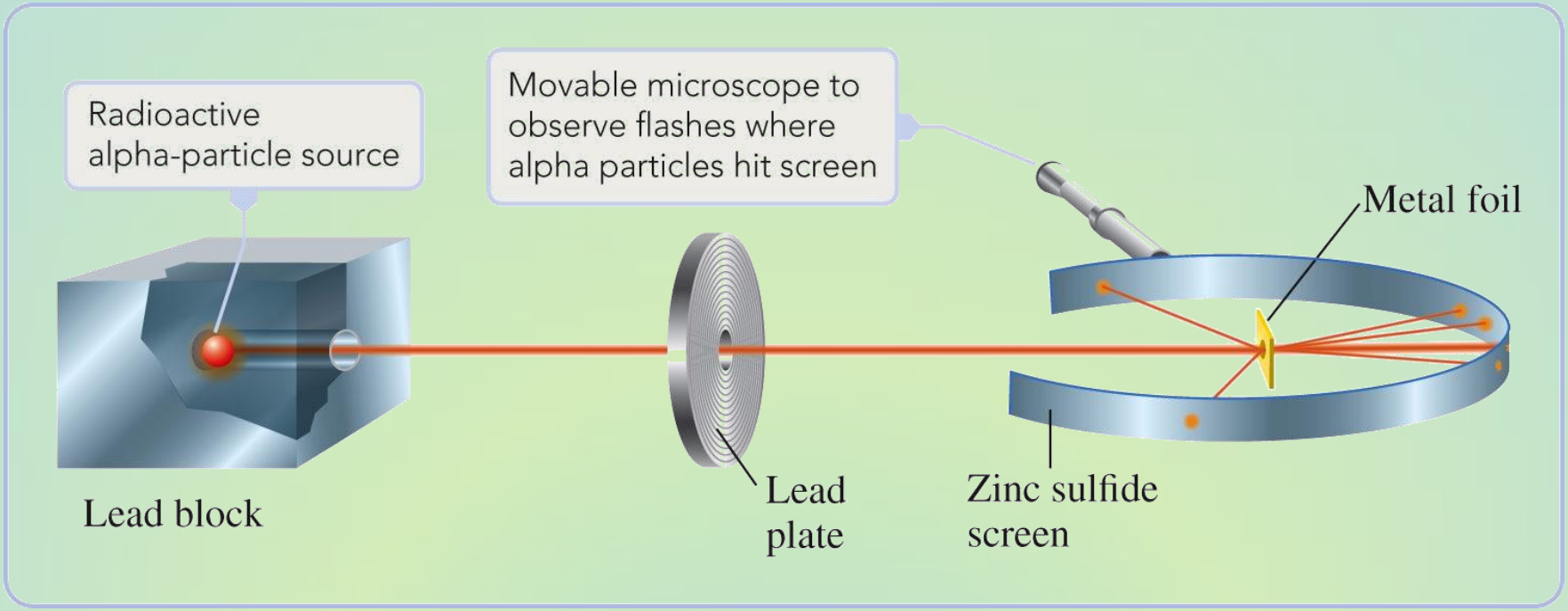
Nuclear Model of the Atom

Experiments done in Ernest Rutherford's laboratory used positively charged alpha particles to bombard a very thin gold (and other metal) foil.

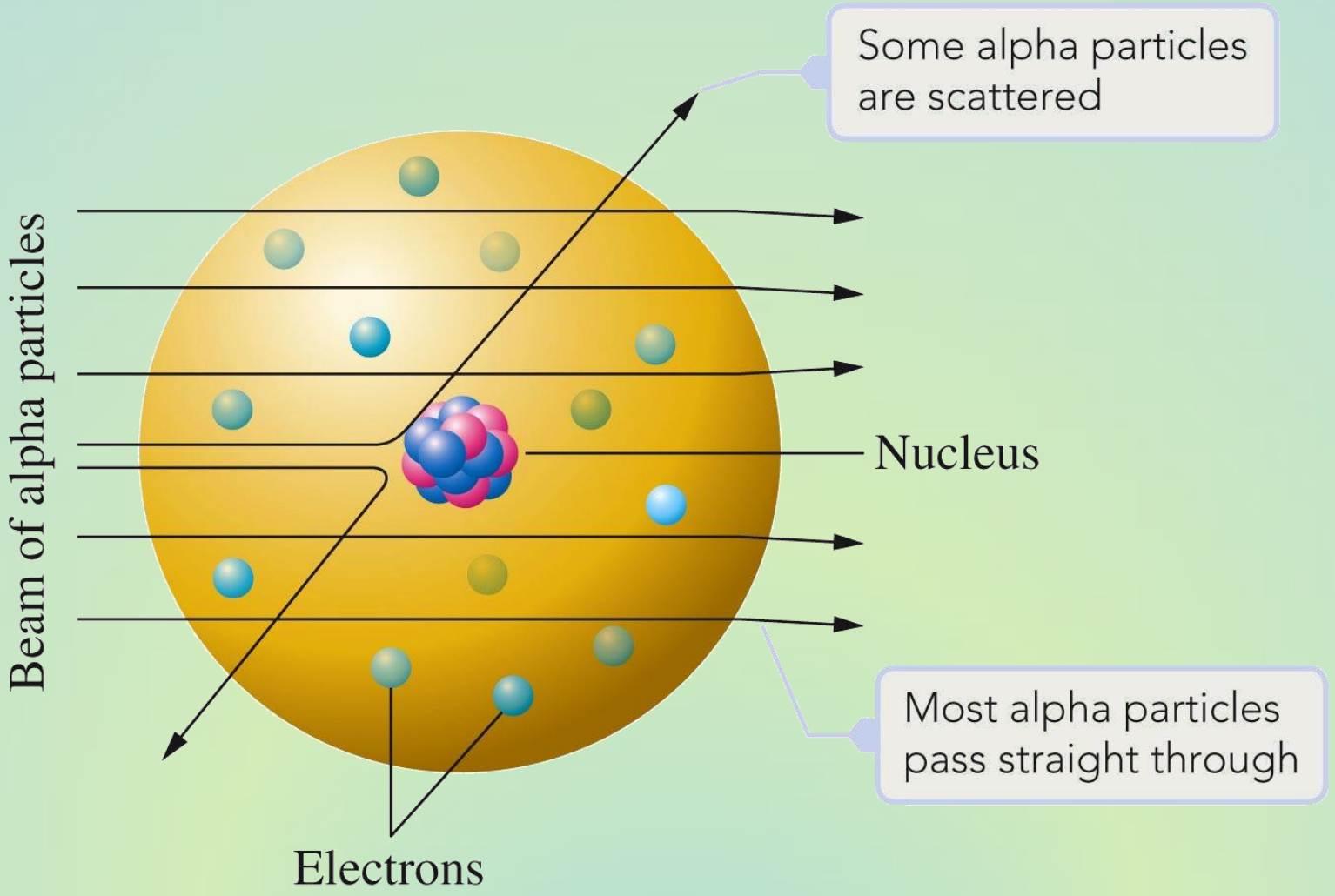
Most alpha particles passed through the foil, but a few were scattered at large angles, sometimes almost backward.

Based on these findings, Rutherford proposed that 99.95% of the atom's mass is in the positively charged nucleus.

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Proton

A nuclear particle that has a positive charge equal in magnitude to that of the electron and a mass more than 1800 times that of the electron.

The number of protons in an atom is called the **atomic number,** *Z.*

An **element** is a substance whose atoms have the same atomic number.

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Neutron

A nuclear particle that has a mass almost equal to that of the proton but no electrical charge.

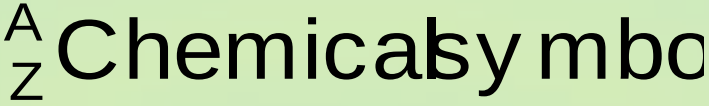
The **mass number**, *A*, is the total number of protons and neutrons in the nucleus.

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Nuclide

An atom characterized by a certain atomic number, *Z*, and mass number, *A*

Nuclide symbol



Isotopes are atoms whose nuclei have the same atomic number (number of protons) but different mass numbers (numbers of neutrons).

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Write the nuclide symbol for a nucleus that has 38 protons and 50 neutrons.

The element with the atomic number 38 is strontium.
Calculating the mass number,

$$38 + 50 = 88$$

$$^{88}_{38}\mathrm{Sr}$$

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Relative Atomic Weights

The average mass of one atom is relative to the average mass of another.

Atomic Mass Unit (amu)

A mass unit equal to exactly one-twelfth the mass of a carbon-12 atom

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Atomic Weight

The average atomic mass for the naturally occurring element, expressed in atomic mass units

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Mass Spectrometry

Helps calculate the atomic weight of an element, as well as all of the isotopic masses and the fractional abundance of each isotope

Fractional Abundance

The fraction of the total number of atoms that is composed of a particular isotope

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Chromium, Cr, has the following isotopic masses and fractional abundances:

Mass number	Isotopic Mass (amu)	Fractional Abundance
50	49.9461	0.0435
52	51.9405	0.8379
53	52.9407	0.0950
54	53.9389	0.0236

Determine the atomic weight of chromium.

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Multiplying each isotopic mass by its fractional abundance and summing up the products

$$
\begin{aligned}
49.9461\ \text{amu} \times 0.0435 &= 2.17\ \text{amu} \\
51.9405\ \text{amu} \times 0.8379 &= 43.52\ \text{amu} \\
52.9407\ \text{amu} \times 0.0950 &= 5.03\ \text{amu} \\
53.9389\ \text{amu} \times 0.0236 &= 1.27\ \text{amu} \\
&\underline{\qquad\qquad} \\
&51.99\ \text{amu}
\end{aligned}
$$

The atomic weight of chromium is 51.99 amu.

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An **ionic compound** is composed of cations and anions. The attraction between positive and negative charges holds the ions in a consistent arrangement, forming a crystal.

The formula of an ionic compound gives the smallest possible integer number of ions in the substance (without writing charges) so that the combination is electrically neutral.

The **formula unit** of a substance is the group of atoms or ions explicitly symbolized in the formula.

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Determine the formula of chromium (III) oxide.

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Chromium (III) oxide comprises Cr^{3+} and O^{2-} ions.

Unit charge on $O^{2-} = 2$

Unit charge on $Cr^{3+} = 3$

Combining the total charges of 2 Cr^{3+} ions and 3 O^{2-} ions

$$\underbrace{2 \times (+3)}_{\text{Positive charge}} + \underbrace{3 \times (-2)}_{\text{Negative charge}} = 0$$

The simplest ratio of Cr^{3+} to O^{2-} is 2 : 3.

The formula is Cr_2O_3.

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Organic Compounds

An important class of molecular substances that contain carbon combined with other elements—notably hydrogen, oxygen, and nitrogen.

Hydrocarbons contain only carbon and hydrogen.

For example, CH_4, C_2H_6, and C_3H_8.

A **functional group** is a reactive portion of a molecule that undergoes predictable reactions.

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Table 2.3 Examples of Organic Functional Groups

Functional Group	Name of Functional Group	Example Molecule	Common Use
—OH	Alcohol	Methyl alcohol (CH_3OH)	Windshield washer
—O—	Ether	Dimethyl ether (CH_3OCH_3)	Solvent
—COOH	Carboxylic acid	Acetic acid (CH_3COOH)	Acid in vinegar

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Chemical nomenclature is the systematic naming of chemical compounds.

Inorganic compounds comprise elements other than carbon.

For example, carbon monoxide, carbon dioxide, carbonates, and the cyanides are some elements that are classified as inorganic compounds.

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Naming Inorganic Compounds

The cation is named first and the anion is named second.

Examples

Cation	Anion	Name
Na^{+}	Br^{-}	Sodium bromide
Mg^{2-}	O^{2-}	Magnesium oxide
Al^{3+}	Cl^{-}	Aluminum chloride

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Monatomic ions

Ions formed from a single atom.

Table 2.4 Common Monatomic Ions of the Main-Group Elements*

	1A	2A	3A	4A	5A	6A	7A
Period 1							H^-
Period 2	Li^+	Be^{2+}	B	C	N^{3-}	O^{2-}	F^-
Period 3	Na^+	Mg^{2+}	Al^{3+}	Si	P	S^{2-}	Cl^-
Period 4	K^+	Ca^{2+}	Ga^{3+}	Ge	As	Se^{2-}	Br^-
Period 5	Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sb	Te^{2-}	I^-
Period 6	Cs^+	Ba^{2+}	Tl^+, Tl^{3+}	Pb^{2+}	Bi^{3+}		

*Elements shown in color do not normally form compounds having monatomic ions.

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Rules for Predicting the Charge on a Monatomic Ion

1. Most **main-group metals** have one monatomic ion with a charge equal to the group number.

Al, in Group IIIA, has one ion, Al^{3+}.

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2. Some metallic elements with high atomic numbers have more than one cation.

   They have common cations with a charge equal to the group minus two.

   They also have a cation with a charge equal to the group number.

      The common ion of lead (group number 4, charge of 4 – 2) is Pb^{2+}.

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3. Most transition metals form more than one cation, each possessing a different charge. One of the ions possess a charge of +2.

   Iron has common cations Fe^{2+} and Fe^{3+}.

4. The charge on a monoatomic anion for a nonmetallic main-group element equals the group number minus 8.

   Oxygen has the monoatomic anion O^{2-}.

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Naming Monatomic Ions

1. Monatomic cations are named after the element if there is only one such ion.

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2. There are two approaches for instances where there are more than one monoatomic cation for an element.

   a. The Stock system names cations after the element and denotes the charge of the ion using a roman numeral.

      Fe^{2+} is called iron (II) ion.

   b. In an older system, the suffix *–ic* denotes ions of higher charge and *–ous* indicates ions of lower charge.

      Cu^{2+} is cupric.

      Cu^{+} is cuprous.

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3. The names of the monatomic anions are obtained from a stem name of the element followed by the suffix *-ide.*

   Br^- is called bromide ion.

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Polyatomic Ions

An ion consisting of two or more atoms chemically bonded together and carrying an electrical charge

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Table 2.5 Common Cations of the Transition Elements

Ion	Ion Name	Ion	Ion Name	Ion	Ion Name
Cr^{3+}	Chromium(III) or chromic	Co^{2+}	Cobalt(II) or cobaltous	Zn^{2+}	Zinc
Mn^{2+}	Manganese(II) or manganous	Ni^{2+}	Nickel(II) or nickel	Ag^{+}	Silver
Fe^{2+}	Iron(II) or ferrous	Cu^{+}	Copper(I) or cuprous	Cd^{2+}	Cadmium
Fe^{3+}	Iron(III) or ferric	Cu^{2+}	Copper(II) or cupric	Hg^{2+}	Mercury(II) or mercuric

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Table 2.6 Some Common Polyatomic Ions

Name	Formula	Name	Formula
Mercury(I) or mercurous	Hg_2^{2+}	Permanganate	MnO_4^-
Ammonium	NH_4^+	Nitrite	NO_2^-
Cyanide	CN^-	Nitrate	NO_3^-
Carbonate	CO_3^{2-}	Hydroxide	OH^-
Hydrogen carbonate (or bicarbonate)	HCO_3^-	Peroxide	O_2^{2-}
Acetate	$C_2H_3O_2^-$	Phosphate	PO_4^{3-}
Oxalate	$C_2O_4^{2-}$	Monohydrogen phosphate	HPO_4^{2-}
Hypochlorite	ClO^-	Dihydrogen phosphate	$H_2PO_4^-$
Chlorite	ClO_2^-	Sulfite	SO_3^{2-}
Chlorate	ClO_3^-	Sulfate	SO_4^{2-}
Perchlorate	ClO_4^-	Hydrogen sulfite (or bisulfite)	HSO_3^-
Chromate	CrO_4^{2-}	Hydrogen sulfate (or bisulfate)	HSO_4^-
Dichromate	$Cr_2O_7^{2-}$	Thiosulfate	$S_2O_3^{2-}$

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Determine the name of the compound Mg_3N_2.

Magnesium is a Group 2A metal; it is expected to form a 2+ ion (Mg^{2+}).
Nitrogen is a Group 5A element; it is expected to form an anion equal to the group number minus 8.
The compound is magnesium nitride.

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Determine the formula for titanium (IV) oxide.

Composition of titanium (IV) oxide:

Titanium (IV) ions - Ti^{4+}

Oxide ions O^{2-}

The formula of titanium (IV) oxide is TiO_2.

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Binary Molecular Compounds

A compound composed of only two elements

Binary compound of a metal and a nonmetal are usually ionic and are generally named as ionic compounds.

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Naming Binary Molecular Compounds

1. The name of the compound has the elements in the order given in the formula.

2. The first element is named using the exact element name.

3. The second element is named by writing the stem name of the element with the suffix *-ide*.

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4. A prefix derived from Greek is added to each element name to denote the subscript of the element in the formula.

For example, SF_4 is sulfur tetrafluoride.

The final vowel for a prefix is often dropped for ease in pronunciation.

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Table 2.7 Greek Prefixes for Naming Compounds

Number	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

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Some compounds have common names that differ from their systematic names

H_2S	hydrogen sulfide (the “di” is omitted)
H_2O	water
NH_3	ammonia

Common names need to be memorized.

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Determine the name of P_4O_6.

Composition of P_4O_6:

4 phosphorus atoms

6 oxygen atoms

The corresponding prefixes are *tetra-* and *hexa-.*

The name of the compound is

tetraphosphorus hexoxide.

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Acids and Corresponding Anions

An acid yields hydrogen ions and an anion for each acid molecule when the acid is dissolved in water.

An oxoacid is an acid containing hydrogen, oxygen, and another element referred to as the central atom.

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Acids and Corresponding Anions

To name an acid from its anion name:

1. Change an –*ate* suffix to –*ic*.
2. Change an –*ite* suffix to –*ous.*
3. Add the word “acid.”

For example:

HNO_3	nitric acid
H_2SO_4	sulfuric acid

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Table 2.8 Some Oxoanions and Their Corresponding Oxoacids

Oxoanion		Oxoacid	
CO_3^{2-}	Carbon*ate ion*	H_2CO_3	Carbon*ic acid*
NO_2^-	Nitr*ite ion*	HNO_2	Nitr*ous acid*
NO_3^-	Nitr*ate ion*	HNO_3	Nitr*ic acid*
PO_4^{3-}	Phosph*ate ion*	H_3PO_4	Phosphor*ic acid*
SO_3^{2-}	Sulf*ite ion*	H_2SO_3	Sulfur*ous acid*
SO_4^{2-}	Sulf*ate ion*	H_2SO_4	Sulfur*ic acid*
ClO^-	*Hypo*chlor*ite ion*	HClO	*Hypo*chlor*ous acid*
ClO_2^-	Chlor*ite ion*	$HClO_2$	Chlor*ous acid*
ClO_3^-	Chlor*ate ion*	$HClO_3$	Chlor*ic acid*
ClO_4^-	*Per*chlor*ate ion*	$HClO_4$	*Per*chlor*ic acid*

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Determine the formula and the name of the corresponding anion of selenic acid, H_2SeO_4.

Removing two H^+ ions from H_2SeO_4 gives SeO_4^{2-}
In the name of the acid, *-ic* is replaced with *-ate.*
The anion is called the selenate ion.

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Hydrate

A compound that contains water molecules weakly bound in the crystals

The formula of a hydrate is written with a dot before including the water molecule(s).

For example, $CuSO_4 \cdot 5H_2O$.

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Hydrates are named from the anhydrous compound followed by a word hydrate. A prefix is added to indicate the number of water molecules per formula unit of the compound.

For example, $CuSO_4 \cdot 5H_2O$ is named copper(II) sulfate pentahydrate.

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Determine the chemical name of Epsom salts, $MgSO_4 \cdot 7H_2O$.

$MgSO_4$ is magnesium sulfate.
$MgSO_4 \cdot 7H_2O$ is magnesium sulfate heptahydrate.

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A **chemical equation** is the symbolic representation of a chemical reaction in terms of chemical formulas.

For example, $2Na + Cl_2 \longrightarrow 2NaCl$

Reactants are the starting materials; they are written on the left side of the equation.

Products are the materials at the end of the reaction; they are written on the right side of the equation.

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In a balanced chemical equation, the numbers of atoms of each element are equal on both sides of the arrow.

To balance the equation, it is necessary to select coefficients that will make the numbers of atoms of each element equal on both sides.

Balancing the atoms for elements that occur in one substance on each side makes the process easier.

A balanced equation can be verified by counting the number of atoms of elements on each side.

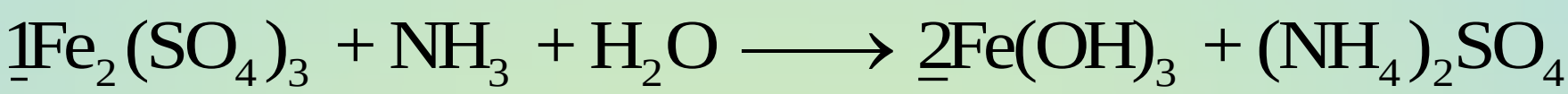
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Balance the following equation:

$$Fe_2(SO_4)_3 + NH_3 + H_2O \longrightarrow Fe(OH)_3 + (NH_4)_2SO_4$$

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Balancing Fe atoms,



Balancing S atoms,



Balancing N atoms,



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To balance the O atoms, count the number of O atoms in substances on the left with known coefficients. There are 12 atoms of oxygen in $Fe_2(SO_4)_3$. The remaining number of O atoms in H_2O must be 18 – 12 = 6.

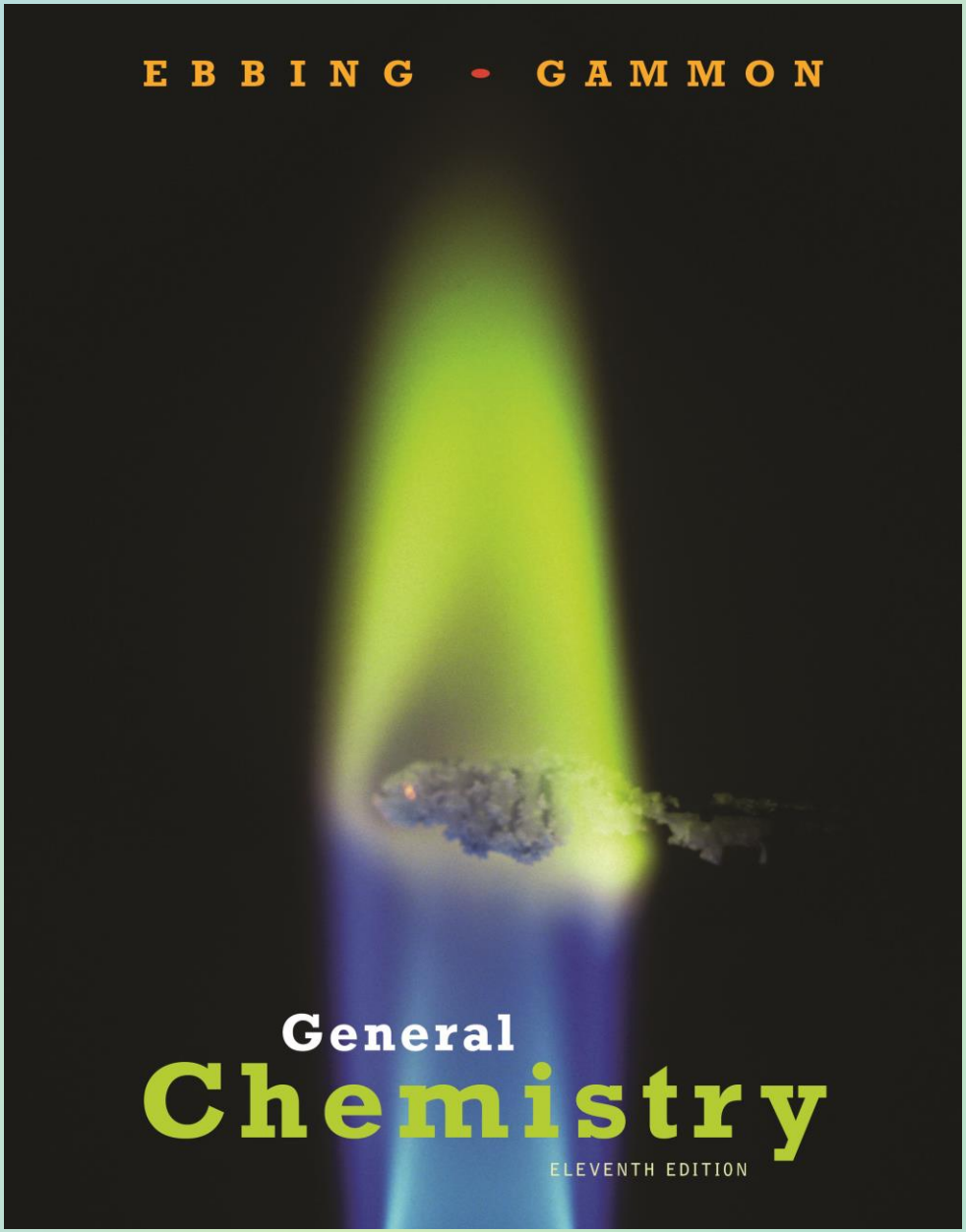
Therefore,

$$1Fe_2(SO_4)_3 + 6NH_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4$$

The balanced equation is:

$$Fe_2(SO_4)_3 + 6NH_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4$$

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Chapter 3 Calculations with Chemical Formulas and Equations

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Molecular Weight (MW)

The sum of the atomic weights of all the atoms in a molecule of the substance.

Formula Weight (FW)

The sum of the atomic weights of all atoms in a formula unit of the compound, whether molecular or not.

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Calculate the formula weight of the following compound using its atomic weight (AW).

Chloroform, ($CHCl_3$)

1× AM of C		=	12.0 amu
1× AM of H		=	1.0 amu
1× AM of Cl	= 3× 35.45 amu	=	106.4 amu
FM of $CHCl_3$		=	119.4 amu

The answer rounded to three figures is 119 amu.

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Mole, mol

The quantity of a given amount of substance that contains as many molecules or formula units as the number of atoms in exactly 12 g of carbon-12.

Avogadro's Number, N_A

The number of atoms in exactly 12 g of carbon-12

$N_A = 6.02 \times 10^{23}$ (to three significant figures).

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Molar Mass

The mass of one mole of substance.

For example,

Carbon-12 has a molar mass of 12 g/mol.

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Determine the mass of a chlorine atom in grams.

Atomic weight of Cl = 35.5 amu
Molar mass of Cl = 35.5 g/mol
Calculating the mass of one Cl atom,

$$\frac{35.5\ \text{g}}{6.02 \times 10^{23}} = 5.90 \times 10^{-23}\ \text{g}$$

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Convert 0.0654 mol of ZnI_2 to grams.

Molar mass of ZnI_2 = 319 g/mol
Converting 0.0654 mol of ZnI_2 to grams,

$$0.0654 \text{ mol } ZnI_2 \times \frac{319 \text{ } ZnI_2}{1 \text{ mol } ZnI_2} = 20.9 \text{ g } ZnI_2$$

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Percentage Composition

The mass percentage of each element in the compound. It helps determine the formula of new compounds.

Mass Percentage

Suppose that A is a part of something—that is, part of a whole.

The mass percentage of A in a substance is the parts of A per hundred parts of the total, by mass.

$$\text{Mass\% A} = \frac{\text{mass of A in the whole}}{\text{mass of the whole}} \times 100\%$$

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Determine the grams of carbon present in CH_2O. Use the following data:

C = 40.0%

H = 6.73%

O = 53.3%

Determining the mass of carbon in 83.5 g CH_2O,

$$83.5\ \text{g} \times 0.400 = 33.4\ \text{g}$$

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The first step in determining the formula of a new substance is obtaining its percentage composition.

Consider analyzing the composition of C, H, and O in compounds containing these three elements.

1. A sample of known mass of the compound is burnt to get CO_2 and H_2O.
2. Masses of CO_2 and H_2O are related to the mases of C and H.
3. Mass percentages of C and H are calculated.

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A 4.24-mg sample of acetic acid is completely burned, giving 6.21 mg of carbon dioxide and 2.54 mg of water. Determine the mass percentage of each element in acetic acid.

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Calculating grams of C,

$$6.21\times10^{-3}\,\text{g}\,\cancel{CO_2}\times\frac{1\,\text{mol}\,\cancel{CO_2}}{44.0\,\text{g}\,\cancel{CO_2}}\times\frac{1\,\text{mol}\,\cancel{C}}{1\,\text{mol}\,\cancel{CO_2}}\times\frac{12.0\,\text{g C}}{1\,\text{mol}\,\cancel{C}}$$

$$=1.69\times10^{-3}\ \text{g C (or 1.69 mg C)} = 39.9\%$$

Calculating grams of H (1 mol H_2O yields 2 mol H),

$$2.54\times10^{-3}\,\text{g}\,\cancel{H_2O}\times\frac{1\,\text{mol}\,\cancel{H_2O}}{18.0\,\text{g}\,\cancel{H_2O}}\times\frac{2\,\text{mol H}}{1\,\text{mol}\,\cancel{H_2O}}\times\frac{1.01\,\text{g H}}{1\,\text{mol H}}$$

$$=2.85\times10^{-4}\ \text{g H (0.285 mg H)} = 6.72\%$$

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Calculating the mass percentage of O_2,

$$\text{Mass\% O} = 100\% - (39.9\% + 6.72\%) = 53.4\%$$

The percentage composition of acetic acid is:

39.9% of carbon

6.72% of hydrogen

53.4% of oxygen

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Empirical Formula (Simplest Formula)

The formula of a substance written with the smallest integer subscripts.

For example,

The empirical formula for H_2O_2 is HO.

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Determining the molecular formula requires:

1. The percentage composition
2. The molecular weight

Determining the empirical formula for a substance involves converting the masses of the elements to moles.

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A compound of nitrogen and oxygen is analyzed and a sample weighing 1.587 g is found to contain 0.483 g N and 1.104 g O. Determine the empirical formula of the compound.

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Converting masses to moles,

$$0.483\,\cancel{g}\,N \times \frac{1\,mol\,N}{14.0\,\cancel{g}\,N} = 0.0345\,mol\,N$$

$$1.104\,\cancel{g}\,O \times \frac{1\,mol\,O}{16.00\,\cancel{g}\,O} = 0.06900\,mol\,O$$

Dividing the bigger mole number by the smaller one results in the smallest integers.

N = 1.00

O = 2.00

As the ratio of N to O is 1:2, the empirical formula is NO_2

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Determining molecular formula from empirical formula

For any molecular compound,

$$\text{Molecular weight} = n \times \text{empirical formula weight}$$

n is the number of empirical formula units in the molecule.

Multiplying the subscripts of the empirical formula by n gives the molecular formula.

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

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Determine the empirical formula and molecular formula of acetic acid using the following data.

Percentage composition of acetic acid:

C = 39.9%

H = 6.72%

O = 53.4%

Molecular weight of acetic acid = 60.0 amu

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100.0 g of acetic acid contains 39.9 g C, 6.72 g H, and 53.4 g O.

Converting into moles gives:

C = 3.33 mol

H = 6.67 mol

O = 3.34 mol

Dividing the mole numbers by the smallest one gives:

C = 1.00

H = 2.00

O = 1.00

The empirical formula of acetic acid is CH_2O.

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Empirical formula weight of CH_2O is 30.0 amu.

Calculating the molecular formula of CH_2O,

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

$$n = \frac{60.0\ \text{amu}}{30.0\ \text{amu}}$$

$$= 2.00$$

The molecular formula of acetic acid is $(CH_2O)_2$ or $C_2H_4O_2$

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Stoichiometry

The calculation of the quantities of reactants and products involved in a chemical reaction.

Interpreting a Chemical Equation

A chemical equation may be interpreted in terms of either:

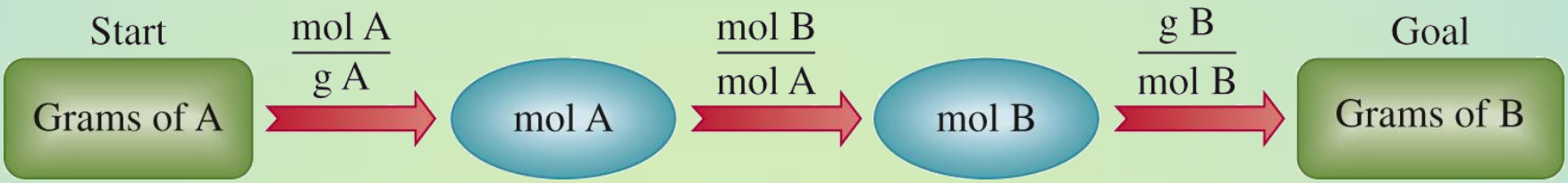
(1) Numbers of molecules (or ions or formula units)

or

(2) Numbers of moles

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Steps in a stoichiometric calculation



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Consider the following reaction and determine the grams of iron that can be produced from 1.00 kg of Fe_2O_3.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

Calculating the amount of Fe_2O_3 required to produce 1.00 kg of iron,

$$1.00 \times 10^3 \text{ g } Fe_2O_3 \times \frac{1 \text{ mol } Fe_2O_3}{160 \text{ g } Fe_2O_3} \times \frac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3} \times \frac{55.8 \text{ g Fe}}{1 \text{ mol Fe}} = 698 \text{ g Fe}$$

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Determine the grams of HCl that react with 5.00 g of manganese dioxide according to the following reaction.

$$4HCl(aq) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

$$5.00\,\text{g}\,MnO_2 \times \frac{1\,\text{mol}\,MnO_2}{86.9\,\text{g}\,MnO_2} \times \frac{4\,\text{mol}\,HCl}{1\,\text{mol}\,MnO_2} \times \frac{36.5\,\text{g}\,HCl}{1\,\text{mol}\,HCl} = 8.40\,\text{g}\,HCl$$

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Limiting Reactant

The reactant that is entirely consumed when a reaction goes to completion.

Once one reactant has been completely consumed, the reaction stops.

The moles of product are always determined by the starting moles of the limiting reactant.

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Steps to solving a limiting-reactant problem

1. Identify the limiting reactant.
2. Calculate the amount of product from the amount of the limiting reactant.

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Consider the following reaction between zinc and hydrochloric acid.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl(aq) + H_2(g)$$

Determine the moles of H_2 produced between 0.30 mol of zinc and 0.52 mol of HCl.

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Identifying the limiting reactant,

$$0.30\ \text{mol Zn} \times \frac{1\ \text{mol H}_2}{1\ \text{mol Zn}} = 0.30\ \text{mol H}_2$$

$$0.52\ \text{mol HCl} \times \frac{1\ \text{mol H}_2}{1\ \text{mol HCl}} = 0.26\ \text{mol H}_2$$

Zinc is the excess reactant.
Hydrochloric acid must be the limiting reactant.

Since Zinc is the limiting reactant, the amount of H_2 produced must be 0.26 mol

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Consider the following reaction:

$$2CH_3CHO(l) + O_2(g) \longrightarrow 2HC_2H_3O_2(l)$$

Determine:

1. The grams of acetic acid that can be produced in a reaction between 20.0 g of CH_3CHO and 10.0 g of O_2.
2. The remainder of excess reactant after the reaction is complete.

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Identify the limiting reactant using the following data:
Molar mass of acetaldehyde = 44.1 g/mol
Molar mass of oxygen = 32.0 g/mol

$$20.0\,\text{g}\,CH_3CHO \times \frac{1\,\text{mol}\,CH_3CHO}{44.1\,\text{g}\,CH_3CHO} \times \frac{2\,\text{mol}\,HC_2H_3O_2}{2\,\text{mol}\,CH_3CHO} = 0.454\,HC_2H_3O_2$$

$$10.0\,\text{g}\,O_2 \times \frac{1\,\text{mol}\,O_2}{32.0\,\text{g}\,O_2} \times \frac{2\,\text{mol}\,HC_2H_3O_2}{1\,\text{mol}\,O_2} = 0.625\,\text{mol}\,HC_2H_3O_2$$

CH_3CHO is the limiting reactant
Amount of $HC_2H_3O_2$ produced = 0.454 mol

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Converting mol to grams,

$$0.454\ \text{mol}\ HC_2H_3O_2 \times \frac{60.1\ \text{g}\ HC_2H_3O_2}{1\ \text{mol}\ HC_2H_3O_2} = 27.3\ \text{g}\ HC_2H_3O_2$$

Determining the amount of excess reactant,

$$0.454\ \text{mol}\ HC_2H_3O_2 \times \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ HC_2H_3O_2} \times \frac{32.0\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 7.26\ \text{g}\ O_2$$

Initial amount of O_2 was 10.0 g; the remaining quantity is:

$$(10.0 - 7.26)\ \text{g}\ O_2 = \boxed{2.7\ \text{g}\ O_2}$$

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Theoretical Yield

The maximum amount of product that can be obtained by a reaction from given amounts of reactants.

This is a *calculated* amount.

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Actual Yield

The amount of product that is actually obtained.

This is a *measured* amount.

Percentage Yield

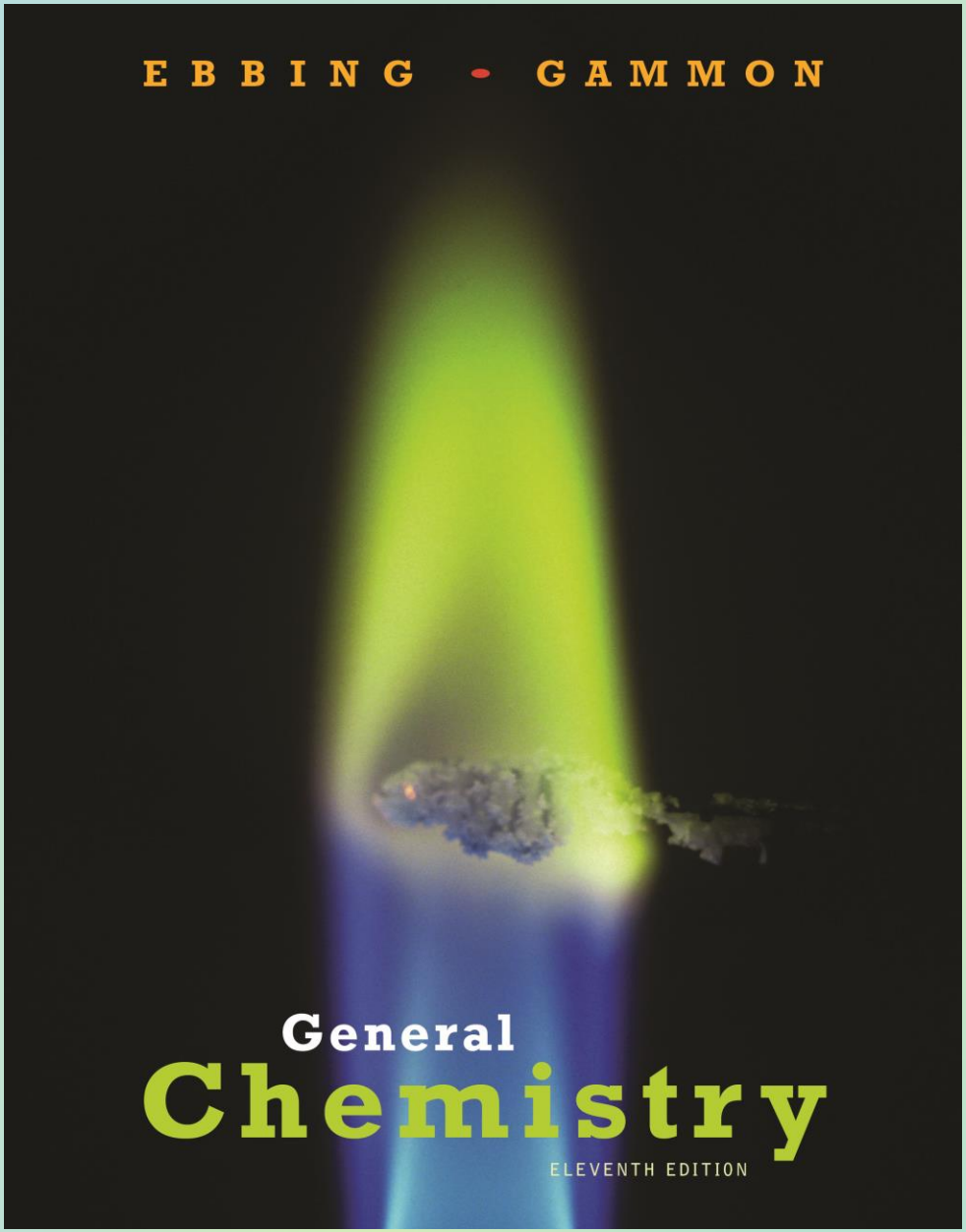
$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

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Examples

- From your textbook

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Chapter 4 Chemical Reactions

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Ionic theory of solutions

Arrhenious proposed the ionic theory of solutions to account for the electrical conductivity of water.

The theory proposed that certain substances produce freely moving ions when they dissolve in water, and these ions conduct electric current in an aqueous solution.

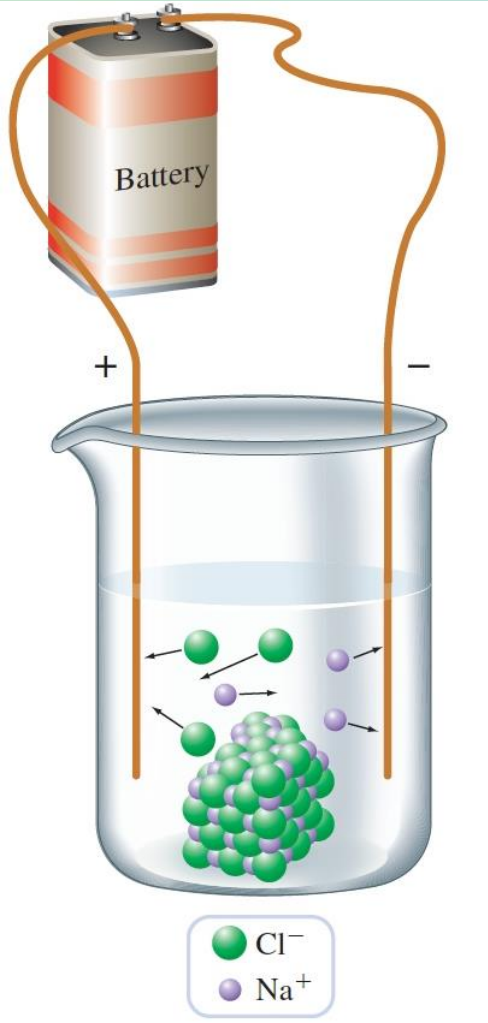
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Electrolyte

It dissolves in water to give an electrically conducting solution.

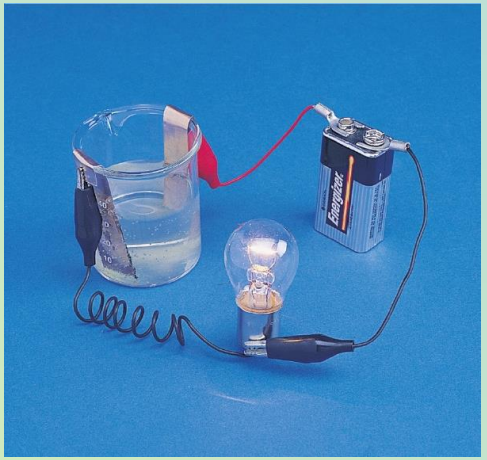
Most ionic solids dissolve in water. Ions in previously fixed states are free to move about, forming an electric current.

A nonelectrolyte dissolves in water, producing a poorly conducted solution.



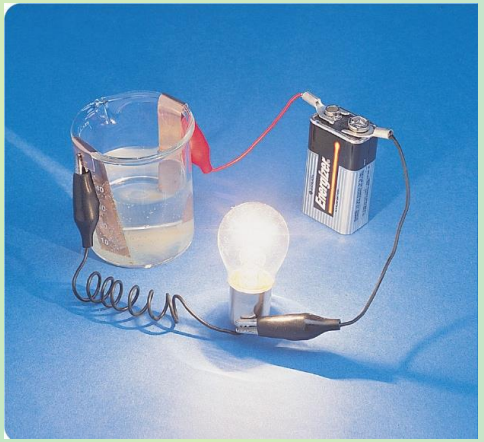
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Solutions that are poor conductors have less or no ions.



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Solutions with good conductivity have plenty of ions.



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A **strong electrolyte** exists in solution almost entirely as ions. This includes almost all soluble ionic substances.

A **weak electrolyte** dissolves in water, yielding a relatively small percentage of ions. Most molecular substances are weak electrolytes.

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Table 4.1 Solubility Rules for Ionic Compounds

Rule	Applies to	Statement	Exceptions
1	Li^+, Na^+, K^+, NH_4^+	Group 1A and ammonium compounds are soluble.	—
2	$C_2H_3O_2^-$, NO_3^-	Acetates and nitrates are soluble.	—
3	Cl^-, Br^-, I^-	Most chlorides, bromides, and iodides are soluble.	AgCl, Hg_2Cl_2, $PbCl_2$, AgBr, $HgBr_2$, Hg_2Br_2, $PbBr_2$, AgI, HgI_2, Hg_2I_2, PbI_2
4	SO_4^{2-}	Most sulfates are soluble.	$CaSO_4$, $SrSO_4$, $BaSO_4$, Ag_2SO_4, Hg_2SO_4, $PbSO_4$
5	CO_3^{2-}	Most carbonates are insoluble.	Group 1A carbonates, $(NH_4)_2CO_3$
6	PO_4^{3-}	Most phosphates are insoluble.	Group 1A phosphates, $(NH_4)_3PO_4$
7	S^{2-}	Most sulfides are insoluble.	Group 1A sulfides, $(NH_4)_2S$
8	OH^-	Most hydroxides are insoluble.	Group 1A hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

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Determine whether the following compounds are soluble or insoluble in water.

a. Hg_2Cl_2

b. KI

a. Hg_2Cl_2 is an exception to Rule 3 of the solubility rules. Therefore, it is not soluble in water.
b. According to Rules 1 and 3, most iodides are soluble. Therefore, it is soluble in water.

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Molecular Equations

They are chemical equations in which the reactants and products are written as if they were molecular substances, even though they may actually exist in solution as ions.

For example

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaOH(aq)$$

It indicates the states of the reactants and products.

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Ionic equations

In a **complete ionic equation**, strong electrolytes are written as separate ions in the solution. Other reactants and products are written in molecular form.

State symbols are included.

Consider the reactants:

$$Ca^{2+}(aq) + 2OH^{-}(aq) + 2Na^{+}(aq) + CO_3^{2-}(aq) \longrightarrow$$

With the products, the ionic form is:

$$Ca^{2+}(aq) + 2OH^{-}(aq) + 2Na^{+}(aq) + CO_3^{2-}(aq) \longrightarrow$$

$$CaCO_3(s) + 2Na^{+}(aq) + 2OH^{-}(aq)$$

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Net Ionic equation

It is an ionic equation from which spectator ions have been omitted.

For example:

$$Ca^{2+}(aq) + 2OH^{-}(aq) + 2Na^{+}(aq) + CO_3^{2-}(aq) \longrightarrow$$
$$CaCO_3(s) + 2Na^{+}(aq) + 2OH^{-}(aq)$$

– The resulting equation is

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

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Write a net ionic equation for the following molecular equation:

$2HClO_4(aq) + Ca(OH)_2(aq) \rightarrow$

Ionic equation $Ca(ClO_4)_2(aq) + 2H_2O(l)$

$2H^+(aq) + 2ClO_4^-(aq) + Ca^{2+}(aq) + 2OH^-(aq) \longrightarrow$

$Ca^{2+}(aq) + 2ClO_4^-(aq) + 2H_2O(l)$

Net ionic equation

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

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Precipitation reactions

A solid ionic substance forms from the mixture of two solutions of ionic substances.

Acid–base reactions

They are the reactions that involve the transfer of a proton between reactants.

Oxidation–reduction reactions

They are the reactions that involve the transfer of electrons between reactants.

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Precipitation Reactions

They occur in aqueous solution.

A **precipitate** is an insoluble solid compound formed during a chemical reaction in solution.

A precipitation reaction, when written as a molecular reaction, has the form of **an exchange reaction**.

An exchange reaction, when written as a molecular equation, appears to involve the exchange of parts between the two reactants.

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Predicting Precipitation Reactions

1. Predict the products (exchange of parts).
2. Determine the state of each product: (*s*), (*l*), (*g*), and (*aq*).
3. If all products are aqueous (*aq*), no net reaction will occur.

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Determine if a precipitation reaction occurs between aqueous solutions of ammonium sulfate and sodium hydroxide. If yes, write the balanced molecular equation and the net ionic equation.

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Balanced equation

$$Al_2(SO_4)_3(aq) + 6NaOH(aq) \longrightarrow 2Al(OH)_3(s) + 3Na_2SO_4(aq)$$

Ionic equation

$$2Al^{3+}(aq) + \cancel{3SO_4^{2-}(aq)} + \cancel{6Na^+(aq)} + 6OH^-(aq) \longrightarrow 2Al(OH)_3(s) + \cancel{6Na^+(aq)} + \cancel{3SO_4^{2-}(aq)}$$

Net ionic equation

$$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$$

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Determining whether a solution is an acid or a base

Acid solutions have a sour taste.

Basic solutions are bitter to taste and soapy to touch.

A dye is used to distinguish between acid and base by the different color changes it undergoes in these solutions.



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An **acid** produces hydrogen ions when dissolved in water.

$$HNO_3(aq) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

A **base** produces hydroxide ions when dissolved in water.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

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Definitions of acid and base according to Brønsted and Lowry

An acid is the species (molecule or ion) that donates a proton to another species in a proton−transfer reaction.

A base is the species (molecule or ion) that accepts a proton from another species in a proton−transfer reaction.

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Strong Acid

It ionizes completely in water.

Examples - Hydrochloric acid and nitric acid

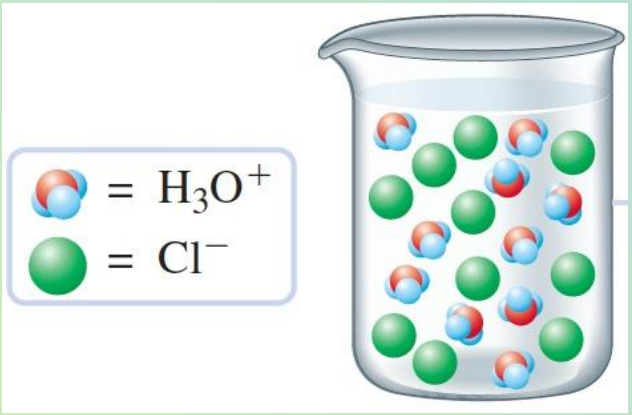
Weak Acid

It partly ionizes in water.

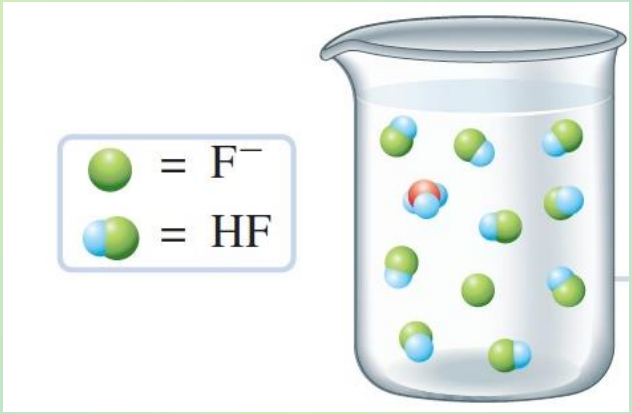
Examples - Hydrocyanic acid and hydrofluoric acid

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In Figure A, a solution of HCl (a strong acid) illustrated on a molecular/ionic level shows the acid in its ionic form.



In Figure B, a solution of HF (a weak acid), also illustrated on a molecular/ionic level, shows mostly molecules with very few ions.



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Strong Base

It is present in an aqueous solution entirely as ions, one of which is OH^-. It is a strong electrolyte, including groups 1A and 2A elements and excluding beryllium hydroxide.

Weak Base

It undergoes partial ionization. It is a weak electrolyte.

Example - Ammonia

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Identify each of the following as a strong acid or a weak base:

a. LiOH
b. $HC_2H_3O_2$
c. HBr
d. HNO_2

a. LiOH is a strong base.
b. $HC_2H_3O_2$ is a weak acid.
c. HBr is a strong acid.
d. HNO_2 is a weak acid.

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Neutralization Reaction

A reaction of an acid and a base that results in an ionic compound and possibly water.

The ionic compound that is a product of a neutralization reaction is called a **salt**.

$$2HCl(aq) + Ca(OH)_2(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

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Write the molecular and net ionic equations for the neutralization of $HNO_2(aq)$ by $NaOH(aq)$.

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Molecular Equation

(Balance the reaction and include state symbols)

$$HNO_2(aq) + NaOH(aq) \longrightarrow NaNO_2(aq) + H_2O(l)$$

Complete Ionic Equation

$$HNO_2(aq) + \cancel{Na^+(aq)} + OH^-(aq) \longrightarrow \cancel{Na^+(aq)} + NO_2^-(aq) + H_2O(l)$$

Net Ionic Equation

$$HNO_2(aq) + OH^-(aq) \longrightarrow NO_2^-(aq) + H_2O(l)$$

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Polyprotic Acid

It is an acid that results in two or more acidic hydrogens per molecule.

For example:

Carbonate Acid

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Salt

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Acid–base reactions with gas formation

Sulfides, carbonates, and sulfites react with acid to form a gas.

$$\underset{\text{Carbonate}}{Na_2CO_3}(aq) + \underset{\text{Acid}}{2HCl}(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Salt

Interchanging the carbonate ion with the chloride ion gives the following equation:

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2CO_3(aq)$$

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Write the molecular, ionic, and net ionic equations for the reaction of zinc sulfide with hydrochloric acid.

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Molecular Equation

(Balance the reaction and include state symbols.)

$$ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$$

Ionic Equation

$$ZnS(s) + 2H^+(aq) + \cancel{2Cl^-(aq)} \longrightarrow Zn^{2+}(aq) + \cancel{2Cl^-(aq)} + H_2S(g)$$

Net Ionic Equation

$$ZnS(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2S(g)$$

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Oxidation Number

This is the actual charge of the atom if it exists as a monoatomic atom, or a hypothetical charge assigned to the atom in the substance using simple rules.

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Rules for Assigning Oxidation Numbers

1. Elements - The oxidation number of an atom in an element is zero.
2. Monoatomic ions - The oxidation number of an atom in a monatomic ion equals the charge on the ion.
3. Oxygen - The oxidation number of oxygen is −2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is −1.)
4. Hydrogen - The oxidation number of hydrogen is +1 in most of its compounds. (The oxidation number of hydrogen is −1 in binary compounds with a metal such as CaH_2.)

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5. Halogens - The oxidation number of fluorine is −1. Each of the other halogens (Cl, Br, I) has an oxidation number of −1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
6. Compounds and ions - The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

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Obtain the oxidation number of the chlorine atom in ClO_3^-.

Using Rule 6:

(Oxidation number of Cl) +3 × (oxidation number of O) = –1

Using rule 3:

(Oxidation number of Cl) +3 × (–2) = –1

Oxidation number of Cl (in ClO_3^-) = –1 –3 × (–2) = +5

In ClO_3^-, the oxidation number of Cl is 5.

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Half-reaction

It is one of two parts of an oxidation–reduction reaction, one part of which involves a loss of electrons (or increase in oxidation number) and the other part of which involves a gain of electrons (or decrease in oxidation number).

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Oxidation

It is the half-reaction in which there is a loss of electrons by a species (or an increase of oxidation number).

Reduction

It is the half-reaction in which there is a gain of electrons by a species (or a decrease of oxidation number).

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Oxidizing Agent

It is a species that oxidizes another species; it is itself reduced.

Reducing Agent

It is a species that reduces another species; it is itself oxidized.

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Common Oxidation–Reduction Reactions

- Combination reaction
- Decomposition reaction
- Displacement reaction
- Combustion reaction

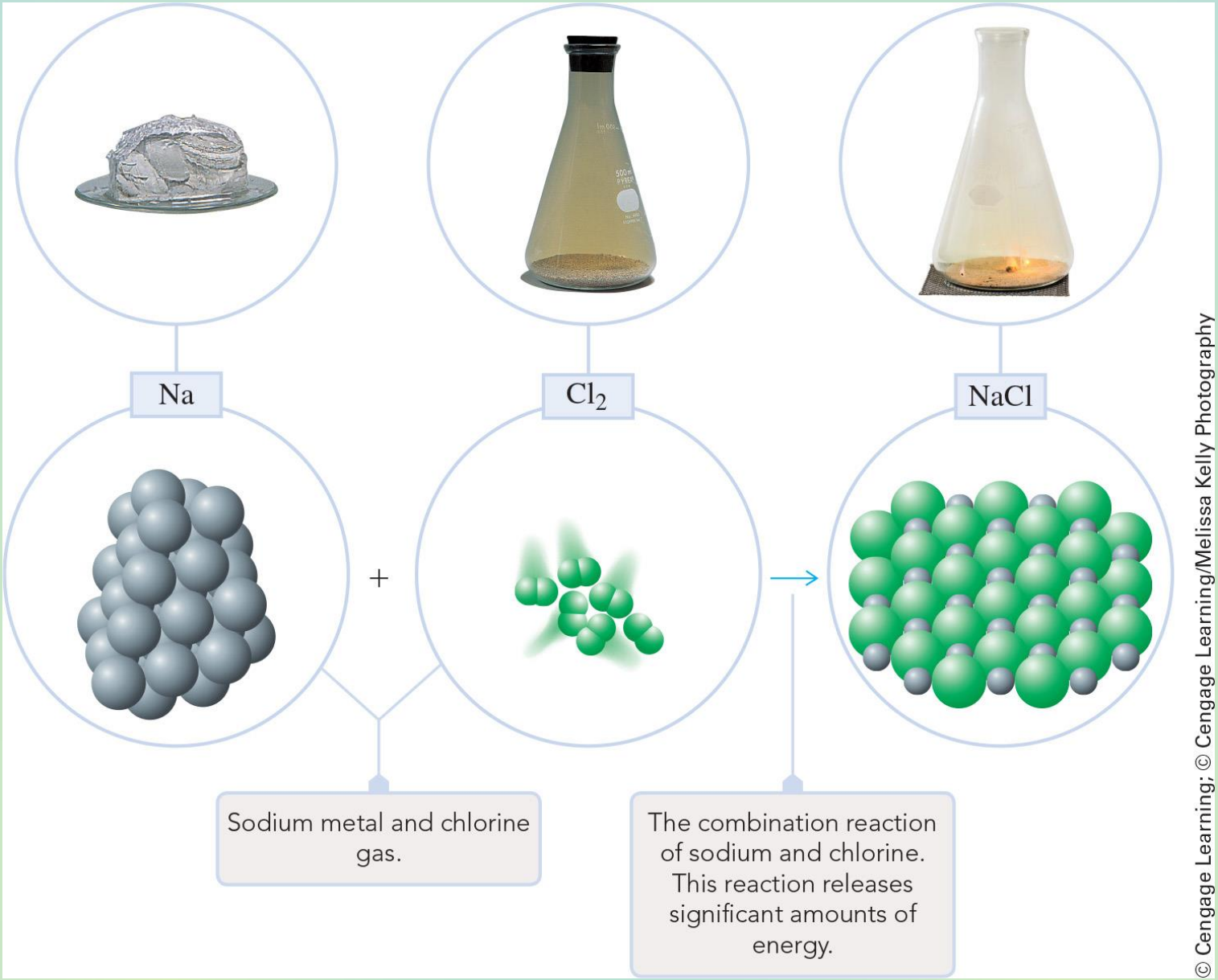
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Combination Reaction

A reaction in which two substances combine to form a third substance.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

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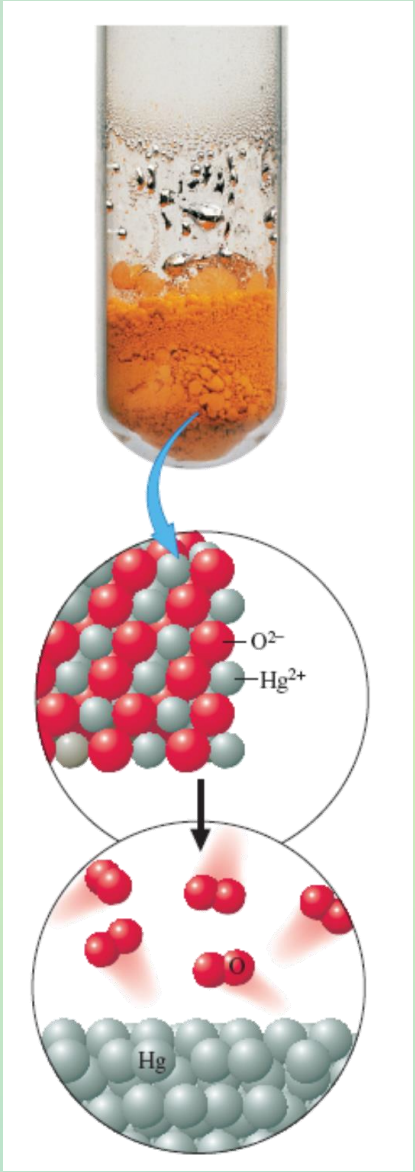
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Decomposition Reaction

It is a reaction in which a single compound reacts to give two or more substances.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

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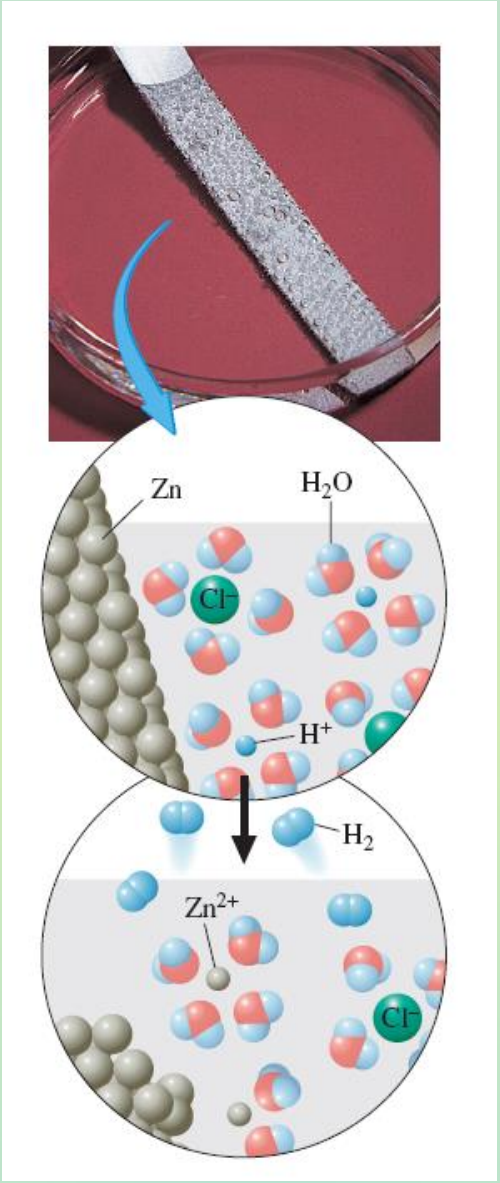
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Displacement Reaction

It is a reaction in which an element reacts with a compound, displacing another element from it.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

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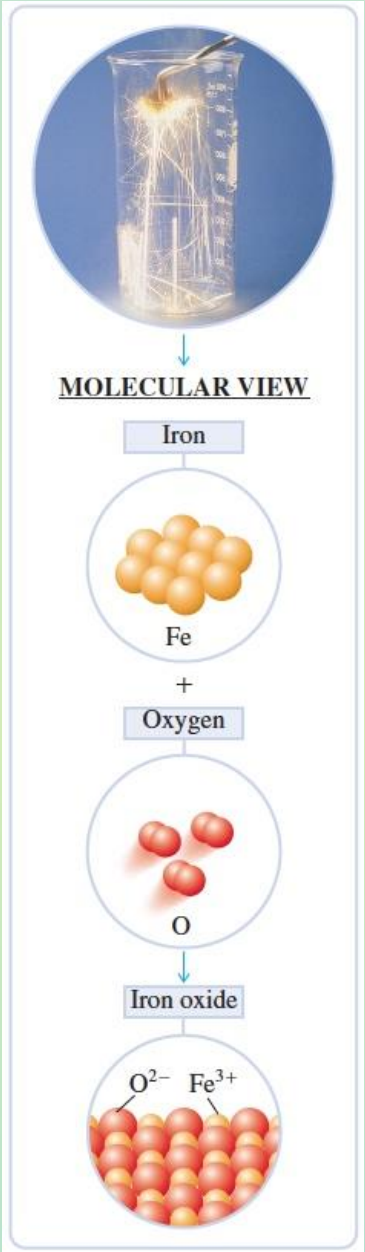
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Combustion Reaction

It is a reaction in which a substance reacts with oxygen, usually with the rapid release of heat to produce a flame.

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O\ (g)$$

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Balancing Simple Oxidation–Reduction Reactions: Half-Reaction Method

First, identify what is oxidized and what is reduced by determining the oxidation numbers.

Balance each half-reaction and combine them to obtain a balanced oxidation reaction.

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For the reaction

$$\underset{0}{Zn}(s) + \underset{+1}{Ag^{+}}(aq) \longrightarrow \underset{+2}{Zn^{2+}}(aq) + \underset{0}{Ag}(s)$$

Zn is oxidized, resulting in Zn^{2}.

Ag^{+} is reduced, resulting in Ag.

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Next, balance the charge in each half-reaction by adding electrons to the more positive side.

$$Zn \longrightarrow Zn^{2+}(aq) + 2e^{-} \quad \text{(oxidation half-reaction)}$$

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag \quad \text{(reduction half-reaction)}$$

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Zinc loses more electrons during oxidation than silver gains during reduction. Since Ag can gain only one electron, the amount of Ag must be doubled for it to accept all the electrons produced by Zn during oxidation. This can be accomplished by multiplying each half-reaction by a factor.

$$1 \times (Zn \longrightarrow Zn^{2+} + 2e^{-})$$
$$2 \times (Ag^{+} + e^{-} \longrightarrow Ag)$$

The electrons cancel, resulting in the balanced oxidation reaction

$$Zn(s) + 2Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

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Use the half-reaction method and balance the following reaction:

$$Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Identifying the oxidation states of the elements

$$\overset{0}{Mg}(s) + \overset{0}{N2}(g) \longrightarrow \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$$

Balancing oxidation and reduction reactions

$$Mg \longrightarrow Mg^{2+} + 2e^- \text{ (balanced oxidation half-reaction)}$$

$$N_2 + 6e^- \longrightarrow 2N^{3-} \text{ (balanced oxidation half-reaction)}$$

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Multiplying each half-reaction by a factor that will cancel the electrons:

$$3 \times (Mg \longrightarrow Mg^{2+}(aq) + 2e^-)$$
$$1 \times (N_2 + 6e^- \longrightarrow 2N^{3-})$$

This gives:

$$3Mg + N_2 + \cancel{6e^-} \longrightarrow 3Mg^{2+} + 2N^{3-} + \cancel{6e^-}$$

Therefore, the balanced combination (oxidation-reduction) reaction is:

$$3Mg + N_2 \longrightarrow 3Mg^{2+} + 2N^{3-}$$

This can also be written:

$$3Mg\,(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

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Molar Concentration, Molarity, (*M*)

Moles of solute per liter of solution

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

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To prepare a solution, add the measured amount of solute to a volumetric flask and then add water to bring the solution to the mark on the flask.



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Diluting Solutions

Attaining a solution with specific aqueous content requires diluting it with a predetermined amount of water. This requires knowledge of the relationship between the molarity of the solution before dilution, and that after dilution.

It is known that:

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

This can be rearranged to give

$$\text{moles of solute} = \text{molarity} \times \text{liters of solution}$$

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This can be rearranged to give:

$$\text{Moles of solute} = M_i \times V_i$$

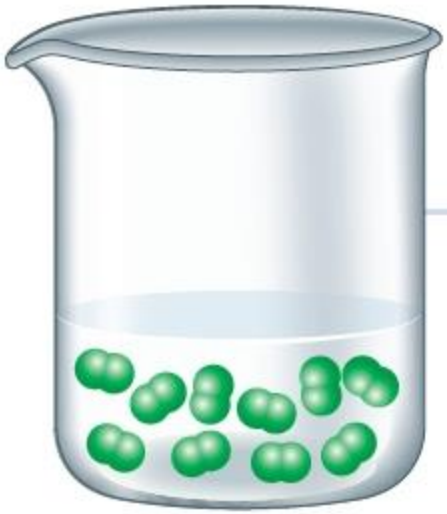
Upon dilution, the concentration and volume changes.

$$\text{Moles of solute} = M_f \times V_f$$

As the moles of solute have not changed during the dilution, it can be observed that:

$$M_i \times V_i = M_f \times V_f$$

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A molecular view of a solution of Cl_2 dissolved in water.

Add more water (solvent)



The solution after performing a dilution by adding water. Note how the number of moles of Cl_2 in the container does not change when performing the dilution; only the concentration changes. In this particular case, the concentration of Cl_2 drops to half of the starting concentration because the volume was doubled.

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The photo on the right shows a volumetric flask used in dilution.



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Determine the milliliters of a solution of 14.8 *M* NH_3 required to produce 100 mL of NH_3 with a molarity of 1.00 *M.*

The initial volume can be determined by rearranging the dilution formula.

$$M_i V_i = M_f V_f$$

$$V_i = \frac{M_f V_f}{M_i}$$

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Substituting the known values:

$$V_i = \frac{1.00\ \cancel{M} \times 100.0\ \text{mL}}{14.8\ \cancel{M}} = \boxed{6.76\ \text{mL}}$$

Two concepts that can help verify the result:

1. The volume of the more concentrated solution should always be less than the volume of the final solution.
2. The initial concentration of a solution is greater than the final concentration after dilution.

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Quantitative Analysis

It is the determination of the amount of a substance or species present in a material.

Volumetric Analysis

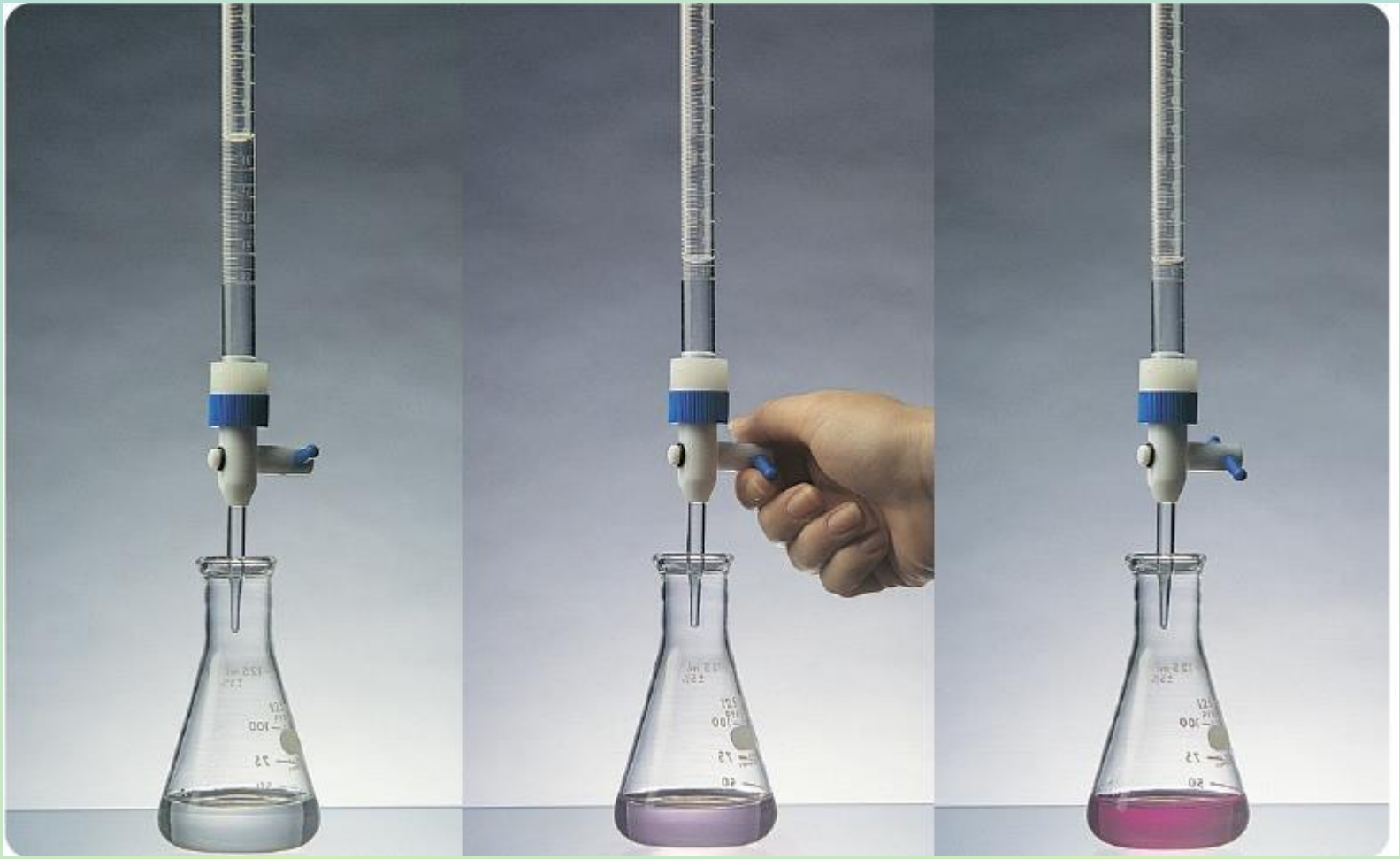
It is a type of quantitative analysis based on titration.

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Titration

It is a procedure for determining the amount of substance A by adding a carefully measured volume with a known concentration of B until the reaction of A and B is just complete.

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In the titration shown above, the indicator changes color to indicate when the reaction is just complete.

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A flask contains an unknown amount of HCl. This solution is titrated with 0.207 *M* NaOH. It takes 4.47 mL of the NaOH solution to complete the reaction. Determine the mass of HCl.

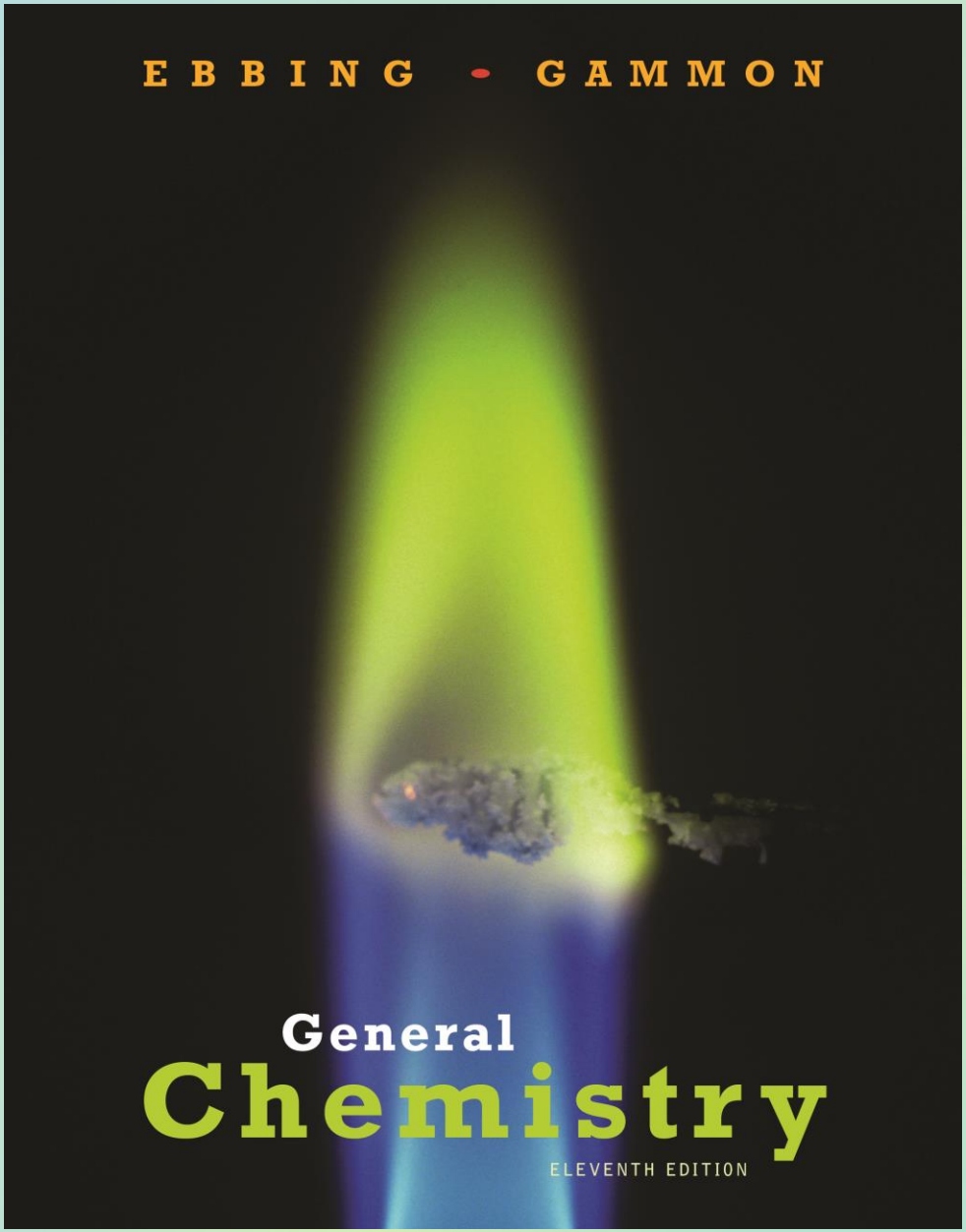
Determine the stoichiometry of the reaction by writing the balanced equation.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Determining the mass of HCl:

$$4.47 \times 10^{-3}\text{L NaOH soln} \times \frac{0.207\text{ mol NaOH}}{1\text{ L NaOH soln}} \times \frac{1\text{ mol HCl}}{1\text{ mol NaOH}} \times \frac{36.5\text{ HCl}}{1\text{ mol HCl}} = 0.0338\text{ g HCl}$$

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Chapter 5
The Gaseous State

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Ideal Gas Law

The ideal gas law is given by the equation

$$PV = nRT$$

The **molar gas constant, R**, is the constant of proportionality that relates the molar volume of a gas to *T*/*P*.

Table 5.5 Molar Gas Constant in Various Units

Value of *R*
0.082058 L·atm/(K·mol)
8.3145 J/(K·mol)*
8.3145 kg·m^2/(s^2·K·mol)
8.3145 kPa·dm^3/(K·mol)
1.9872 cal/(K·mol)*

*The units of pressure times volume are the units of energy—for example, joules (J) or calories (cal).

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Prove the following statement: the pressure of a given amount of gas at a fixed volume is proportional to the absolute temperature. This is sometimes called Amontons' law.

Using the ideal gas law:

$$PV = nRT$$

$$P = \left(\frac{nR}{V}\right)T$$

$$P = \text{constant} \times \text{T}$$

$$\boxed{P \propto T}$$

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Determine the grams of O_2 in a 50.0-L cylinder at 21° C when the O_2 pressure is 15.7 atm.

Variable	*Value*
P	15.7 atm
V	50.0 L
T	(21 + 273) K = 294 K
n	?

Solving the ideal gas law for *n*

$$n = \frac{PV}{RT}$$

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Substituting the data gives

$$n = \frac{15.7\ \text{atm} \times 50.0\ \text{L}}{0.0821\ \text{L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 294\ \text{K}} = 32.5\ \text{mol}$$

Converting moles into mass of oxygen yields

$$32.5\ \text{mol}\ O_2 \times \frac{32.0\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 1.04 \times 10^3\ \text{g}\ O_2$$

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Stoichiometry and Gas Volumes

Use the ideal gas law to find moles from a given volume, pressure, and temperature, and vice versa.

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Air bags in automobiles can be inflated with nitrogen using the rapid reaction of sodium azide, NaN_3, and iron (III) oxide, Fe_2O_3. How many grams of sodium azide would be required to provide 75.0 L of nitrogen gas at 25° C and 748 mmHg?

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The balanced equation is:

$$6NaN_3(s) + Fe_2O_3(s) \longrightarrow 3Na_2O(s) + 2Fe(s) + 9N_2(g)$$

Variable	Value
P	$748\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.984\ \text{atm}$
V	75.0 L
T	(25 + 273) K = 298 K
n	?

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Rearranging the ideal gas law to obtain *n*

$$n = \frac{PV}{RT}$$

Making substitutions from the data available

$$n = \frac{0.984 \cancel{\text{atm}} \times 75.0 \cancel{\text{L}}}{0.0821 \cancel{\text{L}} \cdot \cancel{\text{atm}}/(\cancel{\text{K}} \cdot \text{mol}) \times 298 \cancel{\text{K}}} = 3.02 \text{ mol}$$

$$3.02 \cancel{\text{mol N}_2} \times \frac{6 \text{ mol NaN}_3}{9 \cancel{\text{mol N}_2}} = 2.01 \text{ mol NaN}_3$$

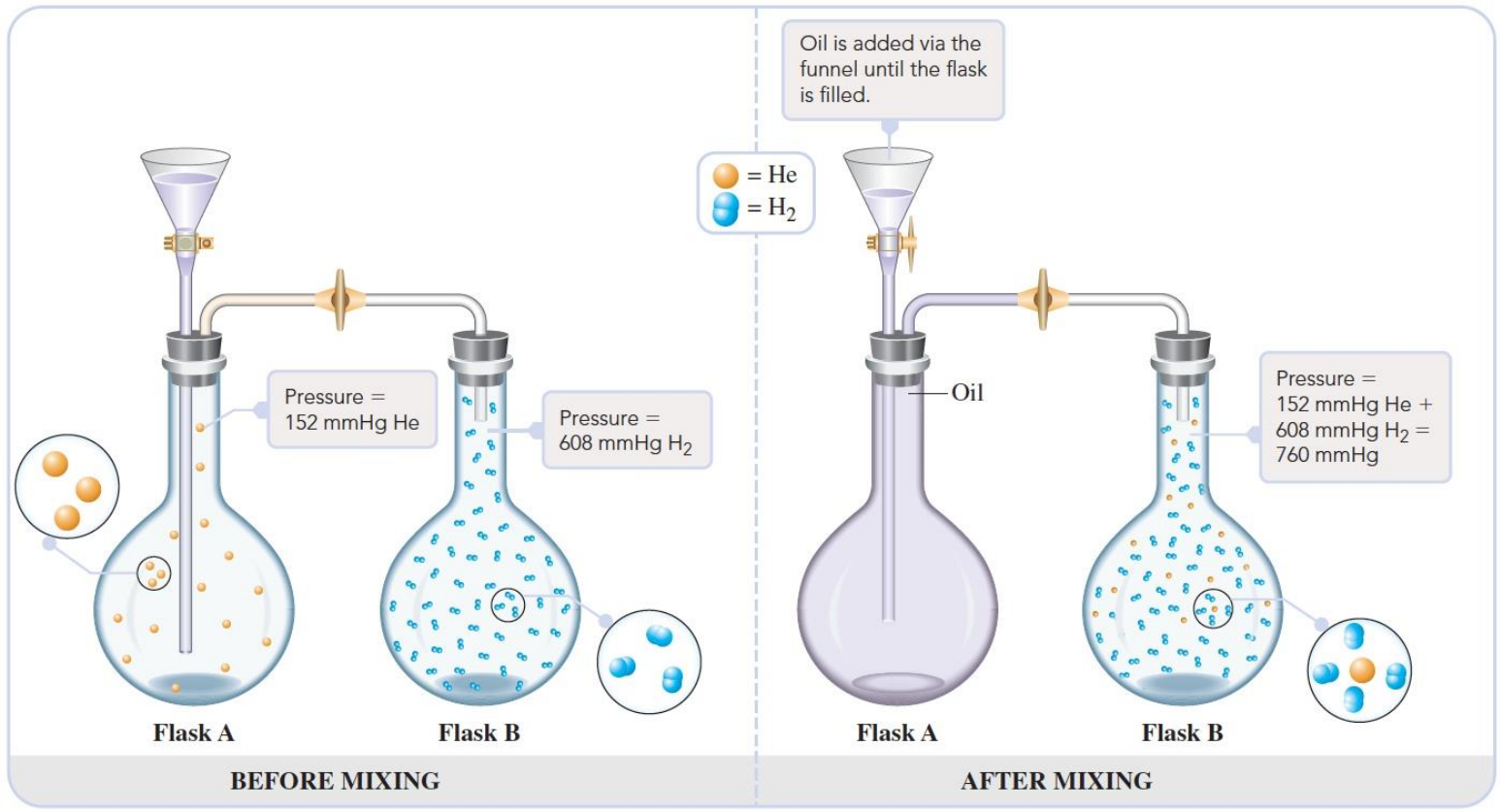
$$2.01 \cancel{\text{mol NaN}_3} \times \frac{65.01 \text{ g NaN}_3}{1 \cancel{\text{mol NaN}_3}} = \boxed{131 \text{ g NaN}_3}$$

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Gas Mixtures

Dalton found that in a mixture of unreactive gases, each gas behaves as if it were the only gas in the mixture as far as pressure is concerned.

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Originally (left), flask A contains He at 152 mmHg and flask B contains O_2 at 608 mmHg. Flask A is then filled with oil forcing the He into flask B (right). The new pressure in flask B is 760 mmHg.

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Partial Pressure

The pressure exerted by a particular gas in a mixture.

Dalton's Law of Partial Pressures

The sum of the partial pressures of all the different gases in a mixture is equal to the total pressure of the mixture:

$$P = P_A + P_B + P_C + \ldots$$

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Mole Fraction

The mole fraction of a component gas is the fraction of moles of that component in the total moles of gas mixture.

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A 1.00-L sample of dry air at 25° C and 786 mmHg contains 0.925 g N_2, plus other gases including oxygen, argon, and carbon dioxide.

Determine the partial pressure (in mmHg) of N_2 in the air sample

Determine the mole fraction and mole percent of N_2 in the mixture.

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Converting 0.925 g N_2 moles to N_2

$$0.925\ \text{g}\ \cancel{\text{N}_2} \times \frac{1\ \text{mol}\ \text{N}_2}{28.0\ \cancel{\text{g}\ \text{N}_2}} = 0.330\ \text{mol}\ \text{N}_2$$

Substituting into the ideal gas law (25° C = 298 K)

$$P_{\text{N}_2} = \frac{n_{\text{N}_2}\text{RT}}{V}$$

$$= \frac{0.0330\ \cancel{\text{mol}} \times 0.0821\ \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 298\ \cancel{\text{K}}}{1.00\ \cancel{\text{L}}}$$

$$= 0.807\ \text{atm}\ (= 613\ \text{mmHg})$$

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Determining the mole fraction of N_2 in the air

$$\text{Mole fraction of } N_2 \quad \frac{P_{N_2}}{P} = \frac{613 \cancel{\text{ mmHg}}}{786 \cancel{\text{ mmHg}}} = 0.780 = \boxed{78.0\%}$$

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A flask equipped with a valve contains 3.0 mol of H_2 gas. You introduce 3.0 mol of Ar gas into the flask via the valve and then seal the flask.

a. What happens to the pressure of just the H_2 gas in the flask after the introduction of the Ar? If it changes, by what factor does it do so?

b. How do the pressures of the Ar and the H_2 in the flask compare?

c. How does the total pressure in the flask relate to the pressures of the two gases?

a. Nothing happens to the pressure of H_2.

b. The pressures are equal because the moles are equal.

c. The total pressure is the sum of the pressures of the two gases.

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Collecting Gas Over Water

Gases are often collected over water. The result is a mixture of the gas and water vapor.

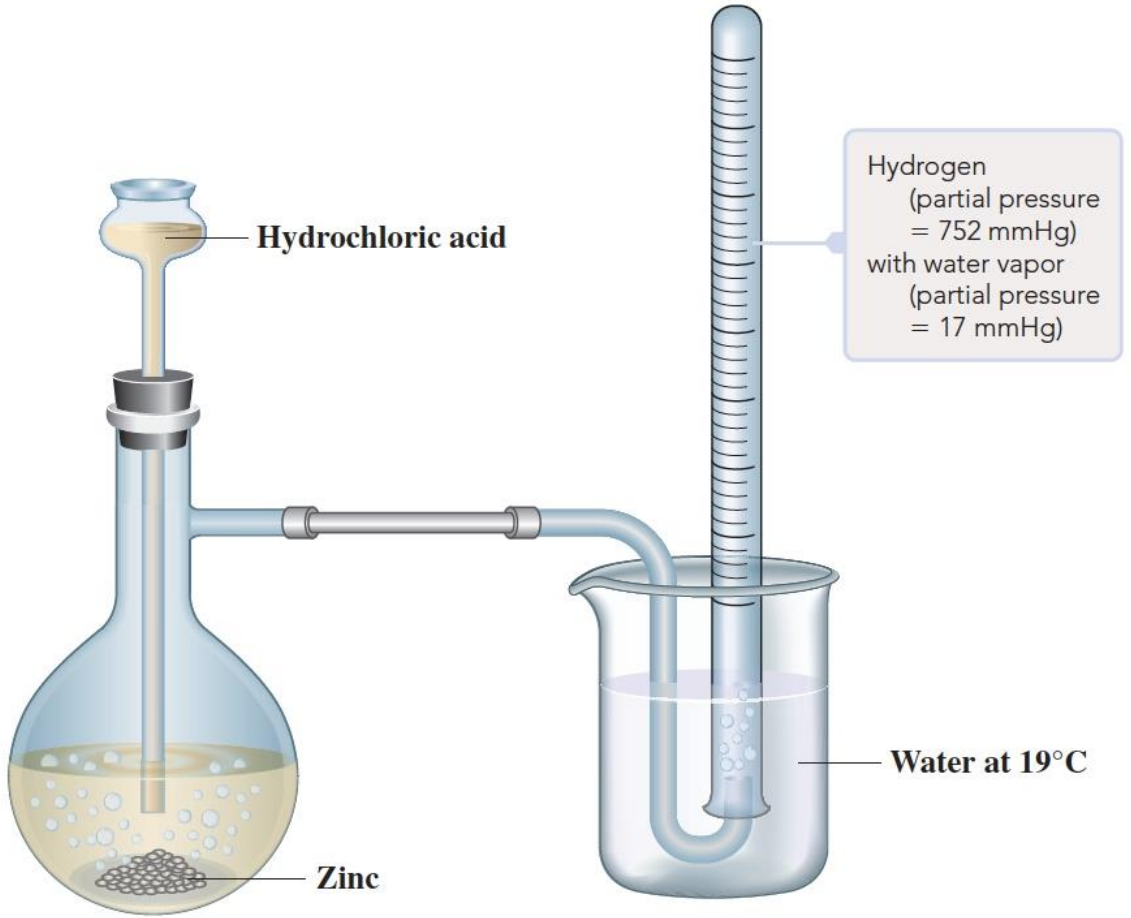
The partial pressure of water depends only on temperature.

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1. Hydrogen, prepared by the reaction of zinc with hydrochloric acid, is led to an inverted tube initially filled with water

2. When the gas-collection tube is adjusted so that the water level in the tube is at the same height as the level in the beaker, the gas pressure in the tube equals the barometric pressure (769 mmHg).

3. The total gas pressure equals the sum of the partial pressure of the hydrogen (752 mmHg) and the vapor pressure of water (17 mm Hg). For clarity, hydrochloric acid is shown in light brown and hydrogen gas in light blue.



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Table 5.6 Vapor Pressure of Water at Various Temperatures*

Temperature (°C)	Pressure (mmHg)
0	4.6
10	9.2
15	12.8
17	14.5
19	16.5
21	18.7
23	21.1
25	23.8
27	26.7
30	31.8
40	55.3
60	149.4
80	355.1
100	760.0

*Appendix B contains a more complete table.

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Hydrogen gas is produced by the reaction of HCl on zinc metal.

$$2HCl\,(aq) + Zn(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

The gas is collected over water. Determine the mass of hydrogen collected if 156 mL of gas is collected at 19° C and 769 mmHg total pressure.

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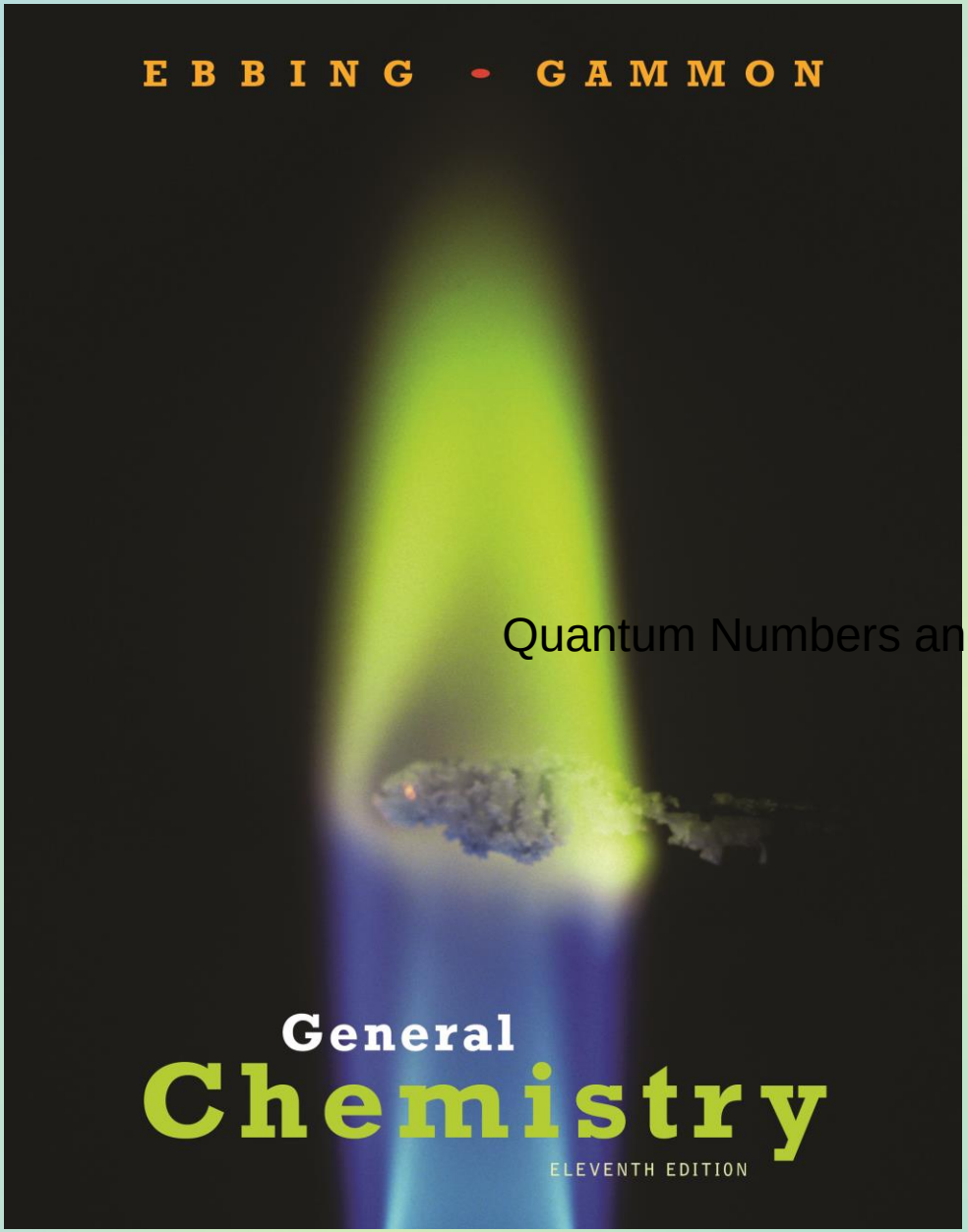
Using Dalton's law of partial pressures,

$$P = P_{H_2} + P_{H_2O}$$

$$P_{H_2} = P - P_{H_2O} = (769 - 16.5)\ \text{mmHg} = 752\ \text{mmHg}$$

Variable	Value
P	$752\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.989\ \text{atm}$
V	156 mL = 0.156 L
T	(19 + 273) K = 292 K
n	?

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Chapter 7
Quantum Theory of the Atom

Quantum Numbers and Atomic Orbitals

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7.5 Quantum Numbers and Atomic Orbitals

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According to quantum mechanics, each electron is described by four quantum numbers:

1. Principal quantum number (n)
2. Angular momentum quantum number (l)
3. Magnetic quantum number (m_l)
4. Spin quantum number (m_s)

The first three define the wave function for a particular electron. The fourth quantum number refers to the magnetic property of electrons.

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A wave function for an electron in an atom is called an atomic orbital (described by three quantum numbers—n, l, m_l).

It describes a region of space where there is high probability of finding the electron.

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Principal Quantum Number, *n*

This quantum number is the one on which the energy of an electron in an atom primarily depends. The smaller the value of *n*, the lower the energy and, in some cases, the smaller the orbital.

The principal quantum number can have any positive value: 1, 2, 3, . . .

Orbitals with the same value for *n* are said to be in the same shell.

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Shells are sometimes designated by uppercase letters:

Letter	*K*	*L*	*M*	*N*	. . .
n	1	2	3	4	

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Angular Momentum Quantum Number, *l*

This quantum number distinguishes orbitals of a given *n* (shell) having different shapes.

It can have any integer value from 0 to *n* –1.

For a given *n*, there will be *n* different values of orbitals with a distinctive shape, *l*.

Orbitals with the same values for *n* and *l* are said to be in different subshells of a certain shell.

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Subshells are sometimes designated by lowercase letters:

Letter	s	*p*	d	f	. . .
l	0	*1*	2	3	. . .

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Magnetic Quantum Number, m_l

This quantum number distinguishes orbitals of a given *n* and *l*—that is, of a given energy and shape but having different orientations.

For $l = 0$, $m_l = 0$.

For $l = 1$, $m_l = -1, 0,$ and $+1$.

Orbitals have the same shape but different orientations in space.

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Spin Quantum Number, m_s

This quantum number refers to the two possible orientations of the spin axis of an electron.

It may have a value of either $+{}^{1}/_{2}$ or $-{}^{1}/_{2}$.

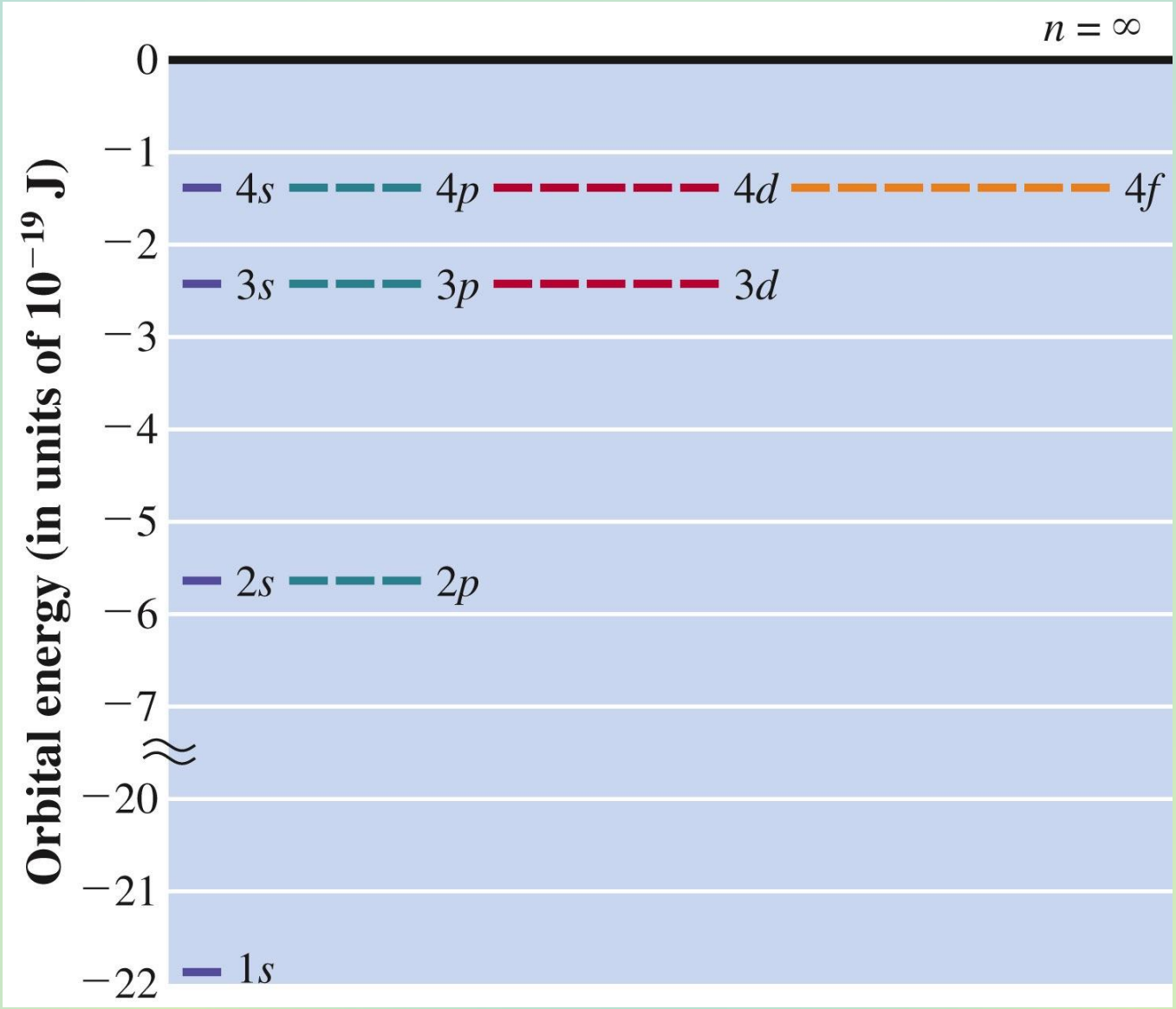
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Table 7.1 Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	−1, 0, +1	2*p*	3
3	0	0	3*s*	1
3	1	−1, 0, +1	3*p*	3
3	2	−2, −1, 0, +1, +2	3*d*	5
4	0	0	4*s*	1
4	1	−1, 0, +1	4*p*	3
4	2	−2, −1, 0, +1, +2	4*d*	5
4	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

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State whether each of the following sets of quantum numbers is permissible for an electron in an atom. If a set is not permissible, explain why.

a. $n = 1, l = 1, m_l = 0, m_s = ½$

b. $n = 2, l = 1, m_l = 0, m_s = ½$

c. $n = 3, l = 1, m_l = –2, m_s = –1/2$

d. $n = 2, l = 0, m_l = 0, m_s = 1$

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a. Not permissible

The *l* quantum number is equal to *n*. It must be lesser than *n.*

b. Not permissible

The magnitude of the m_l number must not be greater than 1.

c. Permissible

d. Not permissible

The m_s quantum number can be only +1/2 or –1/2.

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Atomic Orbital Shapes

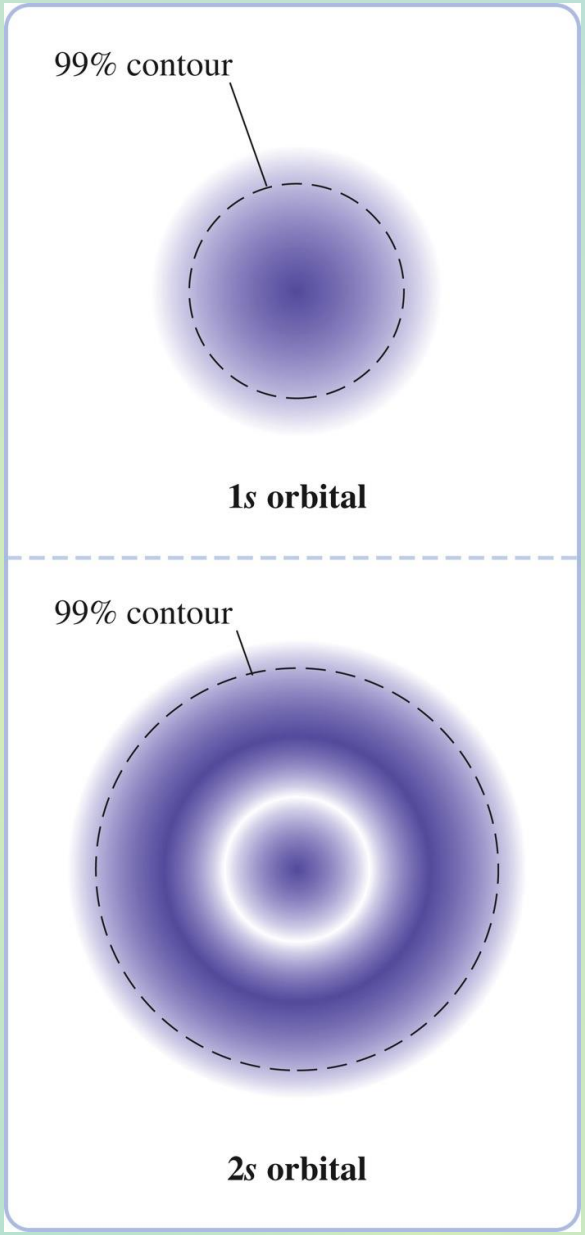
An *s* orbital is spherical.

A *p* orbital has two lobes along a straight line through the nucleus, with one lobe on either side.

A *d* orbital has a more complicated shape than an *s* or a *p* orbital.

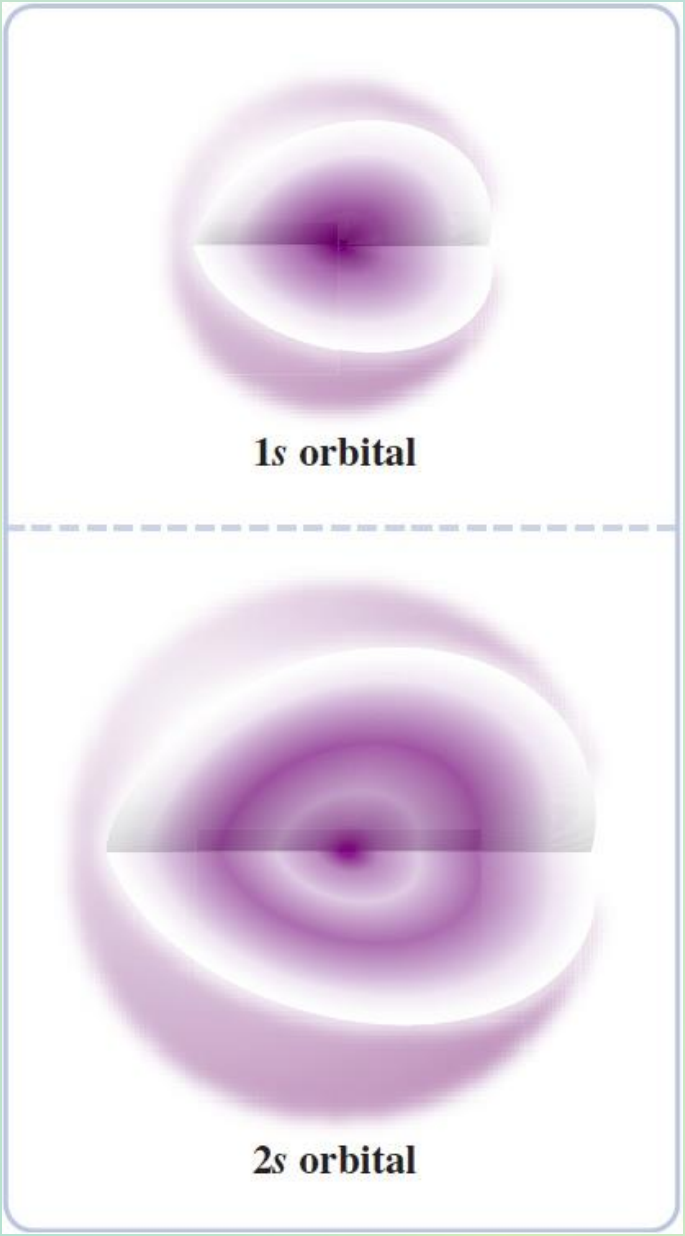
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The cross-sectional view of a 1*s* orbital and a 2*s* orbital highlights the difference in the two orbitals' sizes.



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The cutaway diagrams of the 1*s* and 2*s* orbitals give a better sense of the distribution of the distribution of electrons.



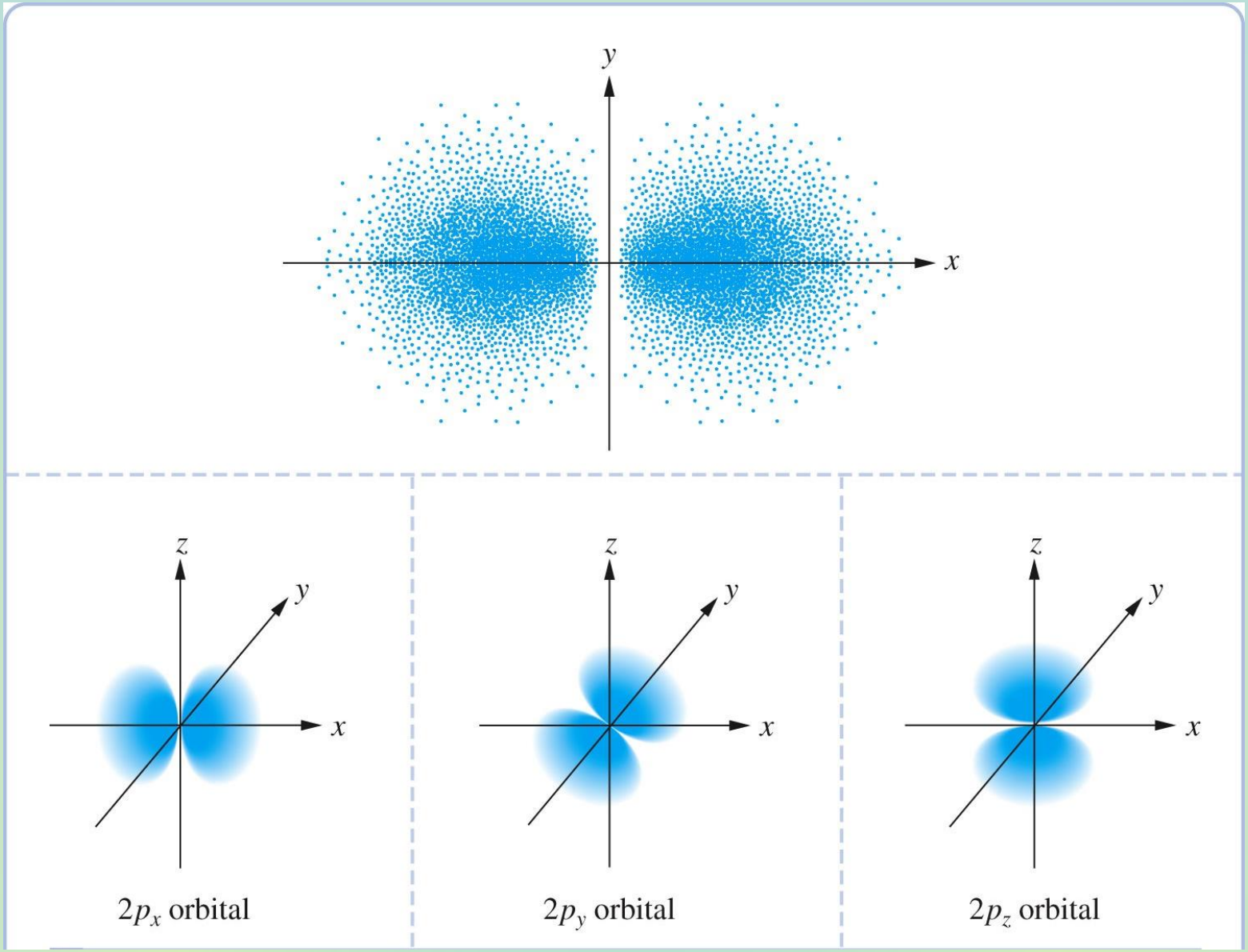
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The next slide illustrates *p* orbitals.

Figure A shows the general shape of a *p* orbital.

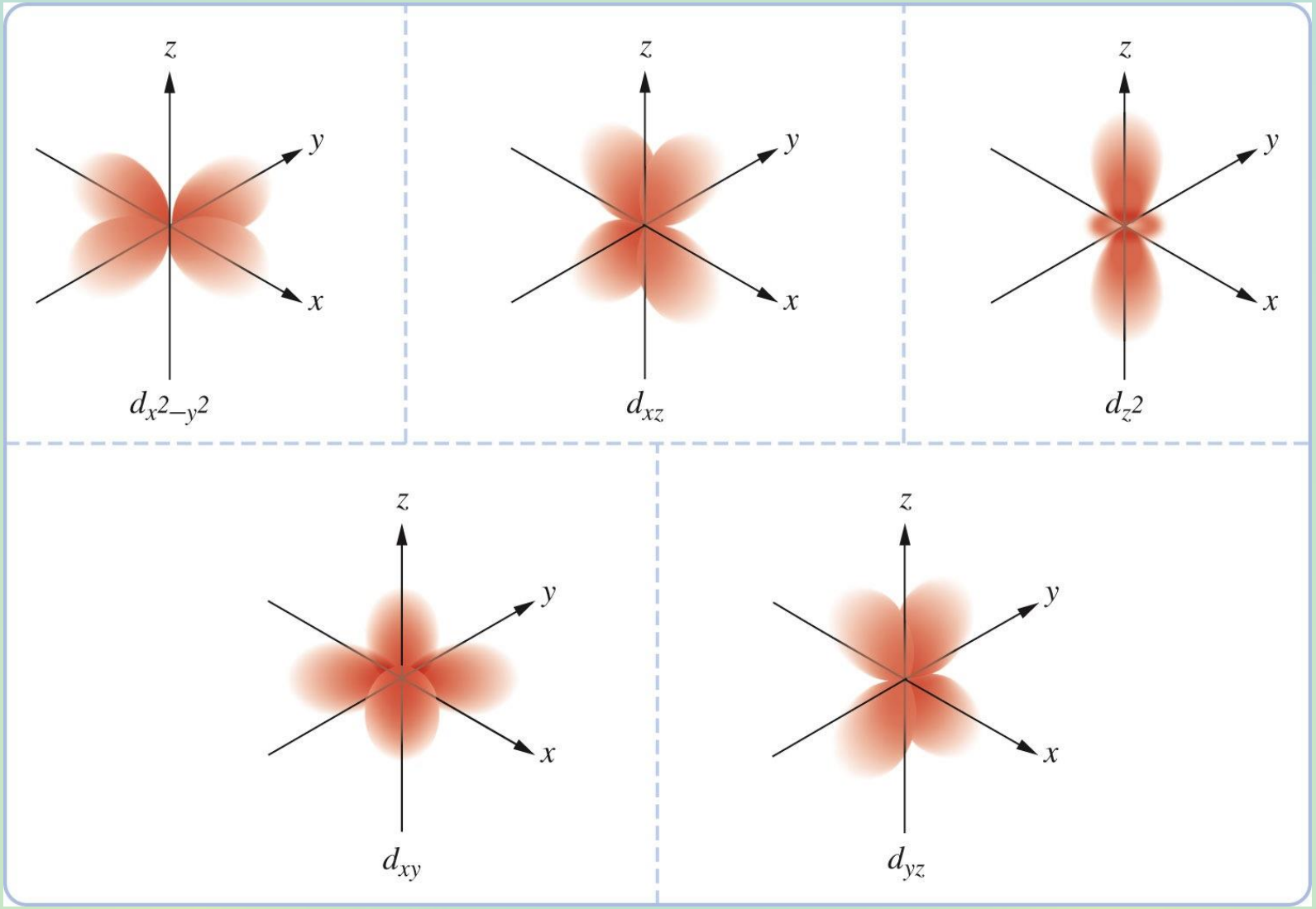
Figure B shows the orientations of each of the three *p* orbitals.

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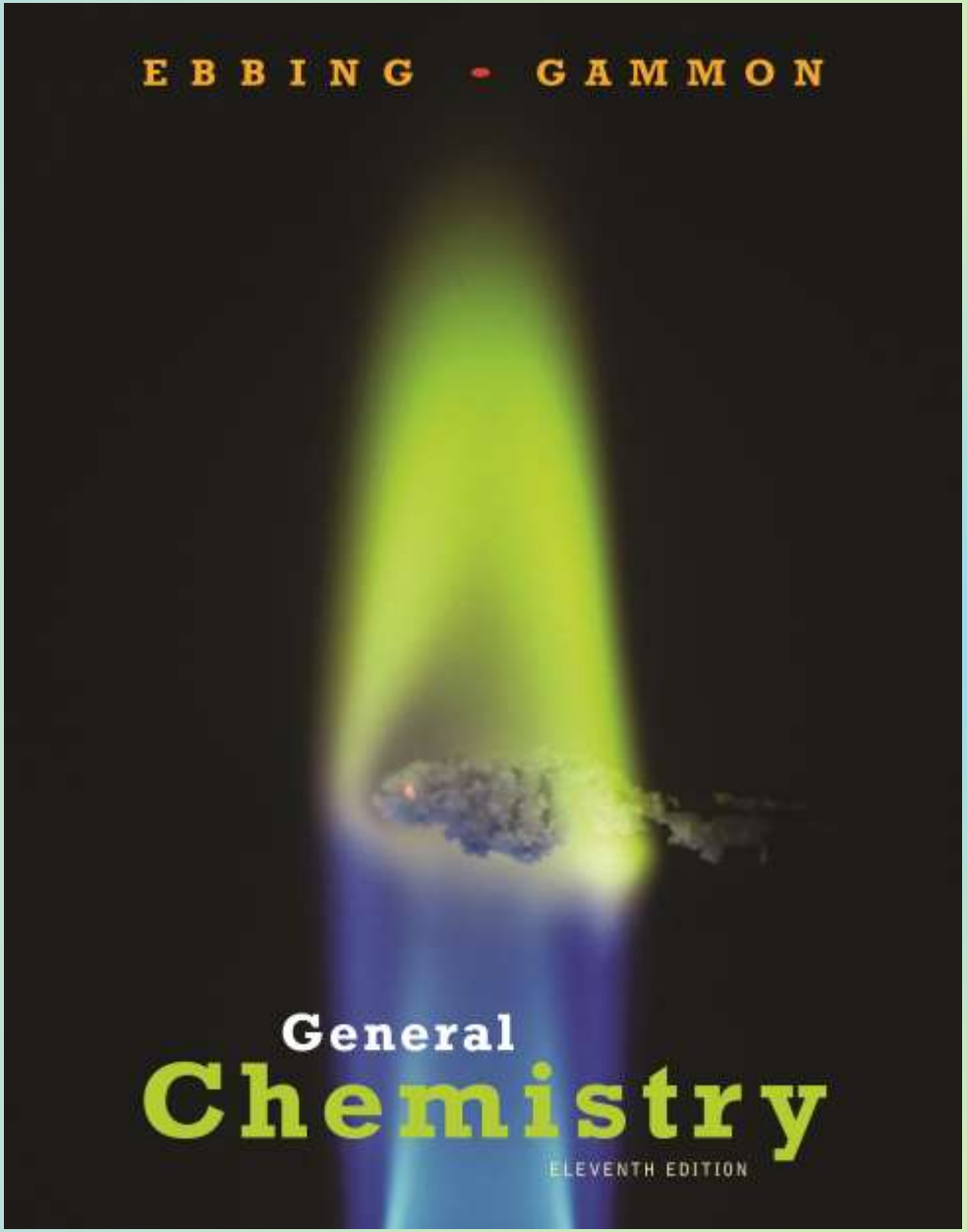


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The complexity of the *d* orbitals can be seen below:



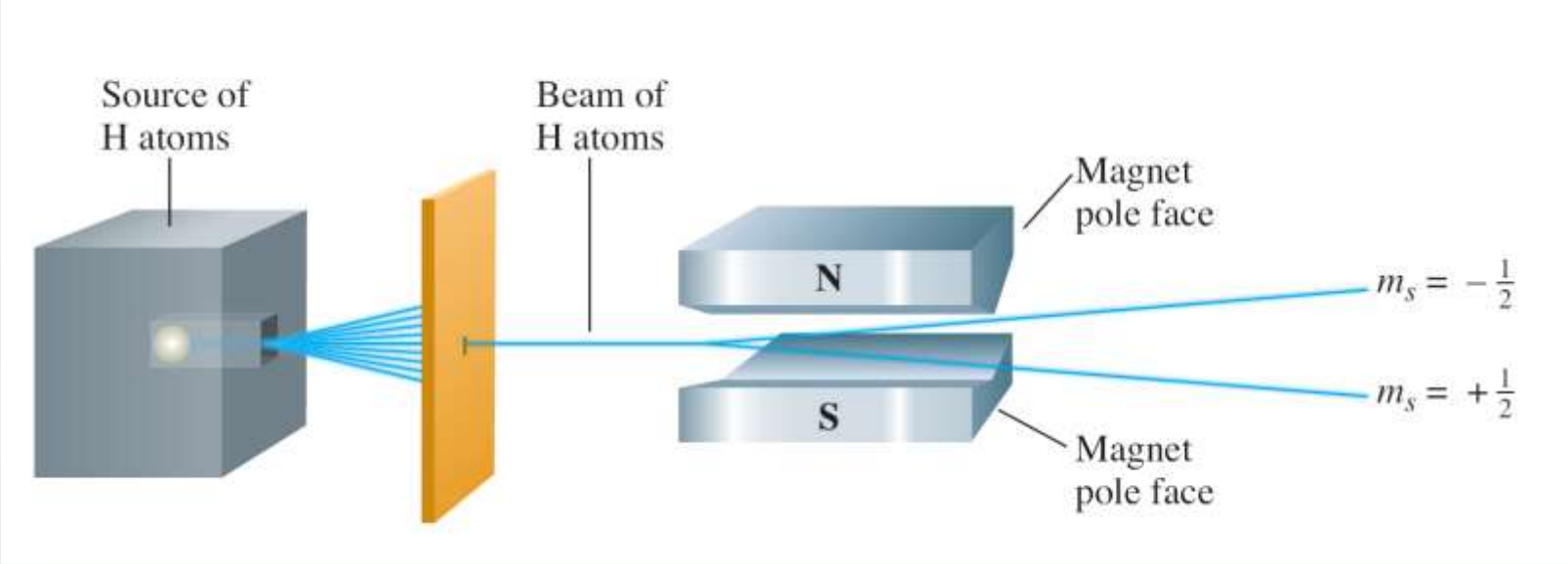
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Chapter 8 Electron Configurations and Periodicity

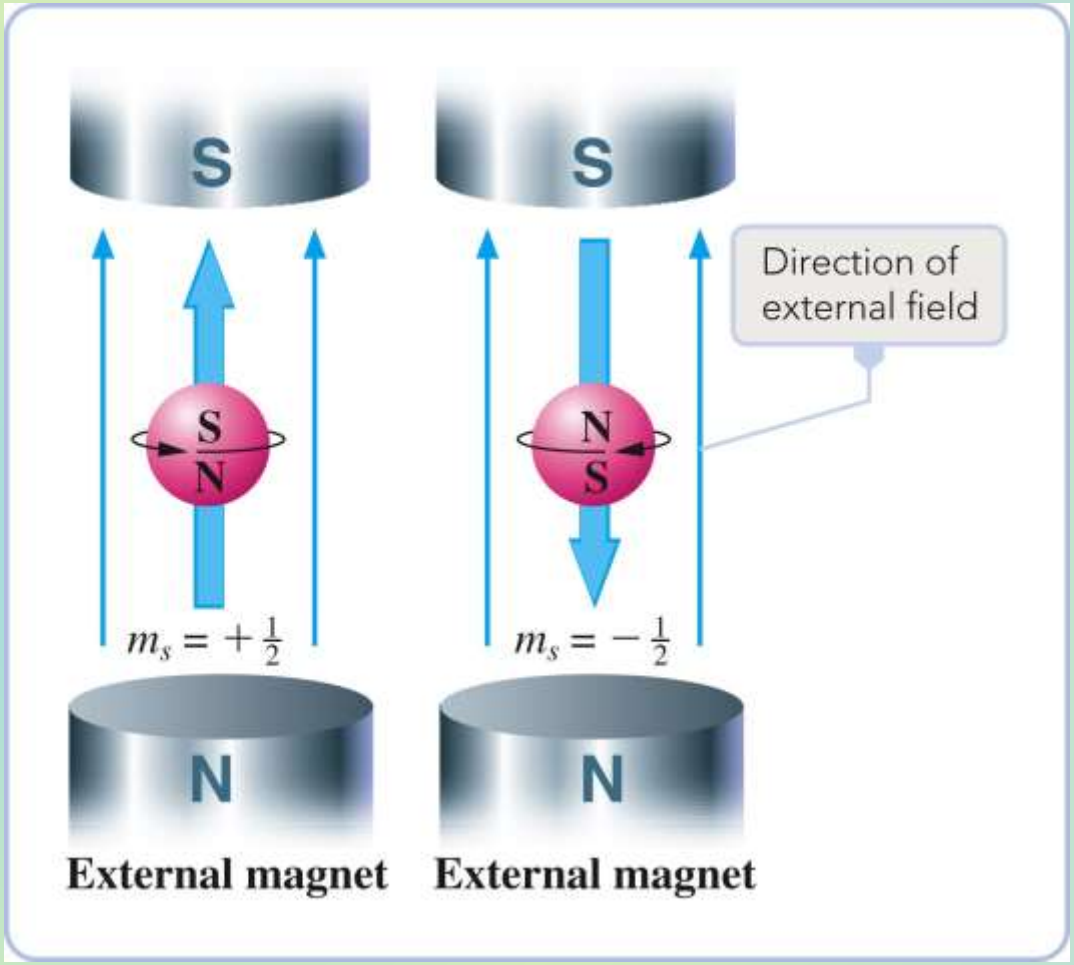
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In 1921, Otto Stern and Walther Gerlach first observed electron spin magnetism. In the diagram below, a beam of hydrogen atoms divides in two while passing through a magnetic field. This correlates with the two values of m_s: +½ and -½.



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The two possible spin orientations of an electron and the conventions for m_s are illustrated here.



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An **electron configuration** of an atom is a particular distribution of electrons among available subshells.

An **orbital diagram** of an atom shows how the orbitals of a subshell are occupied by electrons. Orbitals are represented with a circle; electrons are represented with arrows up for $m_s = +½$ or down for $m_s = -½$.

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The **Pauli exclusion principle** summarizes experimental observations that no two electrons in one atom can have the same four quantum numbers.

That means that within one orbital, electrons must have opposite spin. It also means that one orbital can hold a maximum of two electrons (with opposite spin).

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An *s* subshell, with one orbital,
can hold a maximum of 2 electrons.

A *p* subshell, with three orbitals,
can hold a maximum of 6 electrons.

A *d* subshell, with five orbitals,
can hold a maximum of 10 electrons.

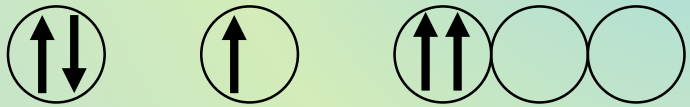
An *f* subshell, with seven orbitals,
can hold a maximum of 14 electrons.

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Determine which of the following orbital diagrams or electron configurations are possible and which are impossible. Provide explanations.

a. 

b. 

c. 

d. $1s^3 2s^1$

e. $1s^2 2s^1 2p^7$

f. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

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a. Possible.
b. Impossible; there are three electrons in the 2*s* orbital.
c. Impossible; there are two electrons is a 2p orbital with the same spin.
d. Impossible; there are three electrons in the 1*s* subshell.
e. Impossible; there are seven electrons in the 2*p* subshell.
f. Possible. The 3*d* subshell can hold as many as three electrons.

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The lowest-energy configuration of an atom is called its **ground state.**

Any other allowed configuration represents an **excited state.**

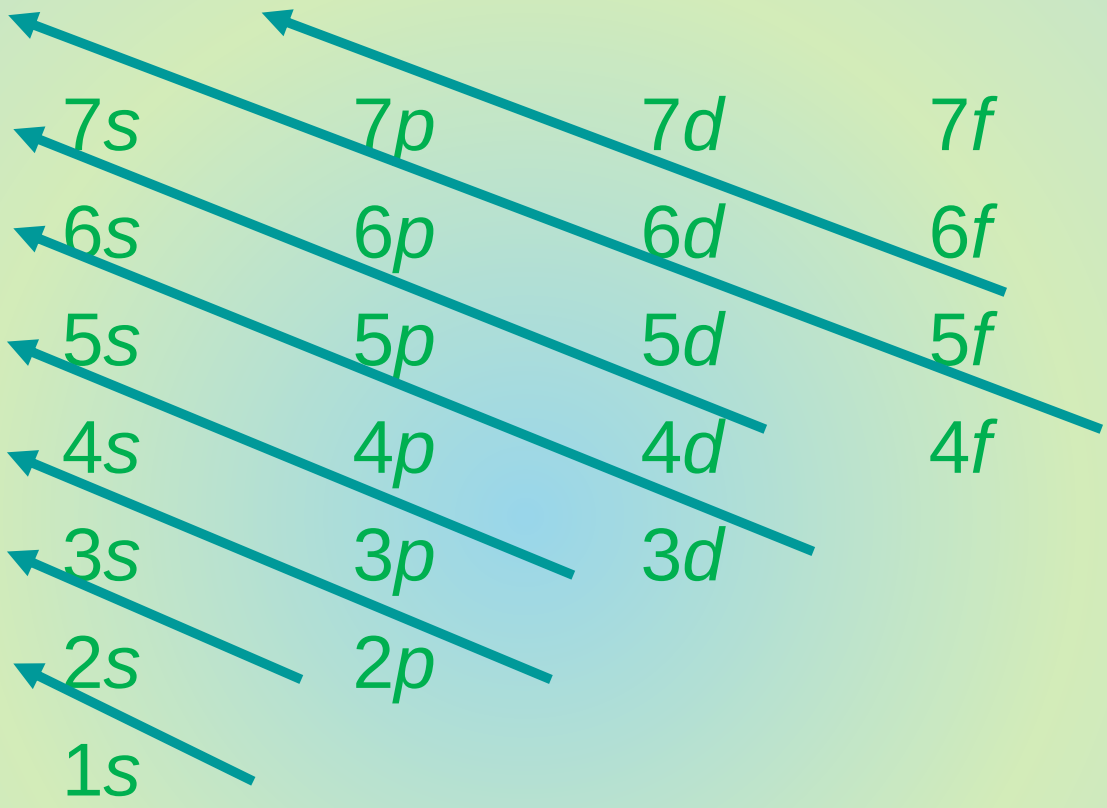
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The **building-up principle** (or aufbau principle) is a scheme used to reproduce the ground-state electron configurations by successively filling subshells with electrons in a specific order (the building-up order).

The ground state of the atom can be obtained by filling orbitals of lowest energy first.

Ground-state configurations are determined by the total energies of the atoms.

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This results in the following order:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*.

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The pattern that develops among the ground-state electron configurations of the atoms, explains the periodic table.

Noble gases (Group 8A periodic table) are relatively unreactive. These elements have a configuration in which a P subshell has just filled.

Example, Helium, Neon, Argon Krypton

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Alkaline earth metals (Group 2A)

Are moderately reactive elements. Example, Beryllium, Magnesium, Calcium

Contain a **noble-gas core** - An inner-shell configuration corresponding to one of the noble gases.

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Elements such as boron and aluminum have three noble-gas cores as well as three electrons with the configuration ns^2np^1.

The noble-gas core along with the $(n - 1)d^{10}$ electrons are referred to as a **pseudo-noble-gas-core** as these electrons are not involved in chemical reactions.

A **valence electron** is an electron in an atom outside the noble-gas or pseudo-noble-gas core.

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In the periodic table, groups 1A and 2A correspond to the *s* subshell; Groups 3A through 8A correspond to the *p* subshell; the “B” groups correspond to the *d* subshell; and the bottom two rows correspond to the *f* subshell. This is shown on the next slide.

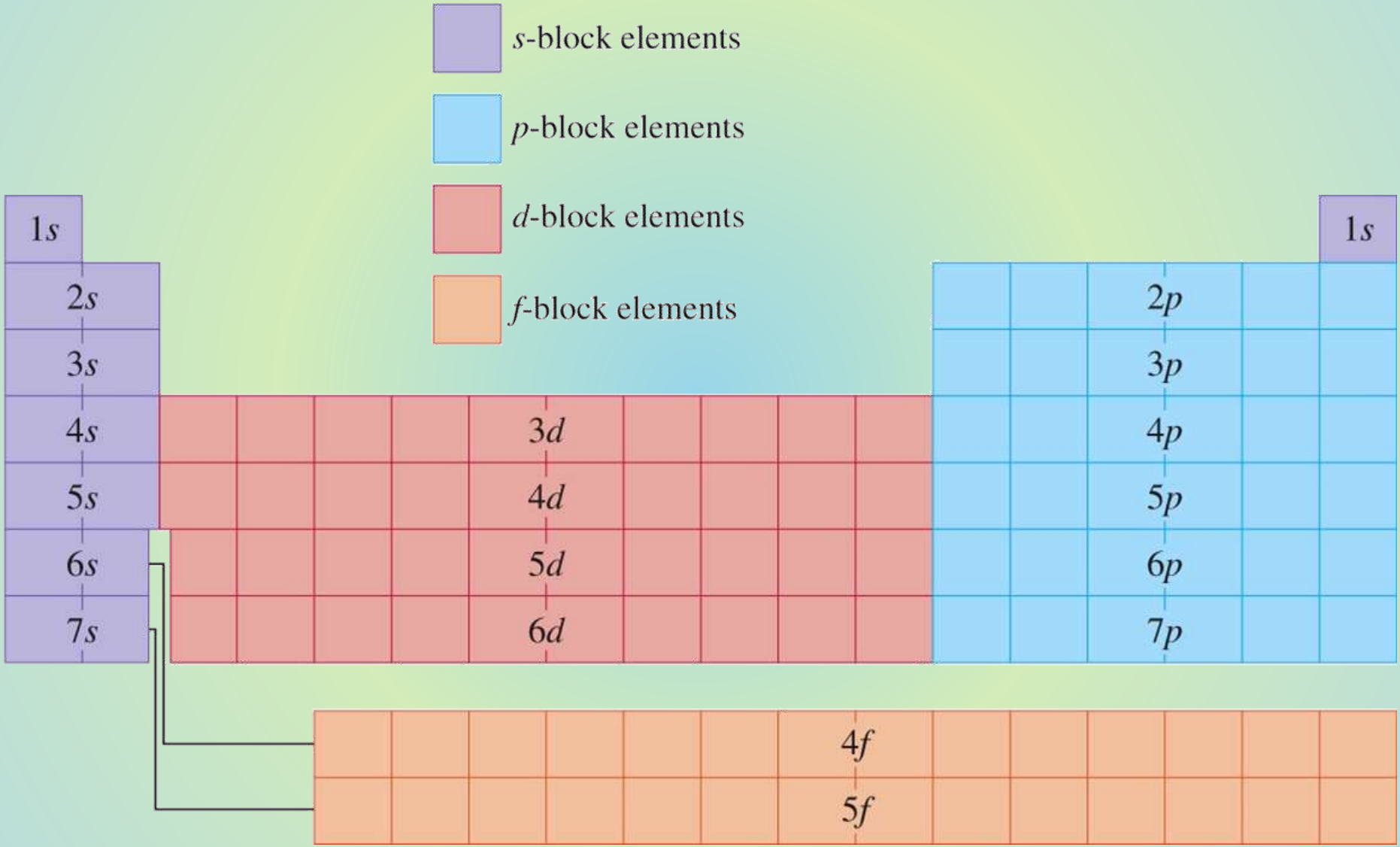
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For main-group (representative) elements, an *s* or a *p* subshell is being filled. The valence configuration is in the form $ns^a np^b$

For *d*-block transition elements, a *d* subshell is being filled.

For *f*-block transition elements, an *f* subshell is being filled.

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There are a few exceptions to the building-up order prediction for the ground state.

According to the building-up principle, the configuration of chromium is [Ar]$3d^4 4s^2$. The actual configuration is [Ar]$3d^5 4s^1$.

There is a difference also in the configuration of copper. The building-up principle predicts a configuration of [Ar]$3d^9 4s^2$ while the actual configuration is [Ar]$3d^{10} 4s^1$.

In essence, the configuration predicted by the building-up principle is very close in energy to the ground-state configuration.

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Write the complete electron configuration of the arsenic atom, As, using the building-up principle.

For arsenic, As, $Z = 33$.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2 4p^3$

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What are the electron configurations for the valence electrons of arsenic and zinc?

Arsenic is in period 4, Group VA.
Its valence configuration is $4s^2 4p^3$.

Zinc, $Z = 30$, is a transition metal in the first transition series.
Its noble-gas core is Ar, $Z = 18$.
Its valence configuration is $4s^2 3d^{10}$.

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Imagine a world in which the Pauli principle is “No more than one electron can occupy an atomic orbital, irrespective of its spin.” How many elements would there be in the second row of the periodic table, assuming that nothing else is different about this world?

When $n = 2$, there are two subshells.

The *s* subshell has one orbital, which could hold one electron.

The *p* subshell has three orbitals, which could hold three electrons.

This would give a total of four elements for the second period.

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Writing Electron Configurations Using the Periodic Table

Recall the structure of the periodic table.

There is a definite pattern to the order of filling subshells as you go through the elements in the periodic table. Refer to Figure 8.12 for this pattern.

When writing the configuration of an atom with its subshells arranged by shells, the orbitals will usually be in order by energy. The subshells describe chemical reactivity at the far right.

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Use the building-up principle to obtain the configuration for the ground state of the gallium atom (Z = 31). Give the configuration in complete form and determine the valence-shell configuration.

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Obtain the following build-up order from the periodic table:

	1*s*	2*s* 2*p*	3*s* 3*p*	4*s* 3*d* 4*p*
Period:	First	Second	Third	Fourth

Fill the subshells with electrons; remember that there is a total of 31 electrons. This gives:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$$

Rearranging gives: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$

The valence shell configuration is $4s^2 4p^1$

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Determine the configurations for the outer electrons for tellurium whose atomic number, Z = 52.

The location of tellurium in a periodic table is Period 5, Group 6A.

Thus, it is a main-group element, and the outer subshells are 5*s* and 5*p*.

Since the group is 6A, the sub-shells contain six electrons.

The valence-shell configuration is $5s^2 5p^4$.

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In 1927, Friedrich Hund discovered, by experiment, a rule for determining the lowest-energy configuration of electrons in a subshell.

Hund's rule states that the lowest-energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before pairing electrons.

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Consider the carbon atom ($1s^2 2s^2 2p^2$)

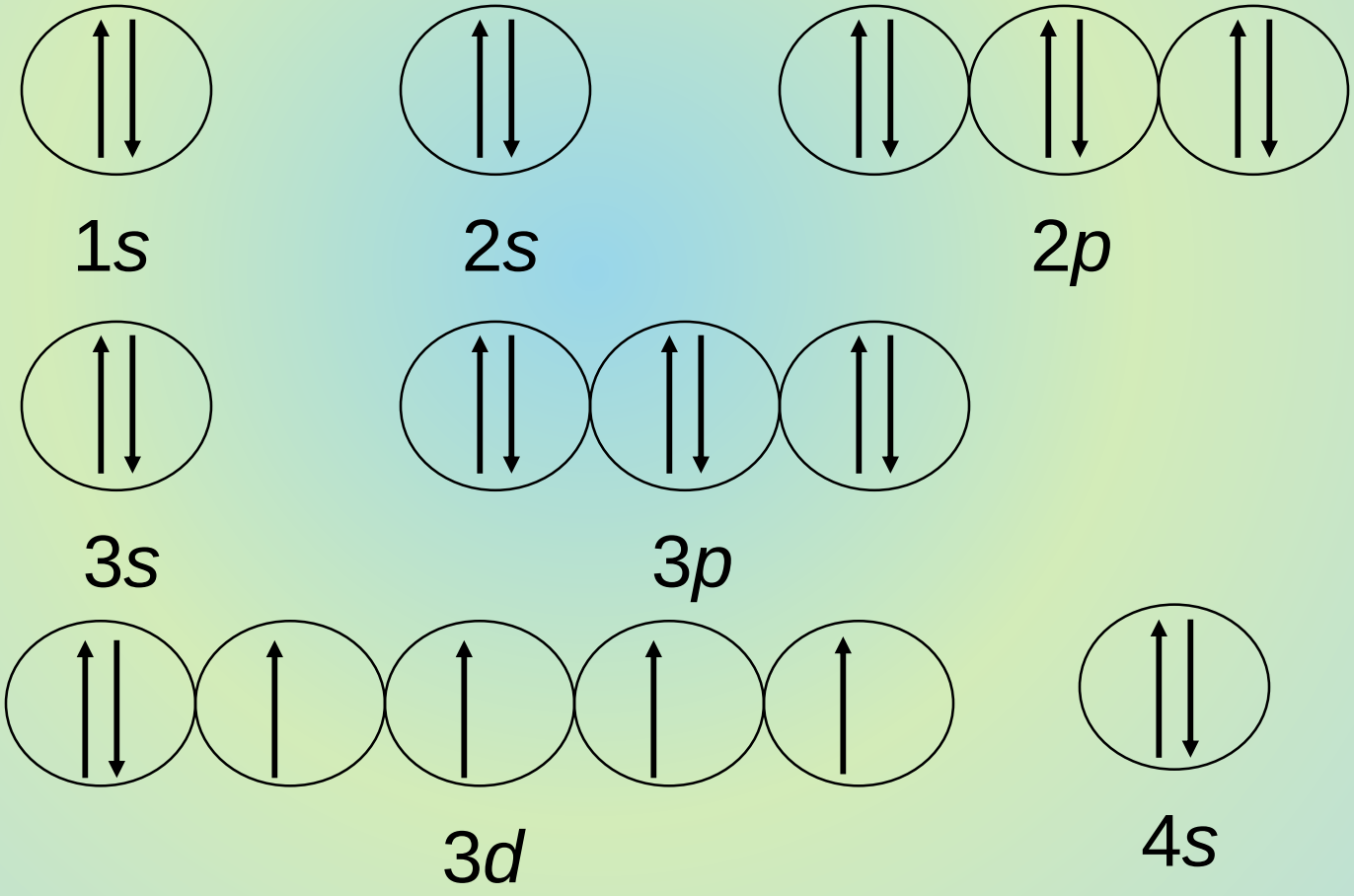


1*s* 2*s* 2*p*

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Write an orbital diagram for the ground state of the iron atom.

For iron, $Z = 26$



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Magnetic Properties of Atoms

Although an electron behaves like a tiny magnet, two electrons that are opposite in spin cancel each other. Only atoms with unpaired electrons exhibit magnetism.

This allows for the classification of atoms based on their behavior in a magnetic field.

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A **paramagnetic substance** is one that is weakly attracted by a magnetic field, usually as the result of unpaired electrons.

A **diamagnetic substance** is not attracted by a magnetic field generally because it has only paired electrons.

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You learned how the organization of the periodic table can be explained by the periodicity of the ground-state configurations of the elements. Now we will look at various aspects of the periodicity of the elements.

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Periodic law states that when the elements are arranged by atomic number, their physical and chemical properties vary periodically.

We will look in more detail at three physical properties of an atom:

- Atomic radius
- Ionization energy
- Electron affinity

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Atomic Radius

It is the maximum in the radial distribution function of the outer shell.

It is the value for that atom in a set of covalent radii assigned to atoms in such a way that the sum of the covalent radii of atoms A and B predicts that approximate A–B length.

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Periodic Trends Observed in Atomic Radii

Within each group (vertical column), the atomic radius increases with the period number.

Within each period (horizontal row), the atomic radius tends to decrease with increasing atomic number (nuclear charge).

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Effective Nuclear Charge

It is the positive charge that an electron experiences from the nucleus. It is equal to the nuclear charge, but is reduced by shielding or screening from any intervening electron distribution.

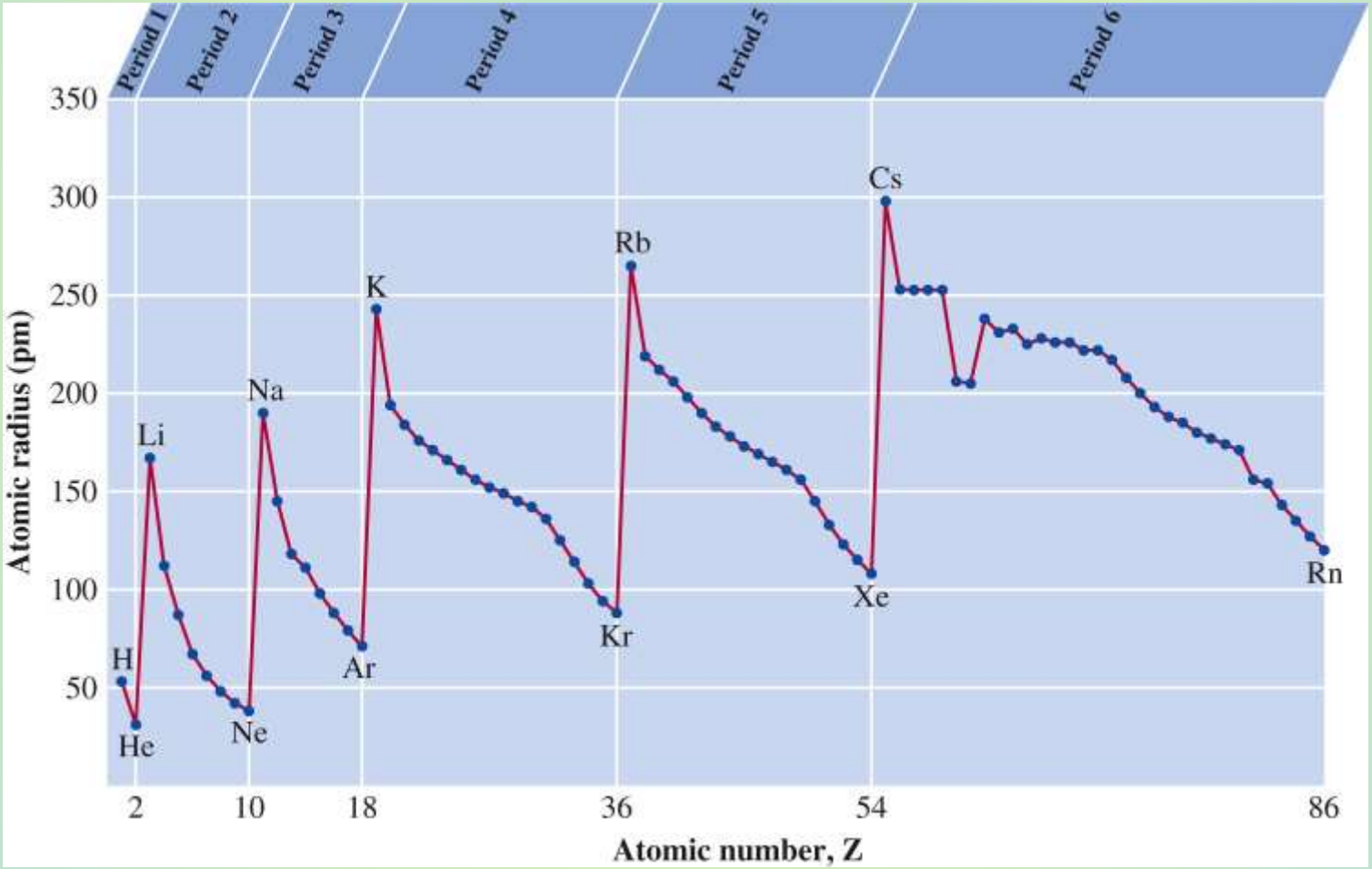
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Effective nuclear charge increases across a period. Because the shell number (*n*) is the same across a period, each successive atom experiences a stronger nuclear charge.

Therefore, the size of the outermost orbital and the radius of the atom decreases with the increase in atomic number.

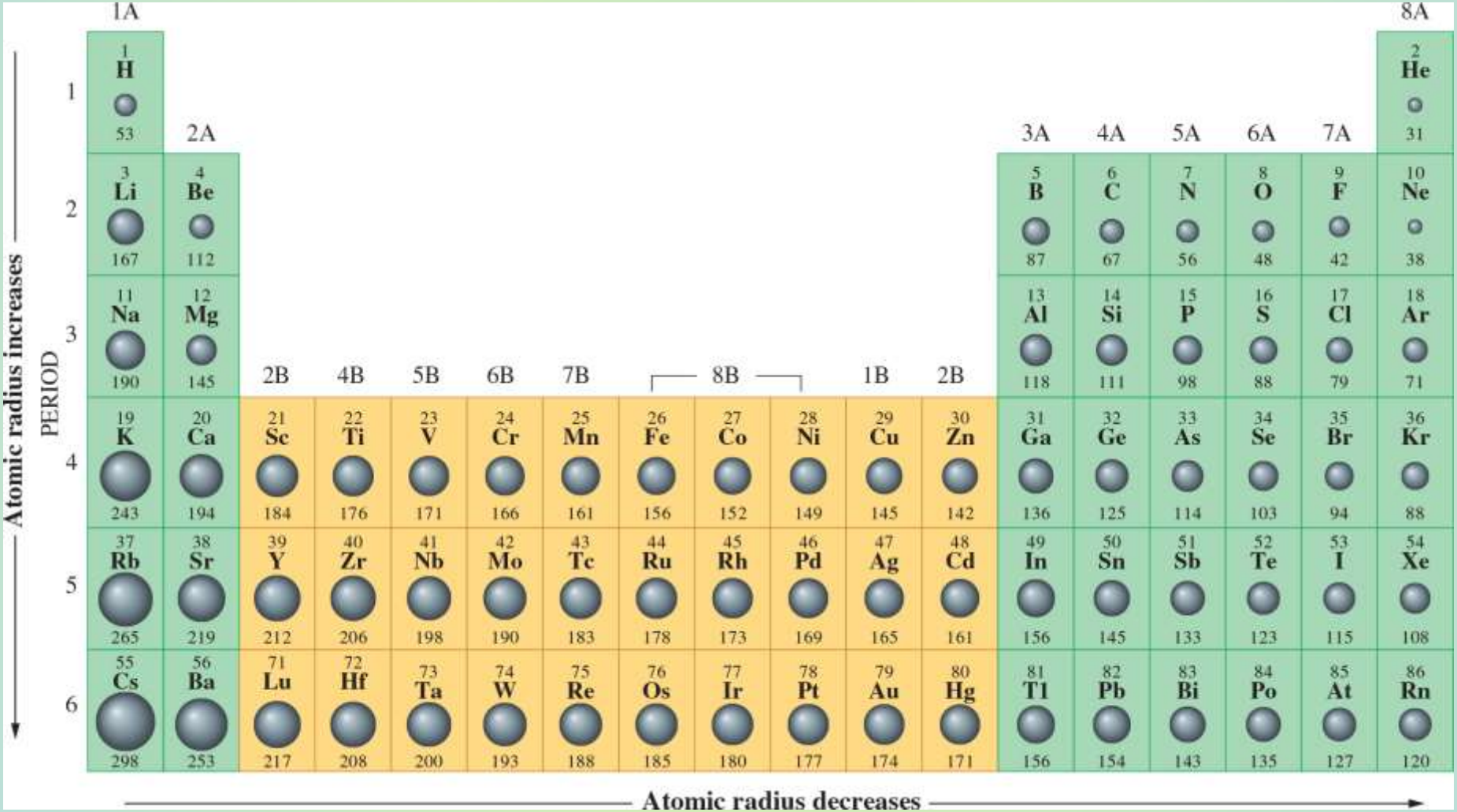
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Atomic radius is plotted against atomic number in the graph below. Note the regular periodic variation.



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A representation of atomic radii is shown below.



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Refer to a periodic table and arrange the following elements in order of increasing atomic radius: Ar, Se, S.

Se is below S group in 6A. Hence, its ionization energy should be less than that of S.

S and Ar are in the same period. Z increases from S to Ar. Hence, the ionization energy of S should be lesser than that of Ar.

Se < S < Ar

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First Ionization Energy (first ionization potential)

The minimum energy needed to remove the highest-energy (outermost) electron from a neutral atom in the gaseous state.

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General trend

Ionization energies tend to increase with the increase in atomic number.

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Generally, ionization energy increases with atomic number.

Ionization energy is proportional to the effective nuclear charge divided by the average distance between the electron and the nucleus.

Because the distance between the electron and the nucleus is inversely proportional to the effective nuclear charge, ionization energy is proportional to the square of the effective nuclear charge.

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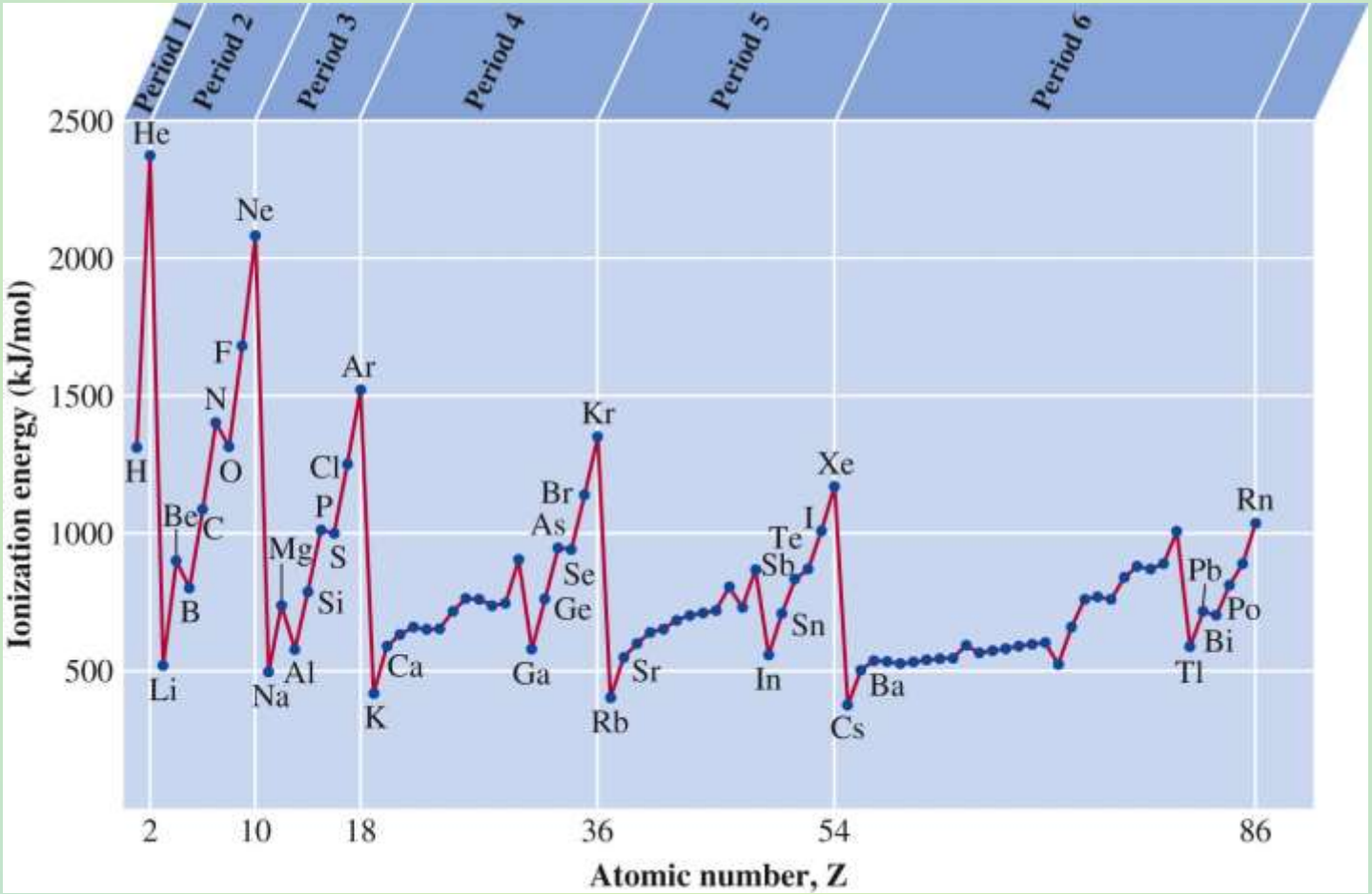
Small deviations occur between Groups 2A and 3A and between Groups 5A and 6A.

A 3A element (ns^2np^1) has a smaller ionization energy than the preceding 2A element (ns^2).

A 6A element (ns^2np^4) has a smaller ionization energy than the preceding 5A element.

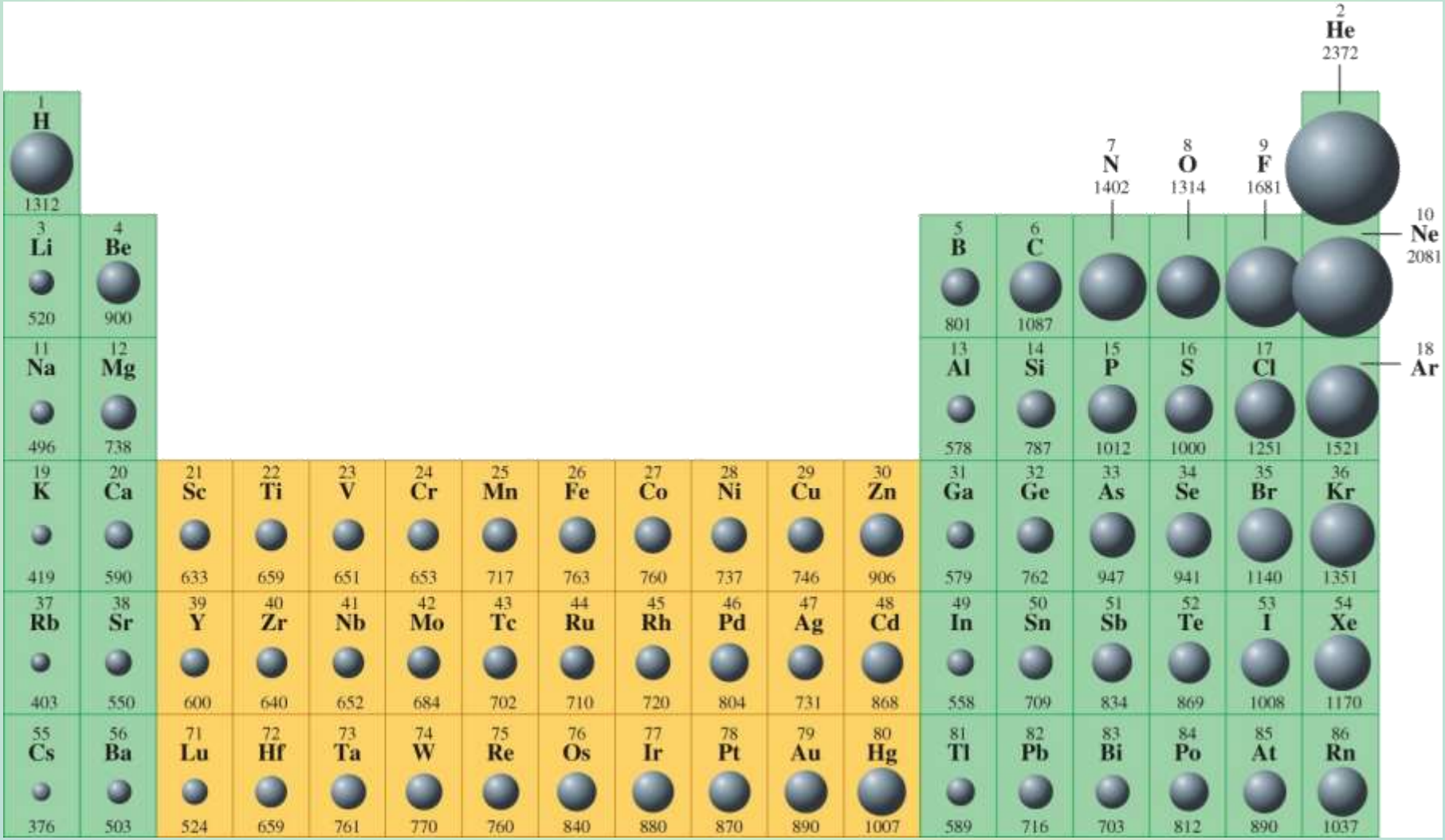
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These trends and reversals are visible in the graph of ionization energy versus atomic number.



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The size of each sphere indicates the size of the ionization energy in the figure below.



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Electrons can be successively removed from an atom. Each successive ionization energy increases, because the electron is removed from a positive ion of increasing charge.

Ionizations become difficult in some elements. This is because once the valence electrons are removed a stable noble-gas configuration is obtained.

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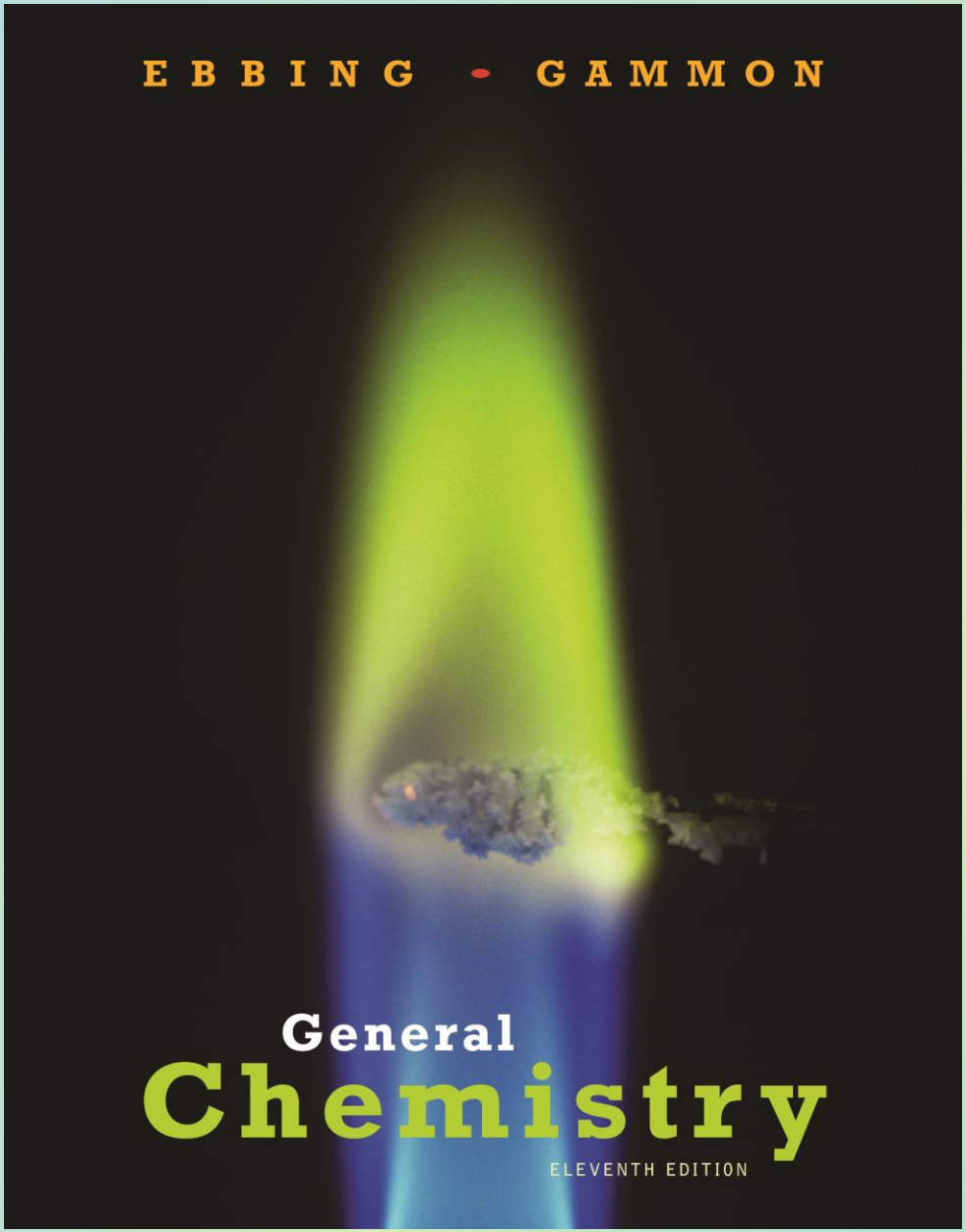
Table 8.3 Successive Ionization Energies of the First Ten Elements (kJ/mol)*

Element	First	Second	Third	Fourth	Fifth	Sixth	Seventh
H	1312						
He	2372	5250					
Li	520	7298	11,815				
Be	900	1757	14,848	21,006			
B	801	2427	3660	25,026	32,827		
C	1086	2353	4620	6223	37,831	47,277	
N	1402	2856	4578	7475	9445	53,267	64,360
O	1314	3388	5300	7469	10,990	13,326	71,330
F	1681	3374	6050	8408	11,023	15,164	17,868
Ne	2081	3952	6122	9371	12,177	15,238	19,999

*Ionization energies to the right of a vertical line correspond to removal of electrons from the core of the atom.

Left of the line, valence shell electrons are being removed. Right of the line, noble-gas core electrons are being removed.

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Chapter 9 Ionic and Covalent Bonding

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A chemical bond is a strong attractive force that exists between certain atoms in a substance.

There are three types of chemical bonds:

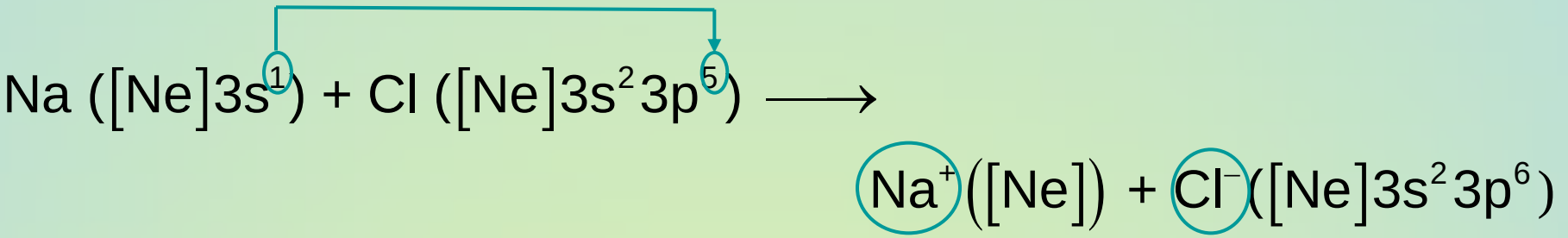
- Ionic bonds
- Covalent bonds
- Metallic bonds

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An **ionic bond** is a chemical bond formed by the electrostatic attraction between positive and negative ions.

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An ionic bond forms when one or more electrons are transferred from the valence shell of one atom to the valence shell of another atom.



The atom that transferred the electron(s) becomes a cation.

The atom that gained the electron(s) becomes an anion.

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A **Lewis electron-dot symbol** is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the chemical symbol of the element.

Note – Dots are placed one to each side, until all four sides are occupied.

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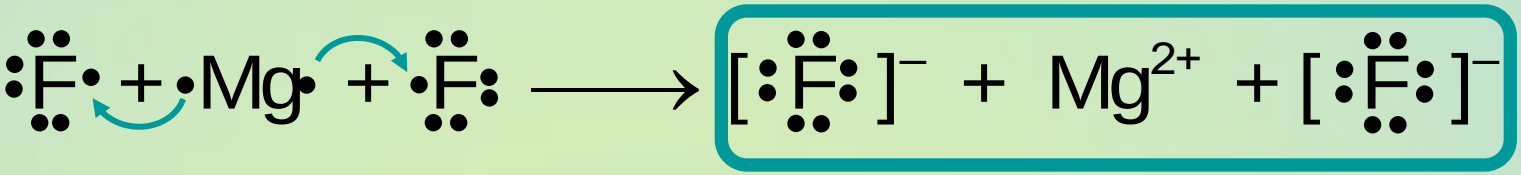
Table 9.1 illustrates the Lewis electron-dot symbols for second- and third-period atoms.

Table 9.1 Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

Period	1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
Second	Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Third	Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:

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Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations.



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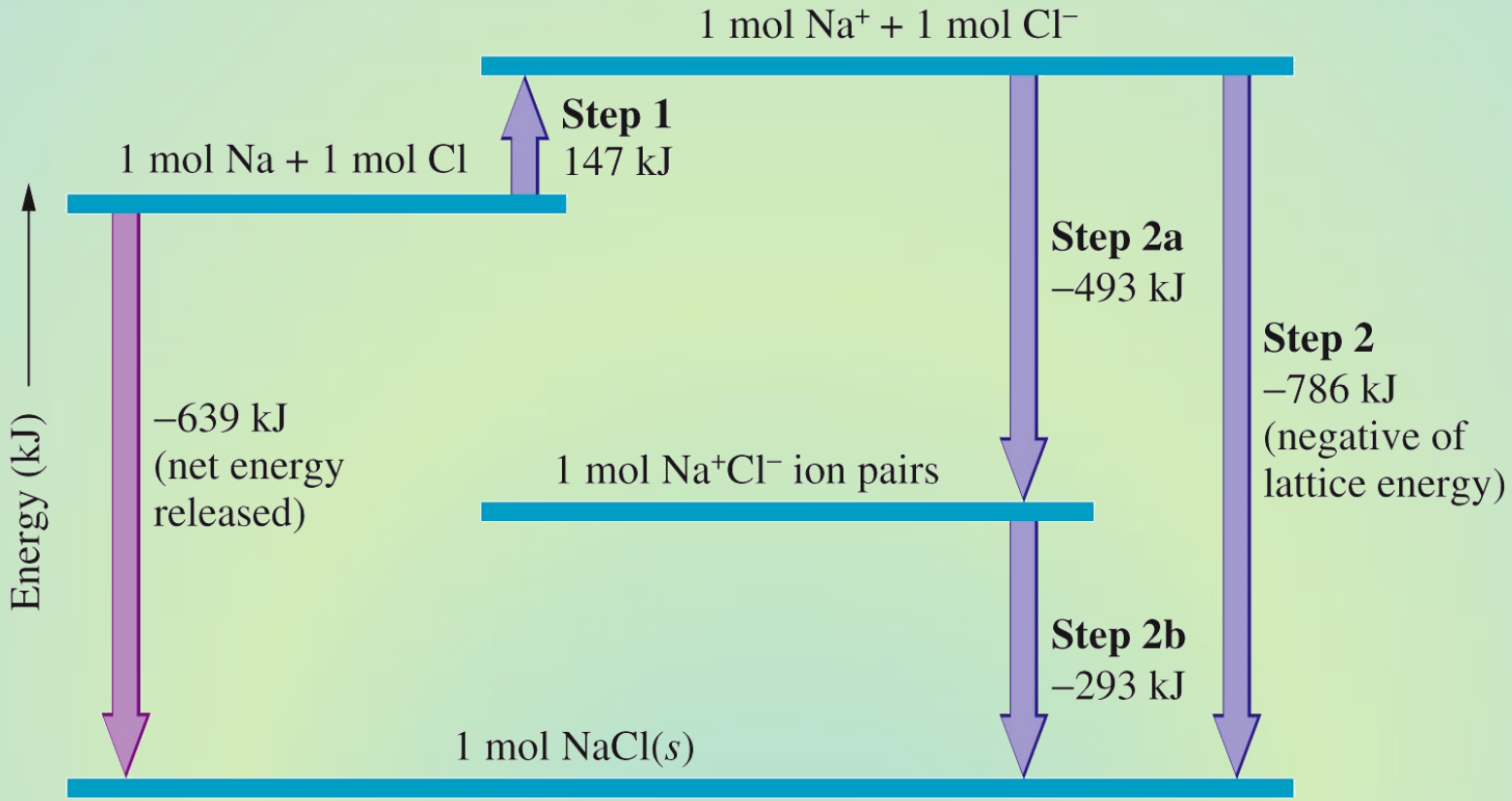
An ionic bond between two atoms is formed in two steps:

1. An electron is transferred between the two separate atoms to give ions.
2. The ions attract one another, forming an ionic bond.

Both steps occur simultaneously.

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For example, to find the lattice energy for NaCl, we can use the following steps.



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Coulomb's Law

The potential energy obtained in bringing two charges Q_1 and Q_2, initially apart, up to a distance r apart is directly proportional to the product of the charges and inversely proportional to the distance between them.

$$E = \frac{kQ_1Q_2}{r}$$

k is a physical constant (8.99 × 109 J·m/C^2).

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Consider the pairing between a Na^+ and a Cl^- ion.

The charge in Na^+ is ^+e

The charge in Cl^- is ^-e

$e = 1.602 \times 10^{-19}\ C$

$$E = \frac{-(8.99 \times 10^9\ J \cdot m/C^2) \times (1.602 \times 10^{-19}\ C)^2}{2.82 \times 10^{-10}\ m} = -8.18 \times 10^{-19}\ J$$

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When we examine the electron configuration of main-group ions, we find that any of these elements that gain or lose electrons attain a noble-gas configuration.

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In cations of Groups 1A to 3A having noble-gas or pseudo-noble-gas configurations, the ion charges equal the group numbers.

In cations of Groups 3A to 5A having ns^2 electron configurations, the ion charges equal the group numbers minus two.

In anions of Groups 5A to 7A having noble-gas or pseudo-gas configurations, the ion charges equal the group numbers minus eight.

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Write the electron configuration and the Lewis symbol for N^{3-}.

The electron configuration for N is [He]$2s^2p^3$. By gaining 3 electrons, the configuration changes to [He]$2s^22p^6$.



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Polyatomic ions are atoms held together by covalent bonds. Most ions are polyatomic in nature.

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Transition metals form several cations.

The atoms generally lose the *ns* electrons before losing the (*n* – 1)*d* electrons.

As a result, most transition metals form the 2+ ion.

Transition elements that lose one (*n* – 1)*d* electrons as well as two *ns* electrons form 3+ ions.

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Give the electron configurations of Fe^{2+} and Fe^{3+}.

The electronic configuration of the Fe atom is [Ar]$3d^6 4s^2$. Removing the $4s^2$ electrons gives the configuration of Fe^{2+}. Removing a $3d$ electron gives the configuration of Fe^{3+}.

The configuration of Fe^{2+} is [Ar]$3d^6$ and that of Fe^{3+} is [Ar]$3d^5$.

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Concept Check 9.1

The following are electron configurations for some ions. Which ones would you expect to see in chemical compounds? State the concept or rule you used to decide for or against any ion.

a. Fe^{2+} [Ar]$3d^{4}4s^{2}$ **b.** N^{2-} [He]$2s^{2}2p^{5}$ **c.** Zn^{2+} [Ar]$3d^{10}$

d. Na^{2+} [He]$2s^{2}2p^{5}$ **e.** Ca^{2+} [Ne]$3s^{2}3p^{6}$

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a. Fe^{2+}: [Ar]$3d^4 4s^2$

No. The $4s^2$ electrons would be lost before the 3*d* electrons.

b. N^{2-}: [He]$2s^2 2p^5$

No. Nitrogen will gain three electrons to fill the shell, forming N^{3-}.

c. Zn^{2+}: [Ar]$3d^{10}$

Yes.

d. Na^{2+}: [He]$2s^2 2p^5$

No. Sodium will lose only its one valence electron, forming Na^+.

e. Ca^{2+}: [Ne]$3s^2 3p^6$

Yes.

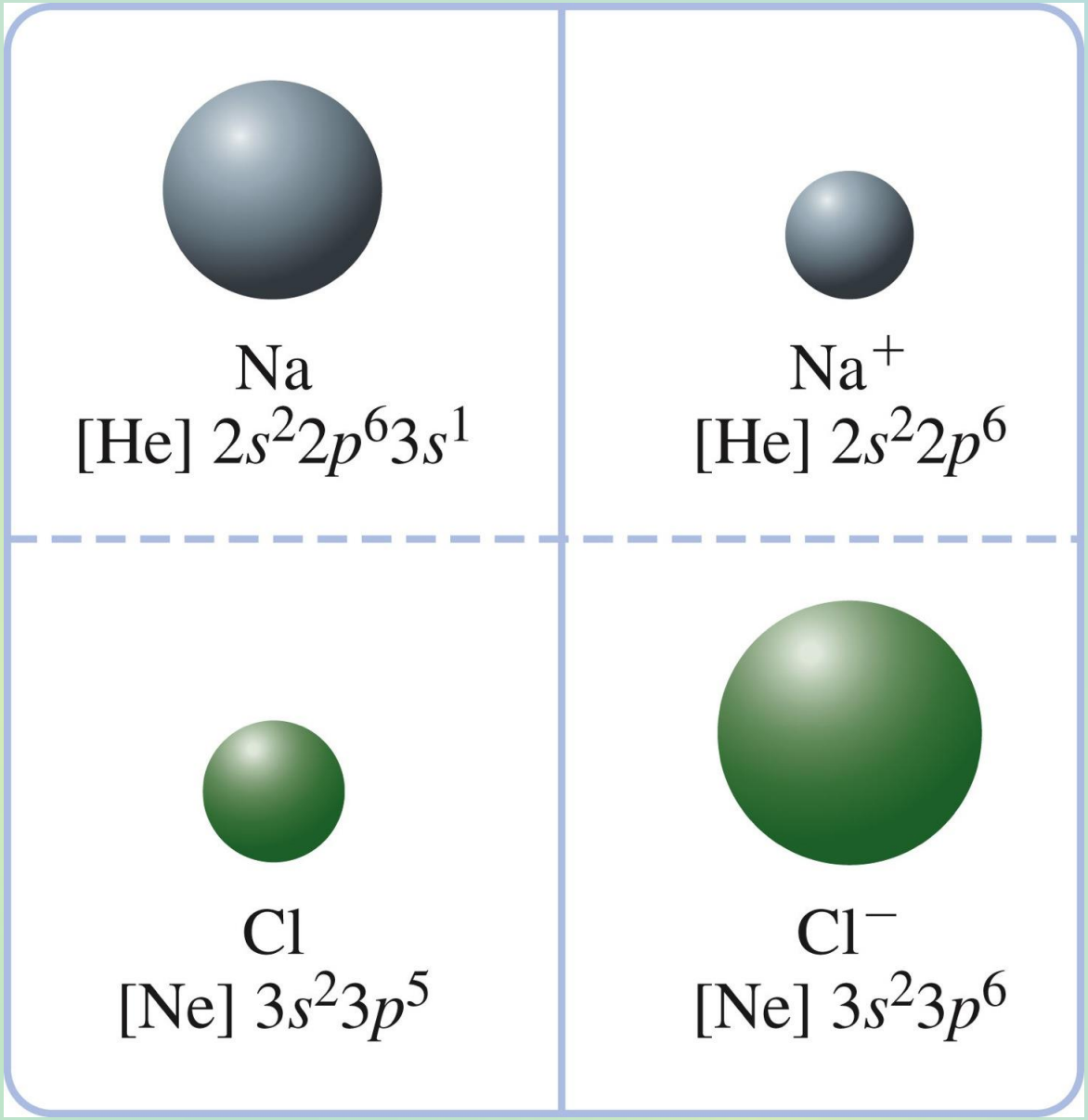
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Ionic radius is a measure of the size of the spherical region around the nucleus of an ion within which the electrons are most likely to be found. While ionic radius, like atomic radius, can be somewhat arbitrary, it can be measured using known distances between nuclei in crystals.

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A cation is always smaller than its neutral atom.

An anion is always larger than its neutral atom.



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The term **isoelectronic** refers to different species having the same number and configuration of electrons.

For example, Na^+, Mg, and Al^{3+} are isoelectronic.

While progressing across a period, the cations decrease in radius. For anions, there is an abrupt increase, followed by a decrease in radius.

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Using the periodic table only, arrange the following ions in order of decreasing ionic radius: F^-, Mg^{2+}, O^{2-}.

These ions are isoelectronic,
so the ion radius decreases with an increase in nuclear charge.

$$O^{2-} < F^- < Mg^{2+}$$

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A **covalent bond** is a chemical bond formed by sharing a pair of electrons.

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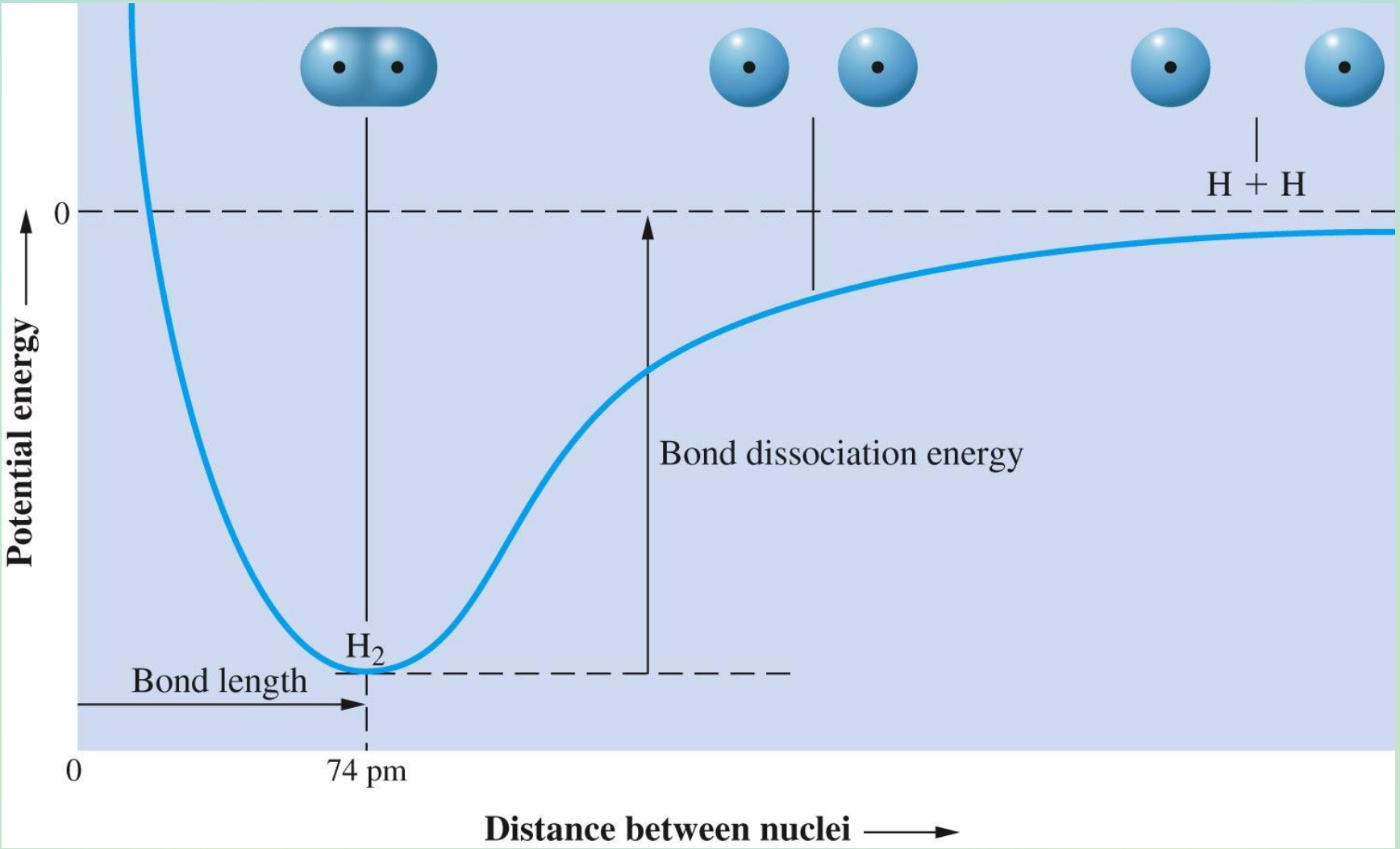
To consider how a covalent bond forms, we can monitor the energy of two isolated hydrogen atoms as they move closer together.

The potential energy decreases—first gradually, and then more steeply—to a minimum. As the atoms continue to move closer, it increases dramatically.

The distance between the atoms when energy is at a minimum is called the bond length.

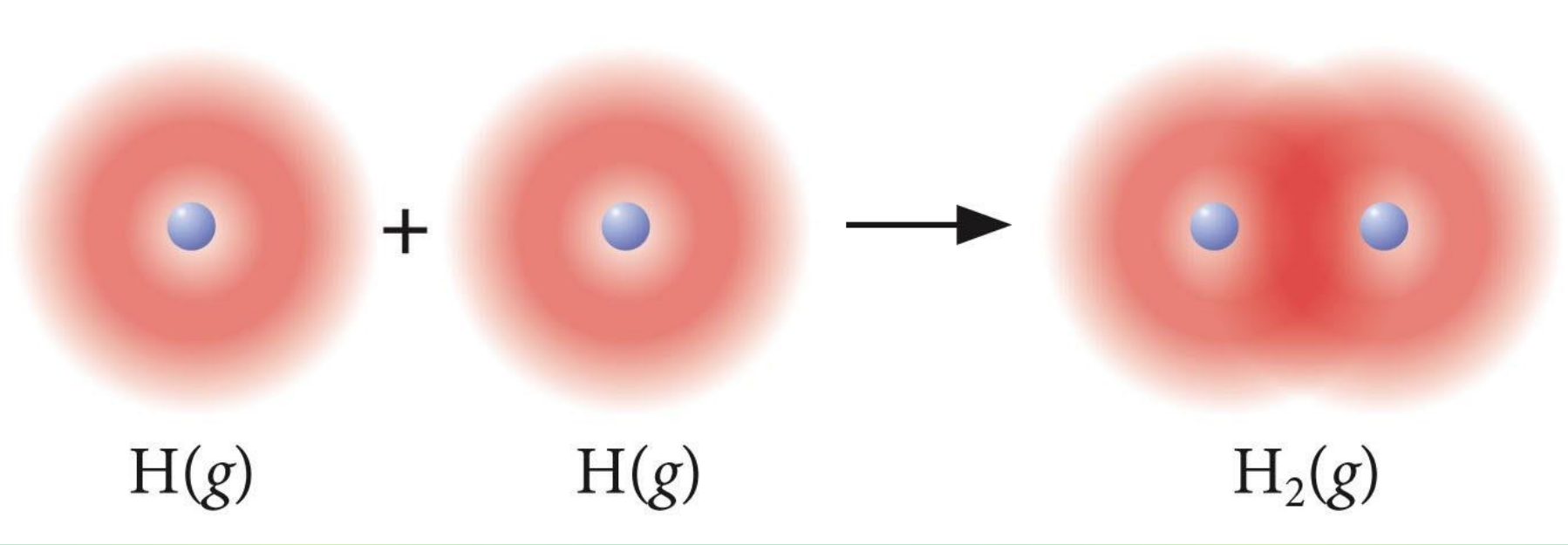
This is illustrated on the following graph, from right to left.

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As the hydrogen atoms move closer together, the electron of each atom is attracted to both its own nucleus and the nucleus of the second atom. The electron probability distribution illustrates this relationship.



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A formula using dots to represent valence electrons is called a **Lewis electron-dot formula.**

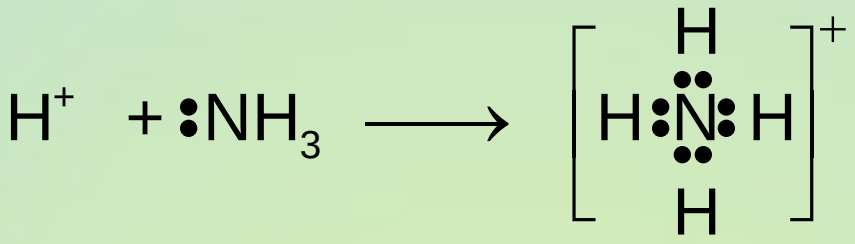
An electron pair is represented by two dots.

An electron pair that is *between* two atoms is a bonding pair. It can also be represented by one line for each bonding pair.

Electron pairs that are not bonding are nonbonding, or lone pair electrons.

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A **coordinate covalent bond** is formed when both electrons of the bond are donated by one atom.



The two electrons forming the bond with the hydrogen on the left were both donated by the nitrogen. Once shared, they are indistinguishable from the other N—H bonds.

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In forming covalent bonds, atoms tend toward having a full eight electrons in their valence shell. This tendency is called the **octet rule.**

Hydrogen is an exception to the octet rule; it has two electrons in its valence shell.

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A **single bond** is a covalent bond in which one pair of electrons is shared by two atoms.

A **double bond** is a covalent bond in which two pairs of electrons are shared by two atoms.

A **triple bond** is a covalent bond in which three pairs of electrons are shared by two atoms.

Double bonds form primarily with C, N, O, and S atoms.

Triple bonds form primarily with C and N atoms.

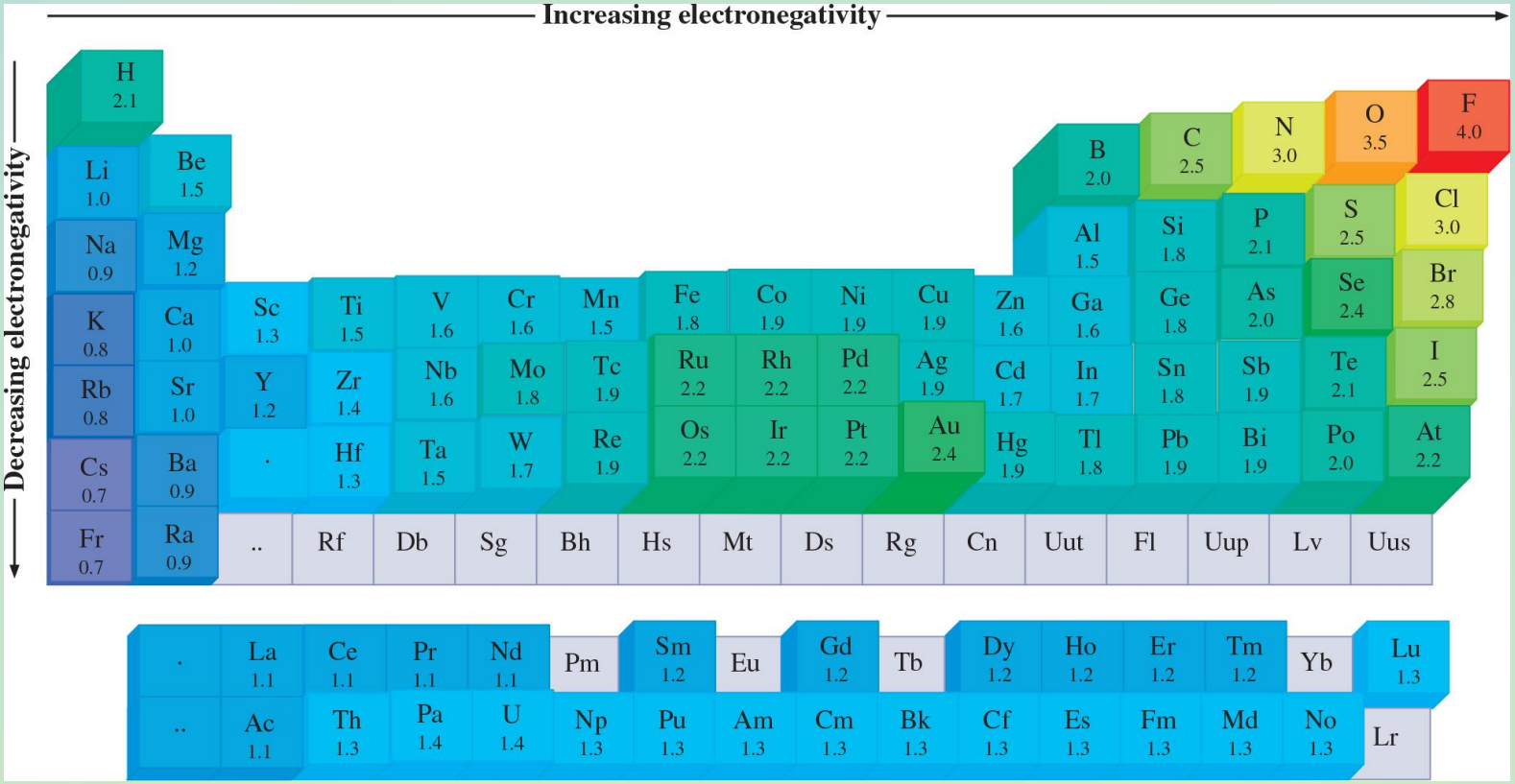
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A **polar covalent bond** (or polar bond) is a covalent bond in which the bonding electrons spend more time near one atom than near the other atom.

Electronegativity, X, is a measure of the ability of an atom in a molecule to draw bonding electrons to itself.

$$X = \frac{I.E. + E.A.}{2}$$

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Electronegativity increases from left to right and from bottom to top in the periodic table. F, O, N, and Cl have the highest electronegativity values.

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The difference in electronegativity between the two atoms in a bond is a rough measure of bond polarity.

A small difference results in a nonpolar bond.

A large difference results in a polar bond.

A very large difference can result in an ionic bond.

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Using electronegativities, arrange the following bonds in order by increasing polarity: P—H, H—O, C—Cl.

The difference for P—H is 0.0

The difference for H—O is 1.4

The difference for C—Cl is 0.5

The order is P—H < C—Cl < H—O

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During bond formation, electrons are piled toward the more electronegative atom. The direction of electrons can be predicted using the electronegativity scale.

In H–Cl bond, electrons are pulled toward the Cl atom (X = 3.0) rather than the H atom (X = 2.1).

The Cl atom acquires a partial negative charge.

The H atom acquires a partial positive charge.

Thus, the HCl molecule is a polar molecule.

$$\overset{\delta+}{\text{H}}\text{—}\overset{\delta-}{\text{Cl}}$$

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Writing Lewis Electron-Dot Formulas

- Calculate the number of valence electrons.
- Write the skeleton structure of the molecule or ion.
- Distribute electrons to the atoms surrounding the central atom or atoms to satisfy the octet rule.
- Distribute the remaining electrons as pairs to the central atom(s).

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Write the Lewis formula for sulfir dichloride; SCl_2.

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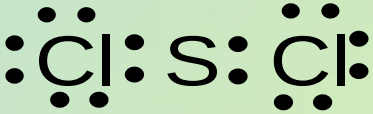
Determine the total number of valence electrons.

Valence electrons in S = 6

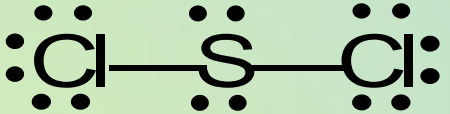
Valence electrons in Cl = 7

Total number of valence electrons = 20

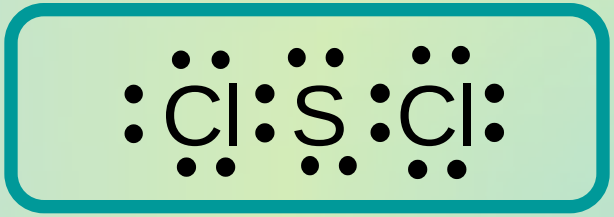
Write the skeletal structure.



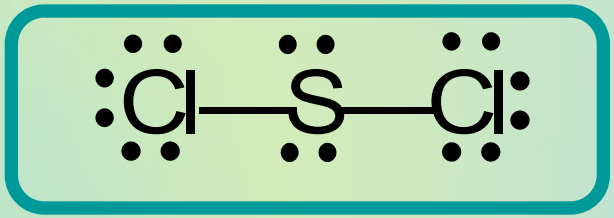
or



Subtracting these 8 pairs from the total gives a difference of 2 pairs, which are placed n the central atom (S). The final Lewis structure is:



or



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Determine the electron-dot formula of $COCl_2$.

Determine the total number of valence electrons.

Valence electrons in C = 4

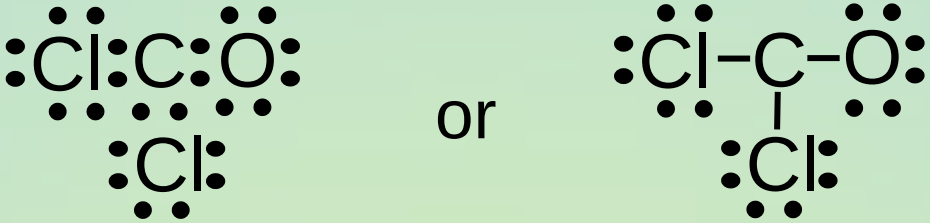
Valence electrons in O = 6

Valence electrons in Cl = 7

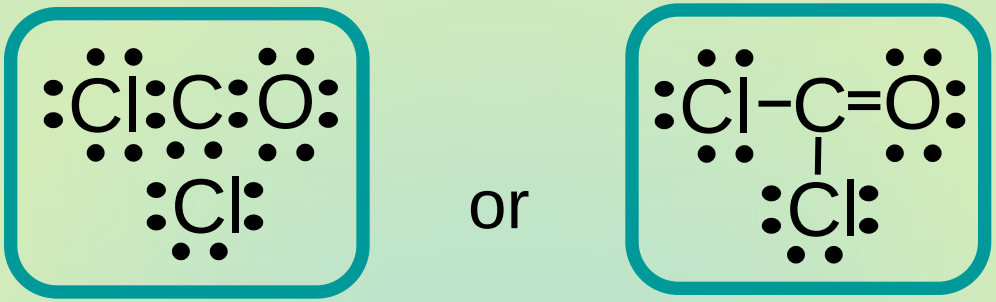
Total number of valence electrons = 24

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Write the skeletal structure.



Since there are not enough electrons to give an octet, transfer an electron pair from an outer atom to form a double bond. This gives:



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Delocalized bonding is a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather than being localized between two atoms.

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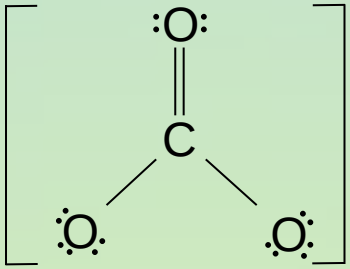
A single electron-dot diagram cannot properly describe delocalized bonding. Using the **resonance description**, the electron structure of a molecule or ion having delocalized bonding is given by writing all possible electron-dot formulas. They are connected with a double-headed arrow.

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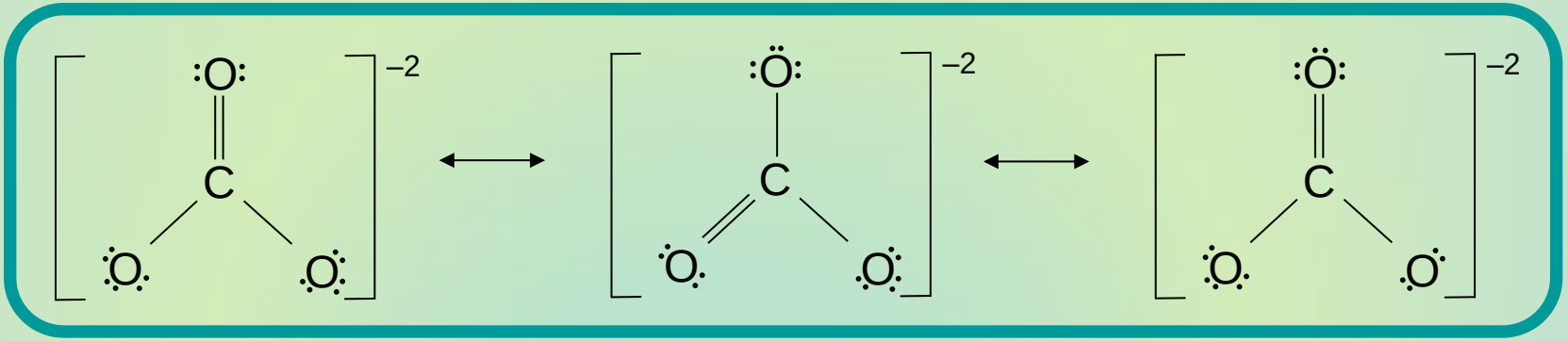
Describe the electron structure of the carbonate ion, CO_3^{2-}, in terms of electron-dot formulas.

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One possible electron-dot formula for the carbonate ion is:



If all carbon–oxygen bonds are expected to be equivalent, the electron structure must be described in resonance terms.

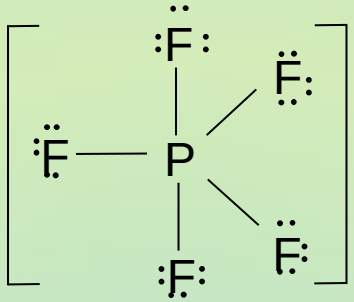


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Some molecules have electron-dot structures that do not satisfy the octet rule. Some have an odd number of electrons, such as NO. Other molecules either have more than eight or less than eight valence electrons around the central atom.

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Phosphorus pentafluoride is a compound that has more than eight valence electrons.



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Determine the electron-dot formula of xenon tetrafluorine, XeF_4.

Determine the total number of valence electrons.

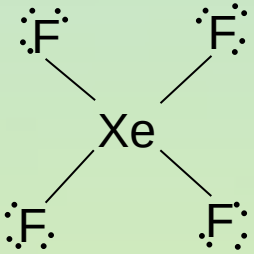
Valence electrons in Xe = 8

Valence electrons in O = 7

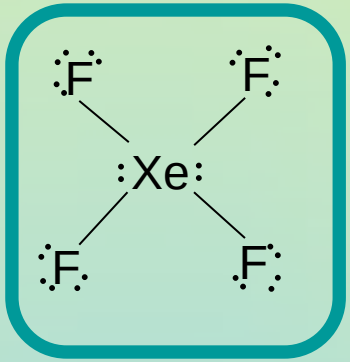
Total number of valence electrons = 36

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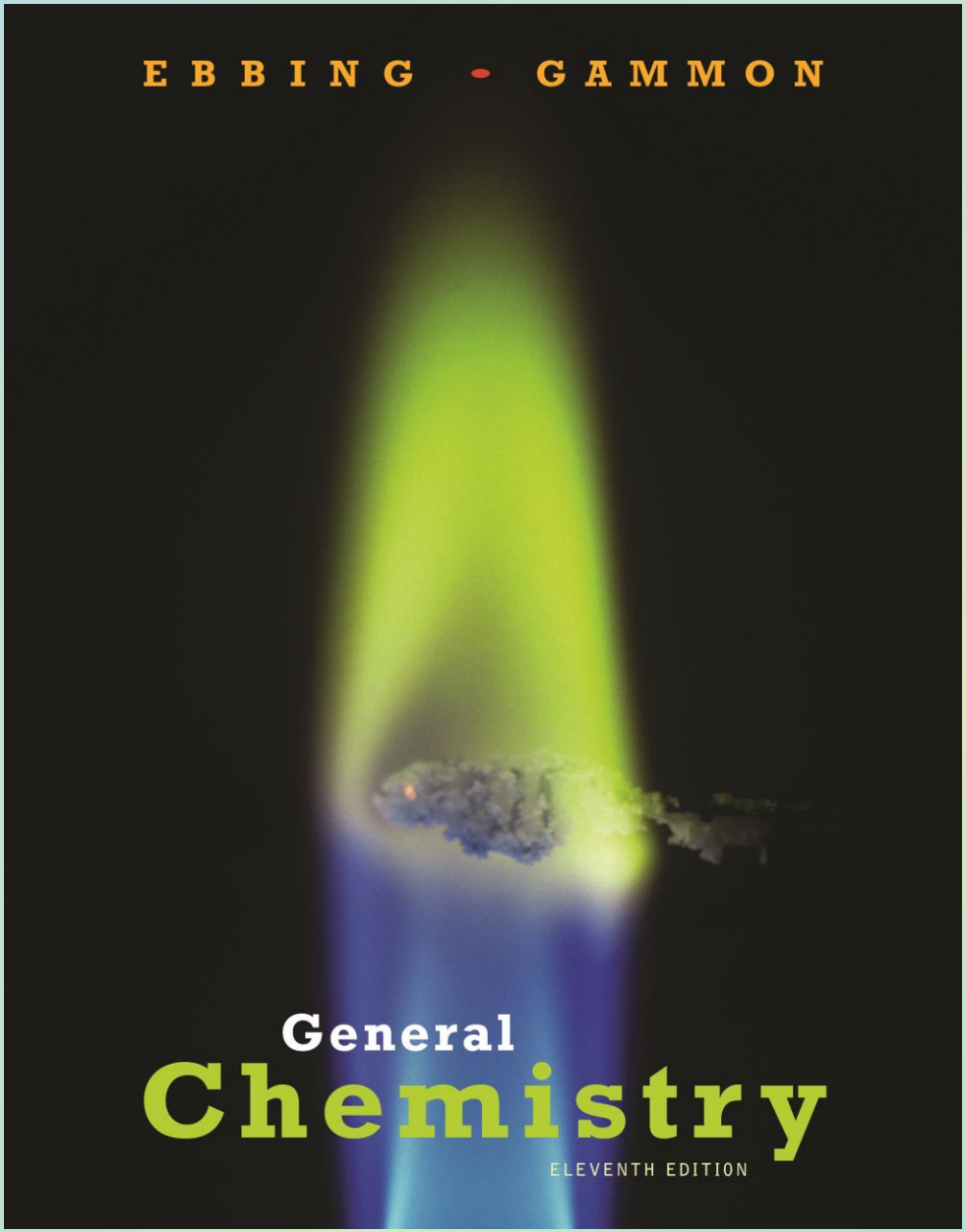
Draw the electron structure and satisfy the octet rule.



This accounts for 16 pairs of electrons. The remaining two pairs of electrons are placed on the Xe atom. This gives:



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Chapter 10 Molecular Geometry and Chemical Bonding Theory

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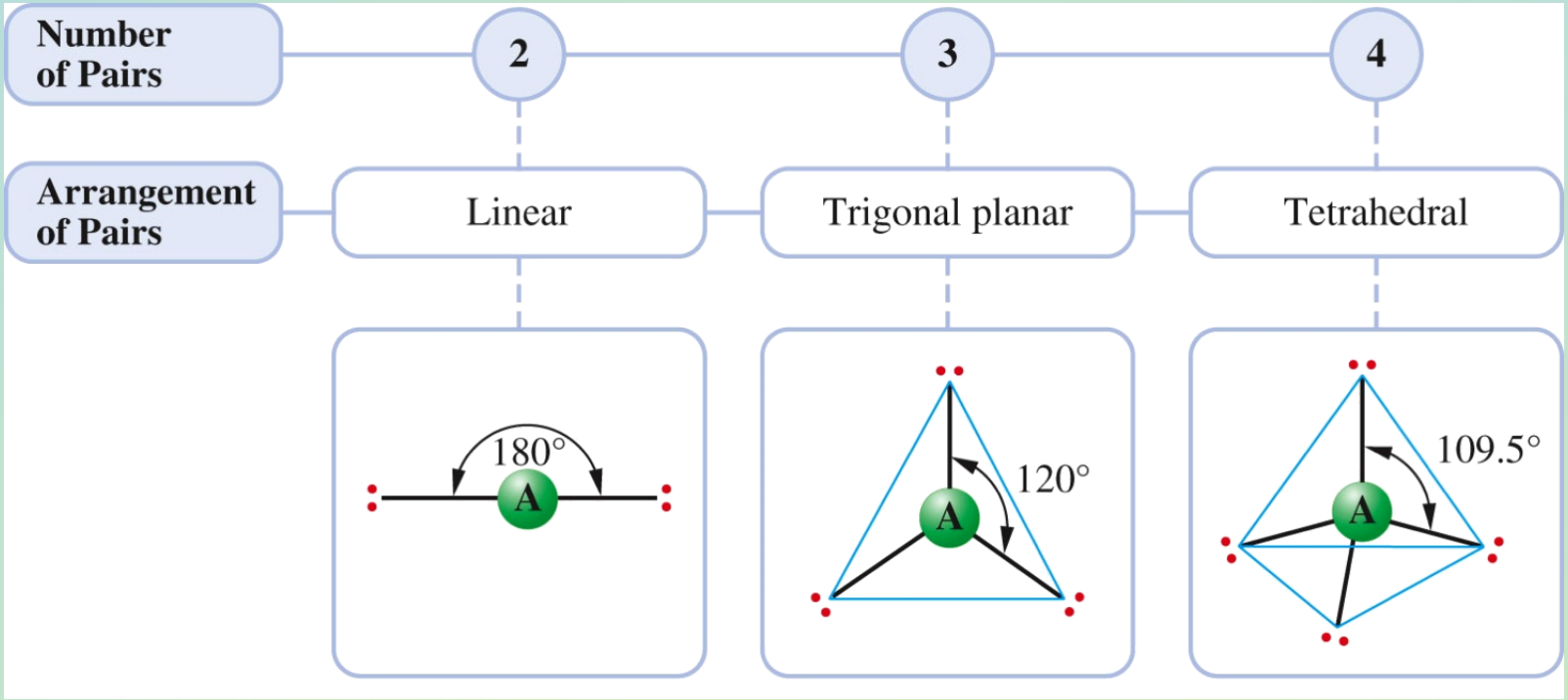
Molecular geometry is the general shape of a molecule, as determined by the relative positions of the atomic nuclei.

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The **valence-shell electron-pair repulsion (VSEPR) model** predicts the shapes of molecules and ions by assuming that the valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thereby minimizing electron pair repulsions.

The diagram on the next slide illustrates this.

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Two electron pairs are 180° apart (a linear arrangement).

Three electron pairs are 120° apart in one plane (a trigonal planar arrangement).

Four electron pairs are 109.5° apart in three dimensions (a tetrahedral arrangement).

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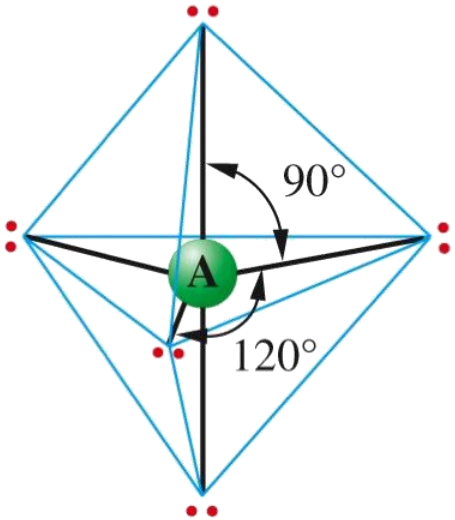
Five electron pairs are arranged with three pairs in a plane 120° apart and two pairs at 90° to the plane and 180° to each other (a trigonal bipyramidal arrangement).

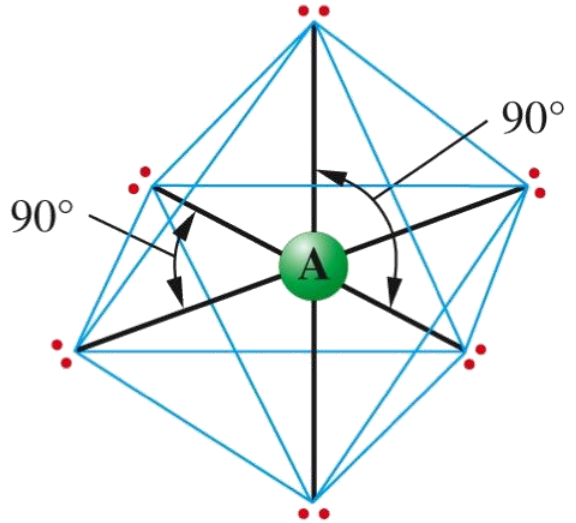
Six electron pairs are 90° apart (an octahedral arrangement).

This is illustrated on the next slide.

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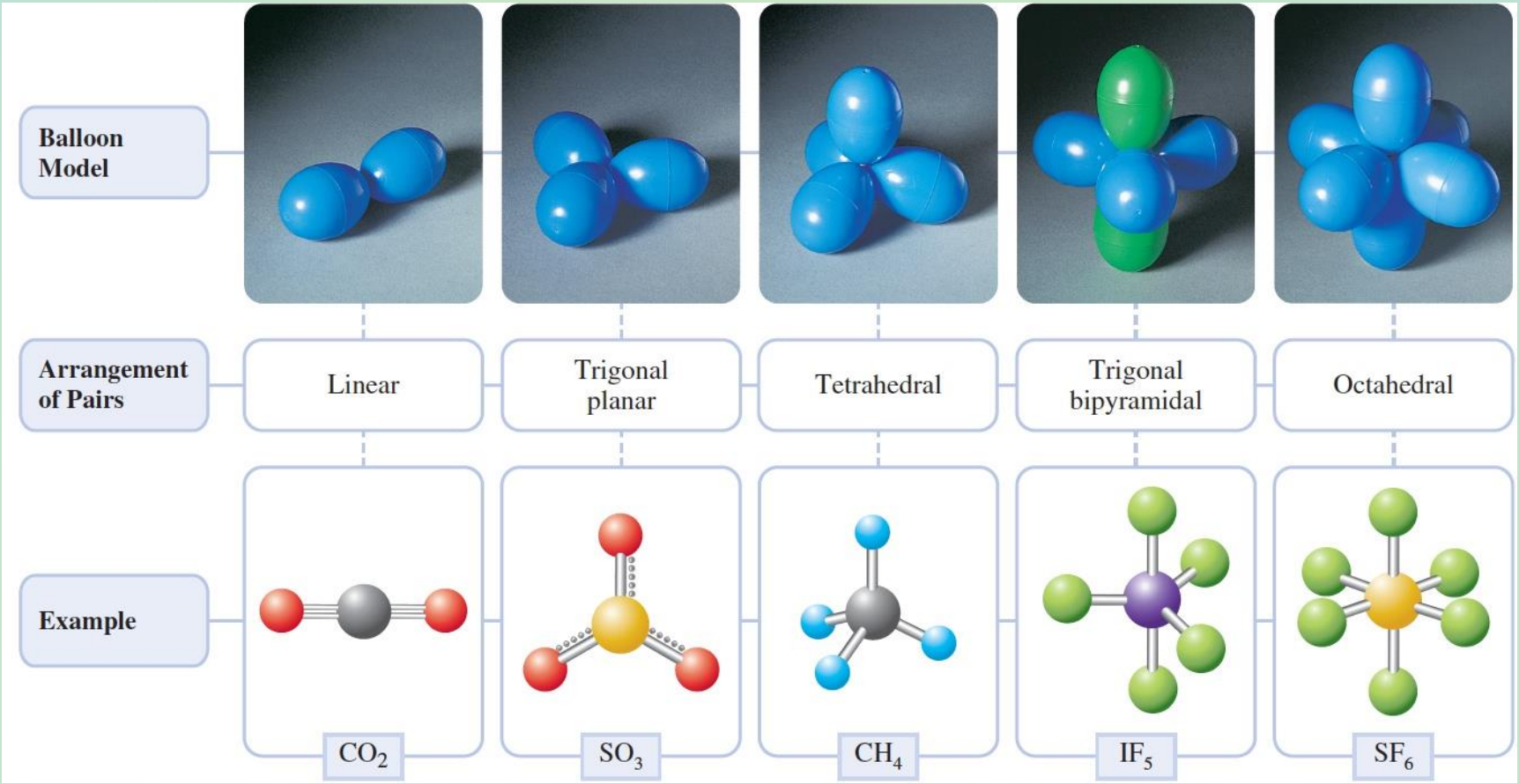
Number of Pairs	5	6
Arrangement of Pairs	Trigonal bipyramidal	Octahedral





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These arrangements are illustrated below with balloons and models of molecules for each.



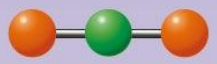
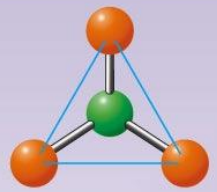
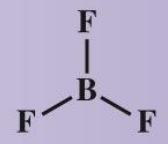
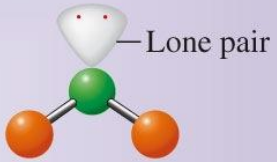
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Experimental determination of molecular geometry involves locating the positions of the atoms, not the electron pairs.

The direction in space of the bonding pairs gives the molecular geometry.

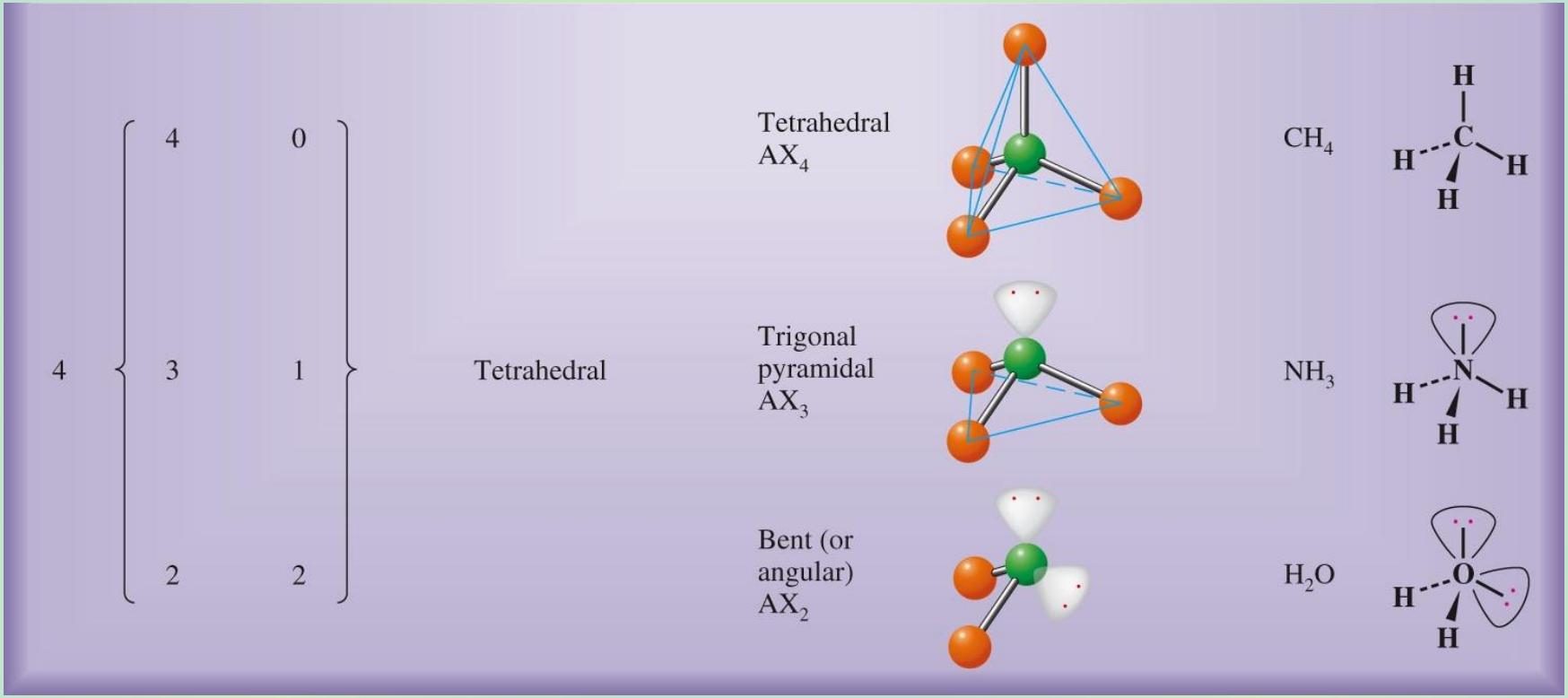
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The following diagrams illustrate molecular geometry and the impact of lone pairs on it for linear and trigonal planar electron-pair arrangements.

Electron Pairs: Total	Electron Pairs: Bonding	Electron Pairs: Lone	Arrangement of Pairs	Molecular Geometry		Example	
2	2	0	Linear	Linear AX_2		BeF_2	F—Be—F
3	3	0	Trigonal planar	Trigonal planar AX_3		BF_3	
	2	1		Bent (or angular) AX_2		SO_2	

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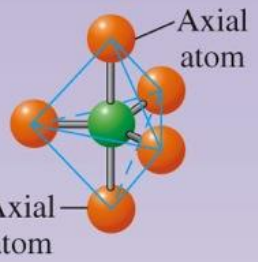
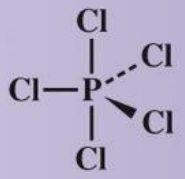
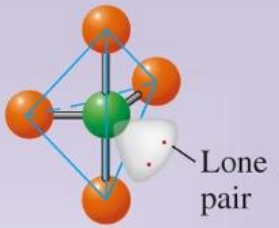
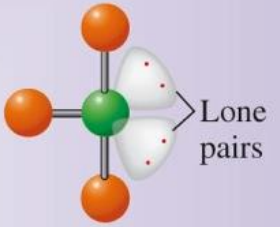
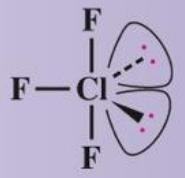
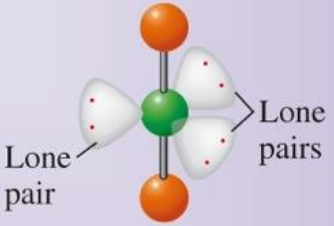
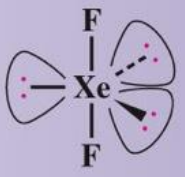
Molecular geometries with a tetrahedral electron-pair arrangement are illustrated below.



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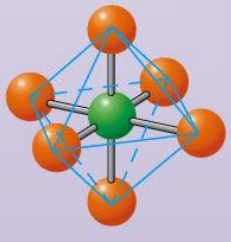
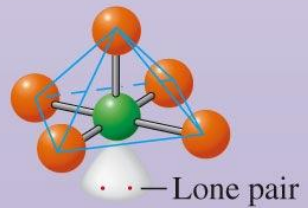
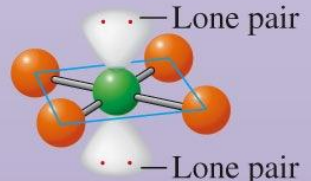
Molecular geometries for the trigonal bipyramidal electron-pair arrangement are shown on the next slide.

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Electron Pairs: Total	Bonding	Lone	Arrangement of Pairs	Molecular Geometry	Example
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal AX_5 	PCl_5 
	4	1		Seesaw (or distorted tetrahedron) AX_4 	SF_4 
	3	2		T-shaped AX_3 	ClF_3 
	2	3		Linear AX_2 	XeF_2 

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Molecular geometries for the octahedral electron-pair arrangement are shown below.

6	6	0	Octahedral	Octahedral AX_6		SF_6 
	5	1		Square pyramidal AX_5		IF_5 
	4	2		Square planar AX_4		XeF_4 

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The VSEPR model considers a double or triple bond as though it were one lone pair.

When resonance structures are required for the electron-dot diagram, you may choose any one to determine the electron-pair arrangement and the molecular geometry.

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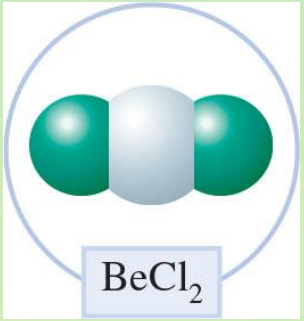
Predicting Molecular Geometry Using VSEPR

- Write the electron-dot formula from the formula.
- Based on the electron-dot formula, determine the number of electron pairs around the central atom (including bonding and nonbonding pairs).
- Determine the arrangement of the electron pairs about the central atom (Figure 10.2).
- Obtain the molecular geometry from the directions of the bonding pairs for this arrangement (Figure 10.4).

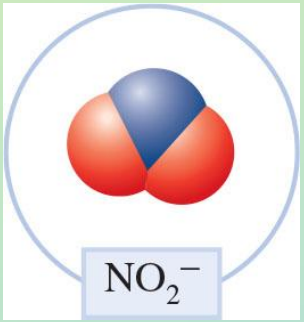
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Use the VSEPR model to predict the geometries of the following molecules:

a. $BeCl_2$



b. NO_2^-



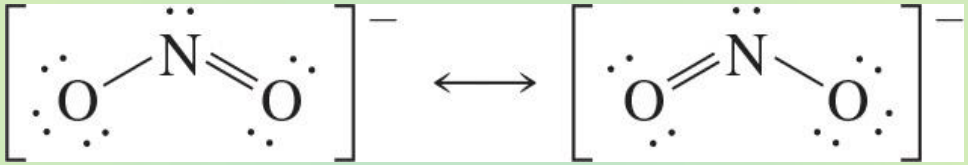
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a. Distribute the valence electrons to the skeleton structure of $BeCl_2$.



The two pairs on Be have a linear arrangement, indicating a linear molecular geometry.

b. Write the resonance description for the nitrite ion.



The molecular geometry of the nitrite ion is bent.

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An atom in a molecule is surrounded by four pairs of electrons: one lone pair and three bonding pairs. Describe how the four electron pairs are arranged about the atom. How are any three of these pairs arranged in space? What is the geometry about this central atom, taking into account just the bonded atoms?

The electron-pair arrangement is tetrahedral.

Any three pairs are arranged as a trigonal pyramid.

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Predicting Bond Angles

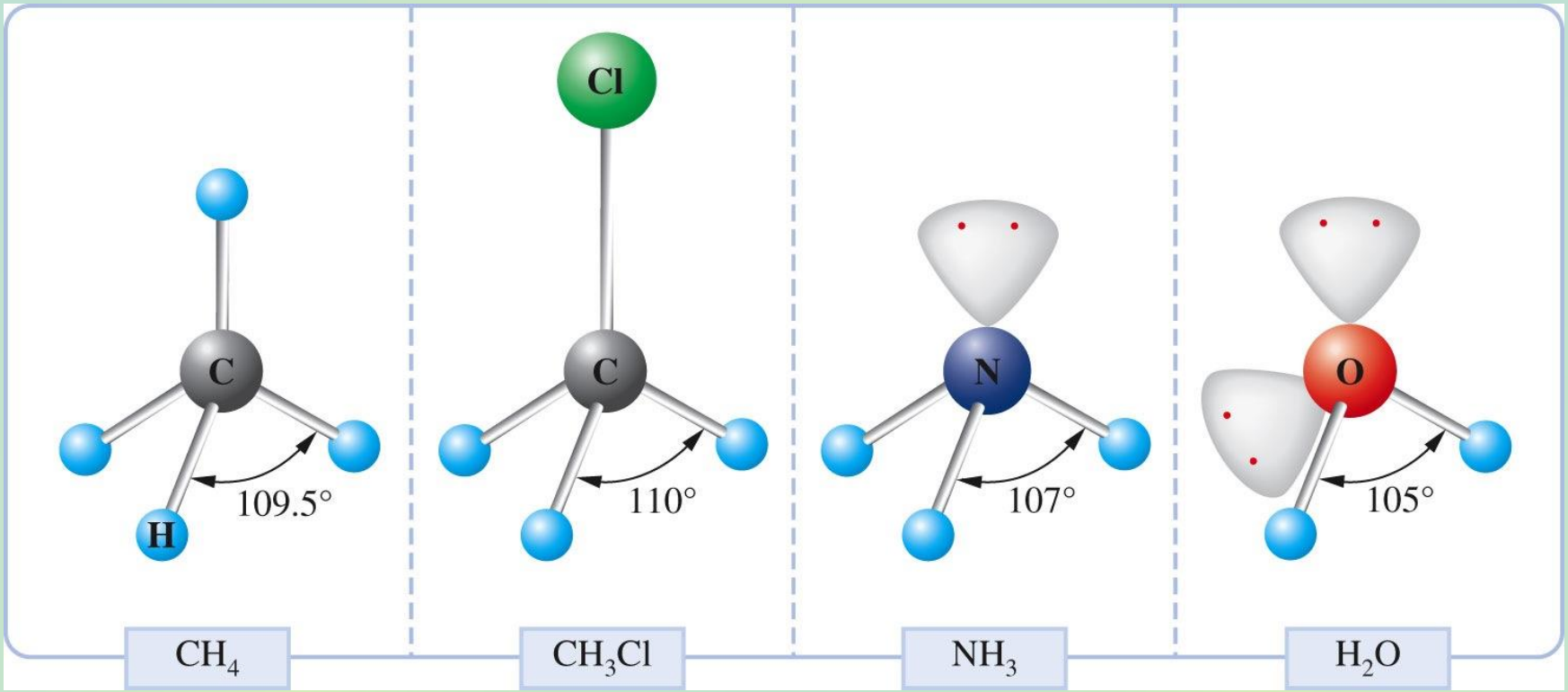
The angles 180°, 120°, 109.5°, and so on are the bond angles when the central atom has no lone pair and all bonds are with the same other atom.

When this is not the case, the bond angles deviate from these values in sometimes predictable ways.

Because a lone pair tends to require more space than a bonding pair, it tends to reduce the bond angles.

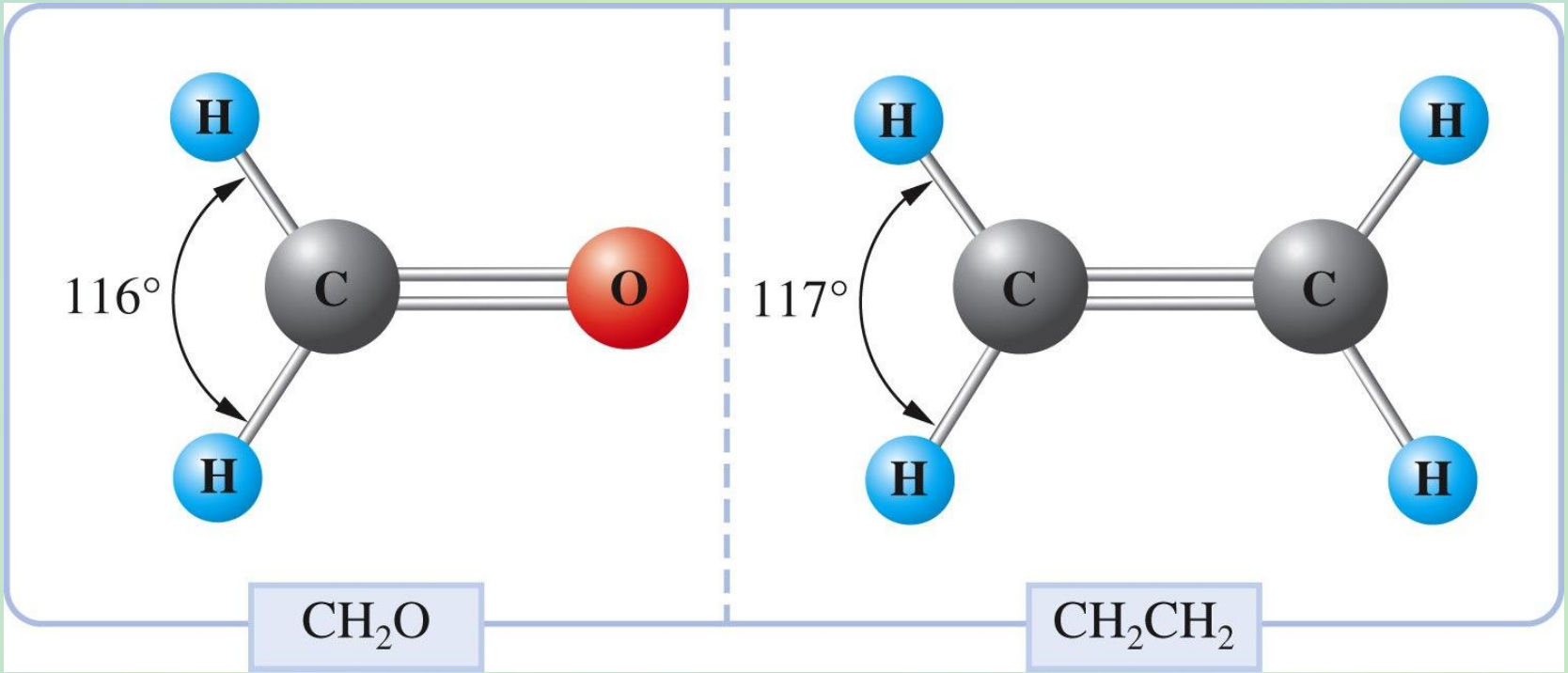
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A lone pair tends to require more space than a corresponding pair.



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Multiple bonds require more space than single bonds and, therefore, constrict the bond angle.



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Large atoms such as phosphorous can accommodate more than eight valence electrons.

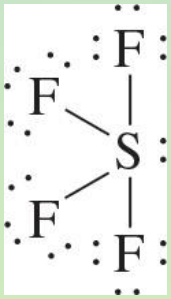
PCl_5 contains five electron pairs in its valence shell, making a trigonal pyramid. Its vertexes are not equivalent due to the different angles between the electron pairs.

Directions that form an axis through the central atom are called axial directions.

Directions that point to the corners of the equilateral triangle lying on a plane though the central atom are equilateral directions.

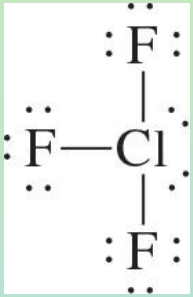
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Consider the SF_4 molecule. The Lewis electron-dot formula is:



The molecule possesses a seesaw (distorted tetrahedral) geometry.

ClF_3 has a T-shaped geometry.

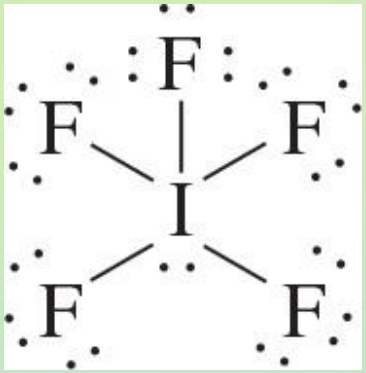


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XeF_2 has a linear geometry.



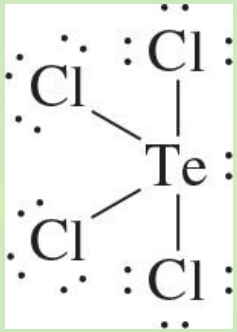
IF_5 has a square pyramidal geometry.



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What do you expect for the geometry of tellurium tetrachloride, $TeCl_4$?

The electron dot formula is:



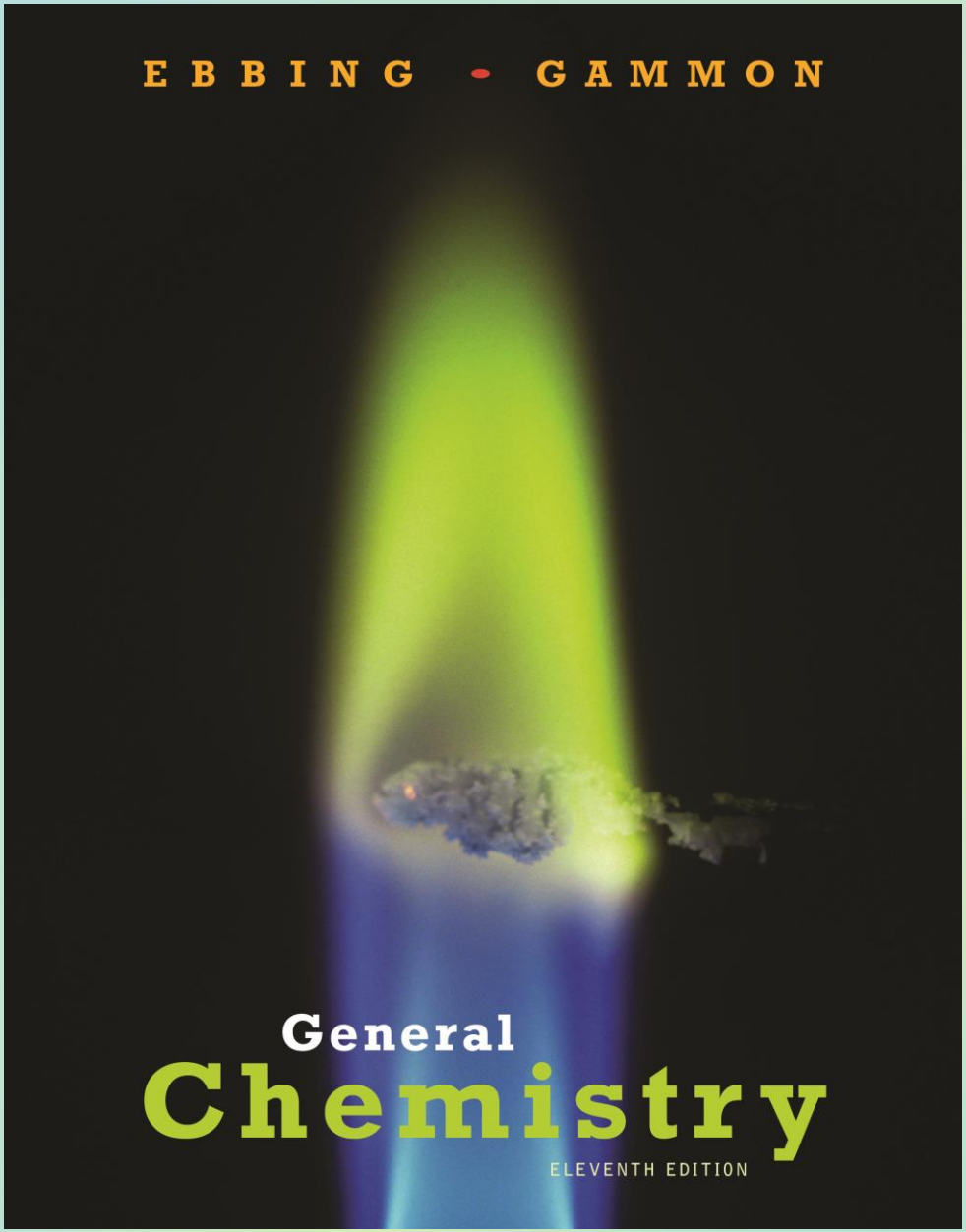
The arrangement of the electron pairs is trigonal bipyramidal.

$TeCl_4$ has a seesaw molecular geometry.

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For large molecules, the VSEPR model is applied by breaking their corresponding electron-dot formulas into smaller sections.

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Chapter 11
States of Matter: Liquids and Solids

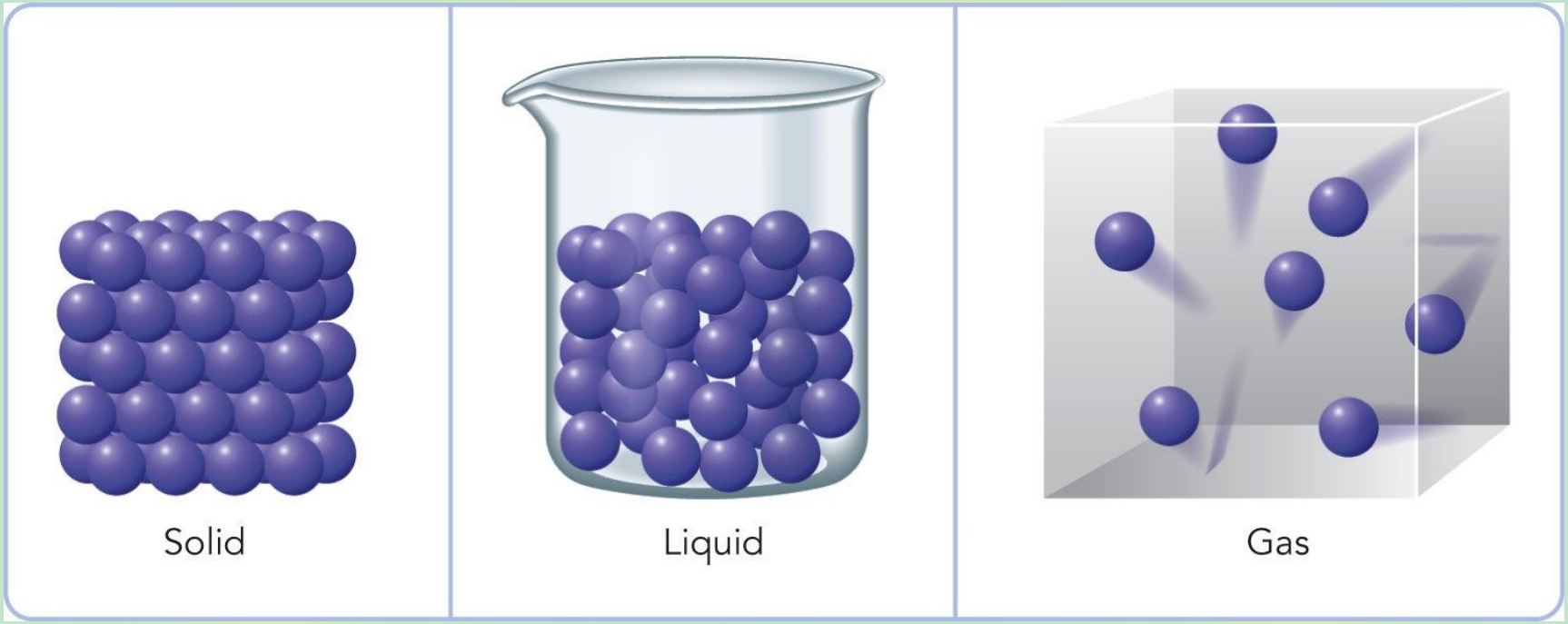
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Comparing Gases, Liquids, and Solids

Gases are compressible fluids.

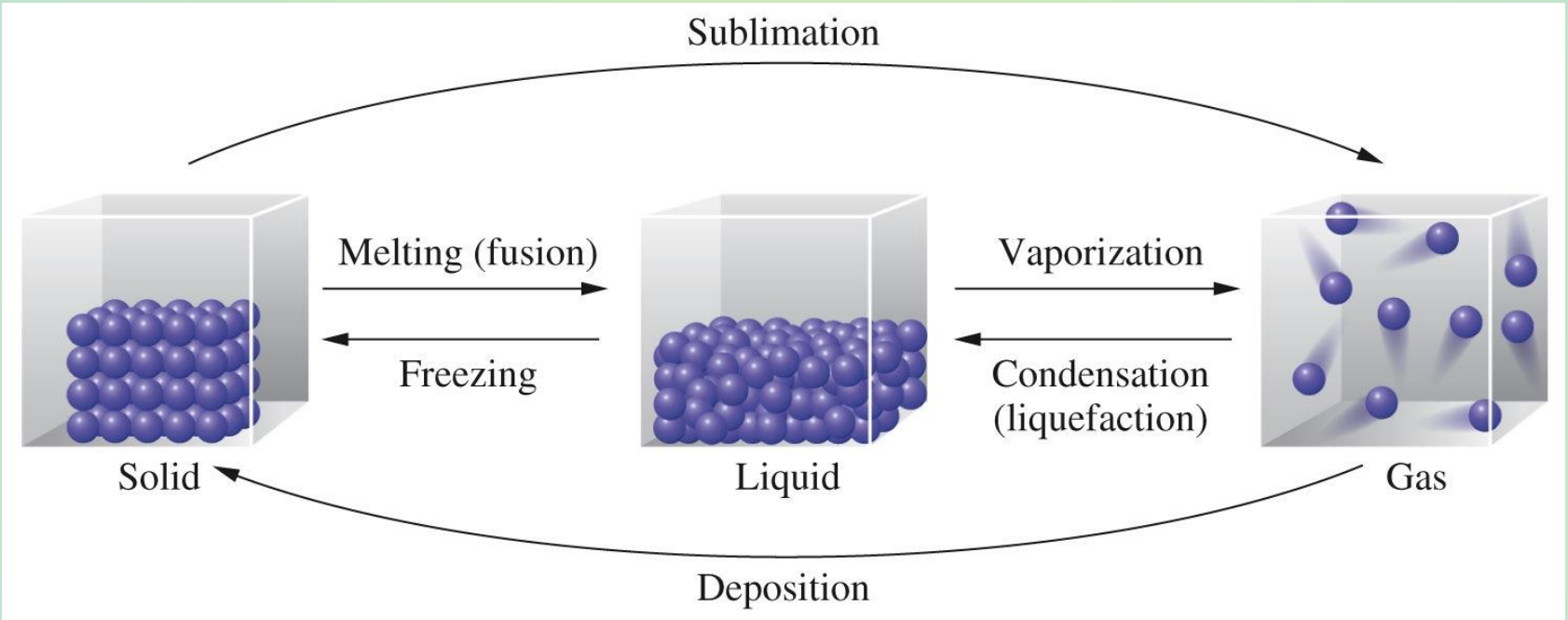
Liquids are relatively incompressible fluids.

Solids are nearly incompressible and rigid.



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A **change of state** or **phase transition** is a change of a substance from one state (solid, liquid, gas) to another. The specific name or names for each of these transitions are given below.



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Melting is the change of a solid to the liquid state.

Freezing is the change of a liquid to the solid state.

Vaporization is the change of a solid to or a liquid to the vapor.

Sublimation is the change of a solid directly to the vapor.

Condensation is the change of a gas to either the liquid or the solid state.

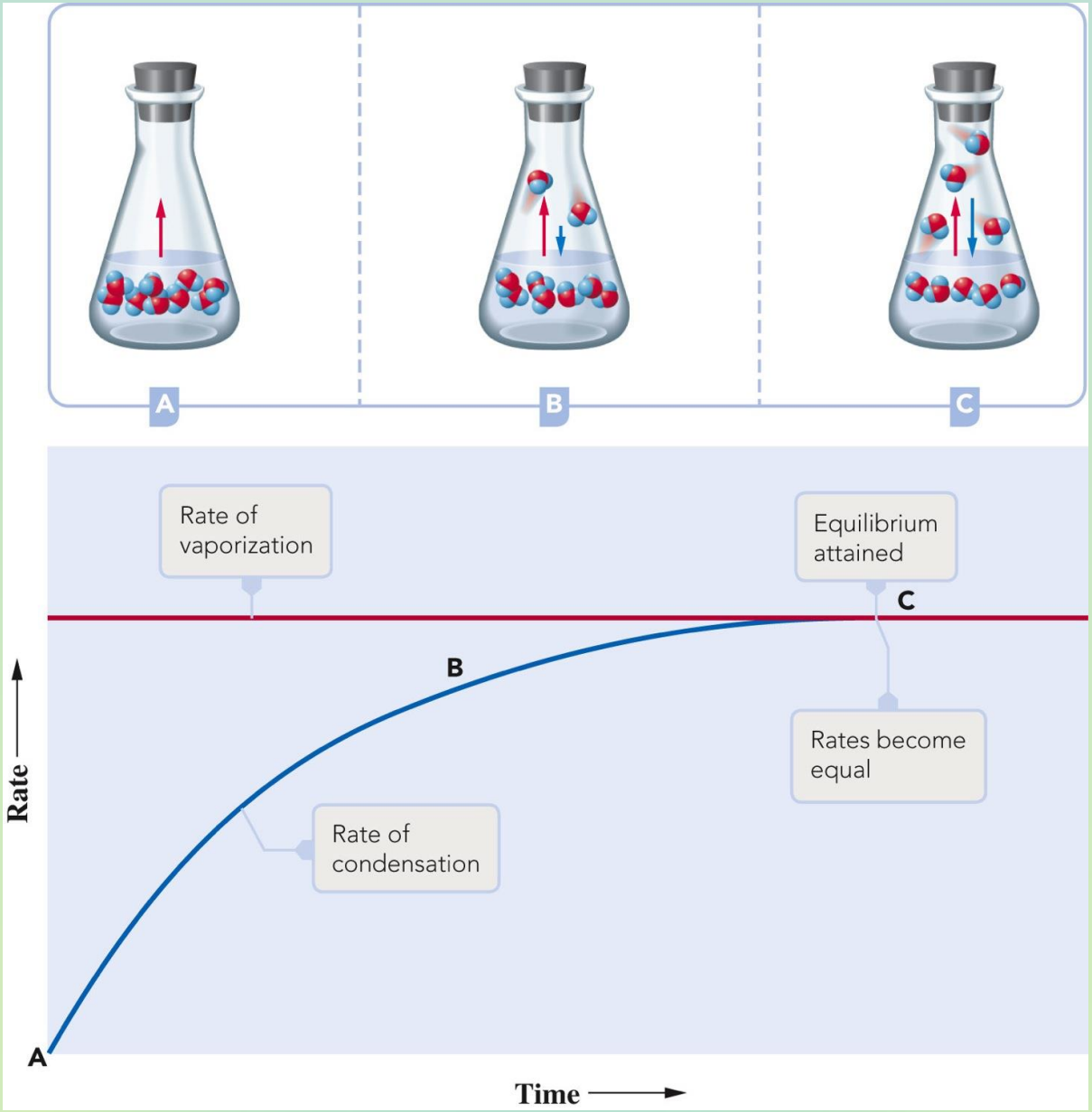
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The **vapor pressure** of a liquid at a particular temperature is the partial pressure of the vapor over the liquid measured at equilibrium.

When a liquid is placed in a closed vessel, condensation and vaporization occurs till the systems reaches equilibrium.

At equilibrium, evaporation and condensation occur at the same rate. This situation, which is called a dynamic equilibrium, is illustrated on the next slide.

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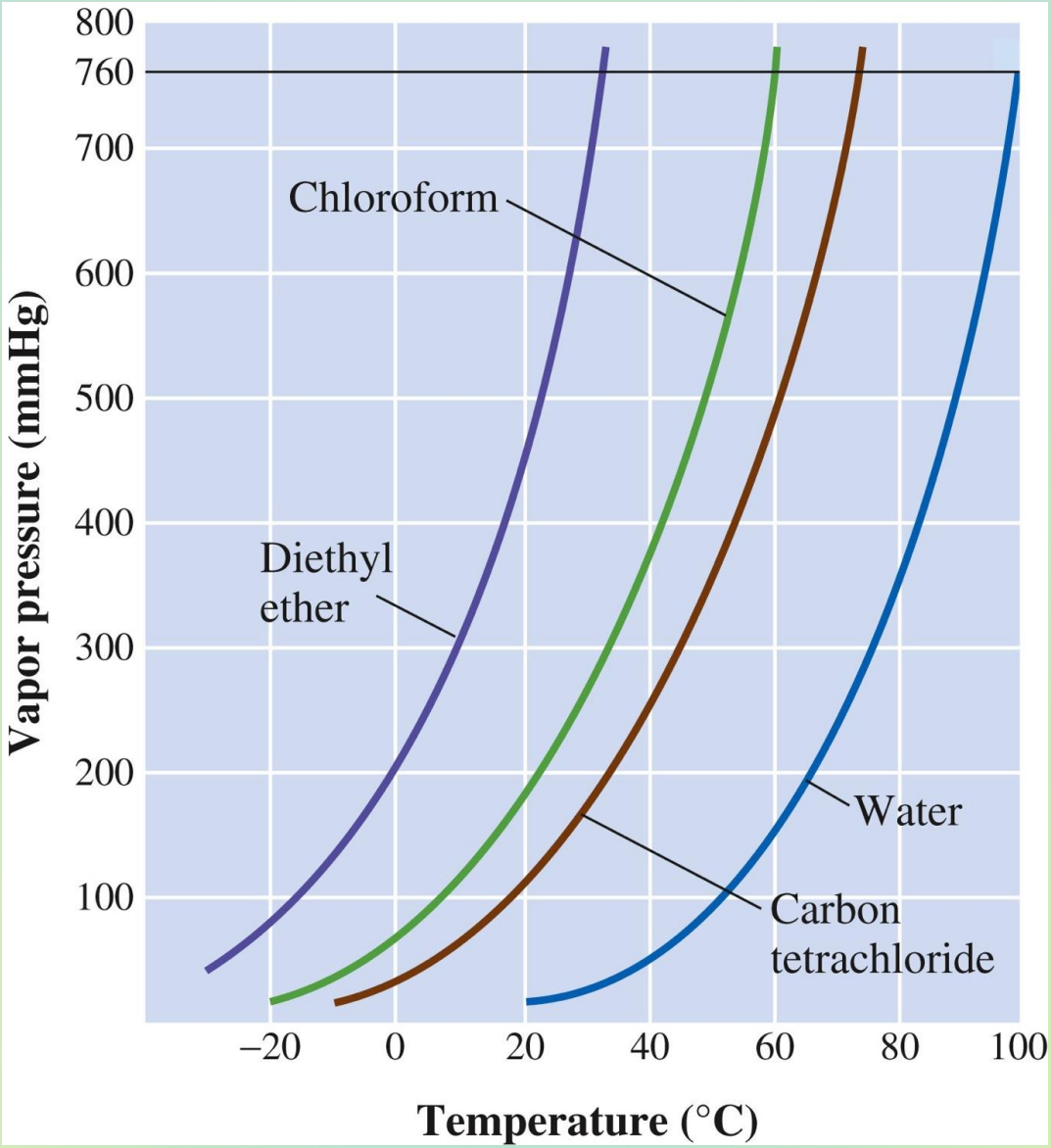
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The vapor pressure depends on the temperature. Note that as temperature increases, vapor pressure increases.

Liquids and solids with relatively high vapor pressure at normal temperatures are considered volatile.

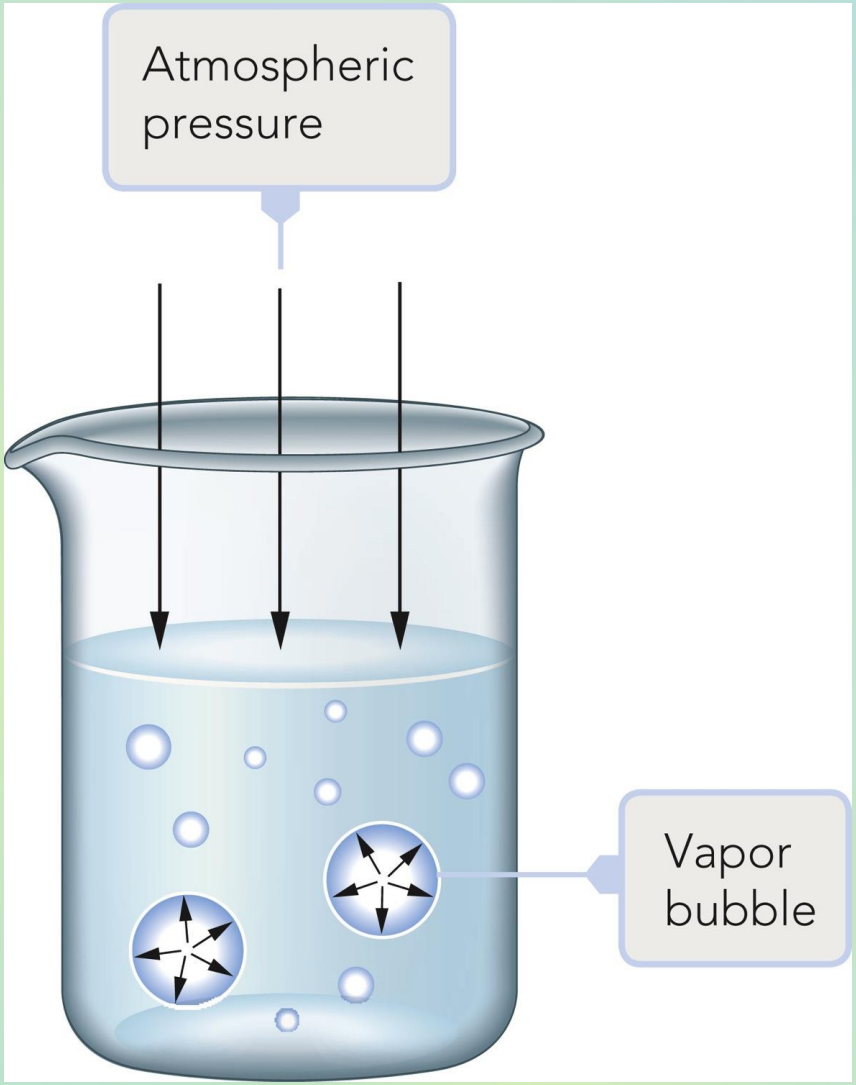
high vaper presser

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The **boiling point** is the temperature at which the vapor pressure is equal to the pressure on the liquid, usually atmospheric pressure. When vapor pressure equals atmospheric pressure, bubbles of gas form within the liquid, as illustrated in the figure.



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When the pressure on the liquid increases, as is the case with a pressure cooker, the boiling point increases.

Conversely, when the pressure on the liquid decreases, as is the case at high altitude, the boiling point decreases.

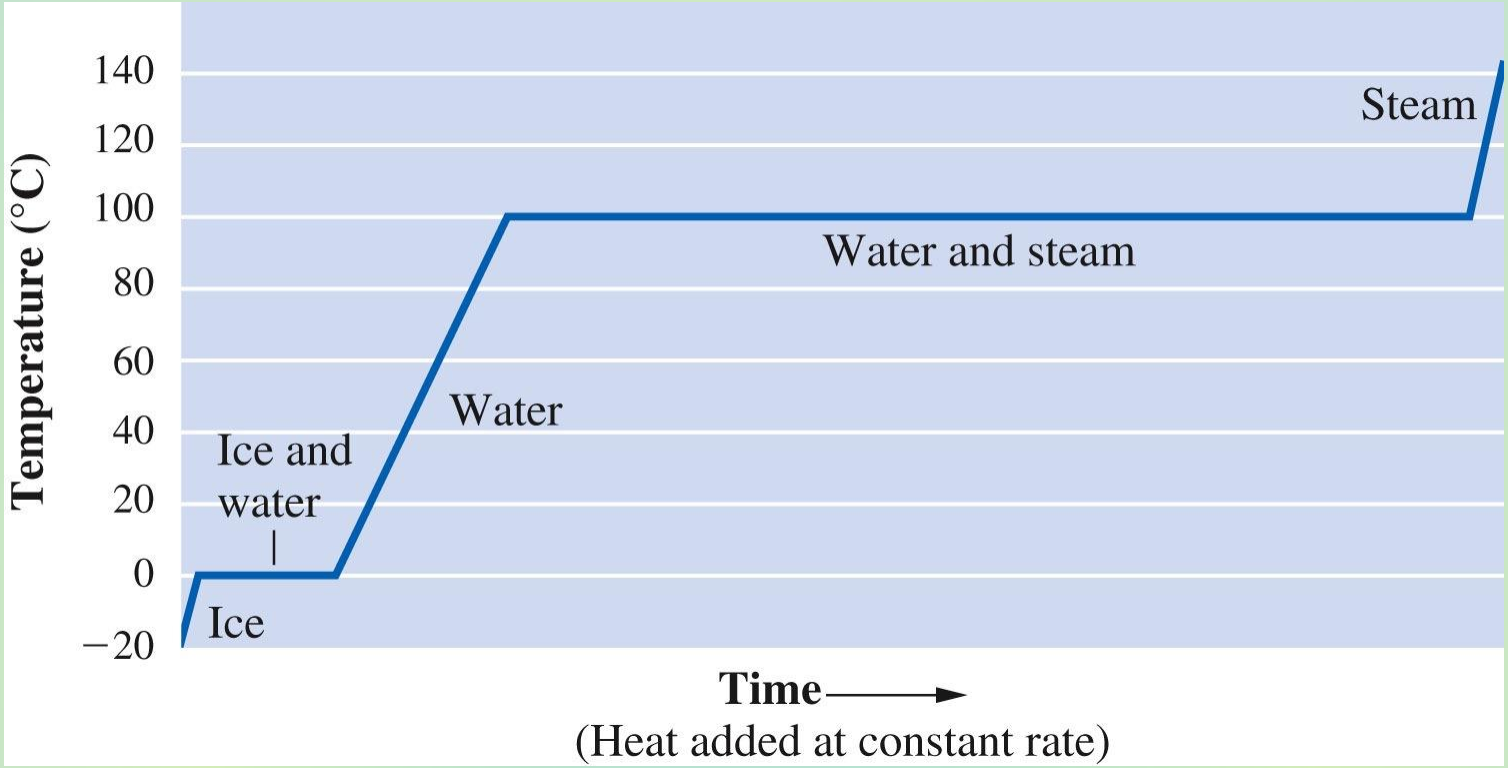
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The **freezing point** is the temperature at which a pure liquid changes to a crystalline solid (or freezes).

The **melting point** is the temperature at which a crystalline solid changes to a liquid (or melts).

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Any change of state requires that energy be added to or removed from the system. As shown in the graph, for water, there are two regions that remain at the same temperature even as heat is added. Those represent regions of phase change.



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The **heat of fusion**, ΔH_{fus}, is the heat needed to melt a solid. It is given in kJ/mol.

For ice, the phase change is represented by

$$H_2O(s) \longrightarrow H_2O(l); \Delta H_{fus} = 6.01 \text{ kJ/mol}$$

The **heat of vaporization**, ΔH_{vap}, is the heat needed to vaporize a liquid. It is given in kJ/mol.

For water, the phase change is represented by

$$H_2O(l) \longrightarrow H_2O(g); \Delta H_{vap} = 40.7 \text{ kJ/mol}$$

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A particular refrigerator cools by evaporating liquefied dichlorodifluoromethane, CCl_2F_2. How many kilograms of this liquid must be evaporated to a freeze tray of water at 0° C to heat ice at 0° C? The mass of water is 525 g, the heat of fusion of ice is 6.01 kJ/mol, and the heat of vaporization of dichlorodifluoroethane is 17.4kJ/mol

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The heat that must be removed to freeze 525 g of water at 0° C is

$$525\ \text{g}\ H_2O \times \frac{1\ \text{mol}\ H_2O}{18.0\ \text{g}\ H_2O} \times \frac{-6.01\ \text{kJ}}{1\ \text{mol}\ H_2O} = -175\ \text{kJ}$$

The mass of CCl_2F_2 vaporized to absorb the heat is:

$$175\ \text{kJ} \times \frac{1\ \text{mol}\ CCl_2F_2}{17.4\ \text{kJ}} \times \frac{121\ \text{g}\ CCl_2F_2}{1\ \text{mol}\ CCl_2F_2} = 1.22 \times 10^3\ \text{g}\ CCl_2F_2$$

1.22 kg of dichlorodifluoromethane must be evaporated.

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Shown to the right is a representation of a closed container in which you have just placed 10 L of H_2O. This is the starting point in time, $t = 0$.

Assume that all of the water is in the liquid phase at this point. The dots represent a few of the H_2O molecules.



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Consider a time t = 1, when some time has passed but the system has not reached equilibrium.

1. How will the level of the liquid H_2O compare to that at t =0?
2. How will the vapor pressure in the flask compare to that at t = 0?
3. How will the number of H_2O molecules in the vapor state compare to that at t = 0?
4. How does the rate of evaporation in this system compare to the rate of condensation?

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Time $t = 1$:

1. The liquid level will be lower than at $t = 0$.
2. The vapor pressure will be higher than at $t = 0$.
3. There will be more molecules of H_2O in the vapor state than at $t = 0$.
4. The rate of evaporation is greater than the rate of condensation.

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Consider a time $t = 2$, when enough time has passed for the system to reach equilibrium.

1. How will the level of the liquid H_2O compare to that at $t = 1$?
2. How will the vapor pressure in the flask compare to that at $t = 1$?
3. How will the number of H_2O molecules in the vapor state compare to that at $t = 1$?
4. How does the rate of evaporation in this system compare to the rate of condensation?

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Time t = 2 (the system is at equilibrium):

1. The liquid level will be lower than at t = 1.
2. The vapor pressure will be higher than at t = 1.
3. There will be more molecules of H_2O in the vapor state than at t = 1.
4. The rate of evaporation is equal to the rate of condensation.

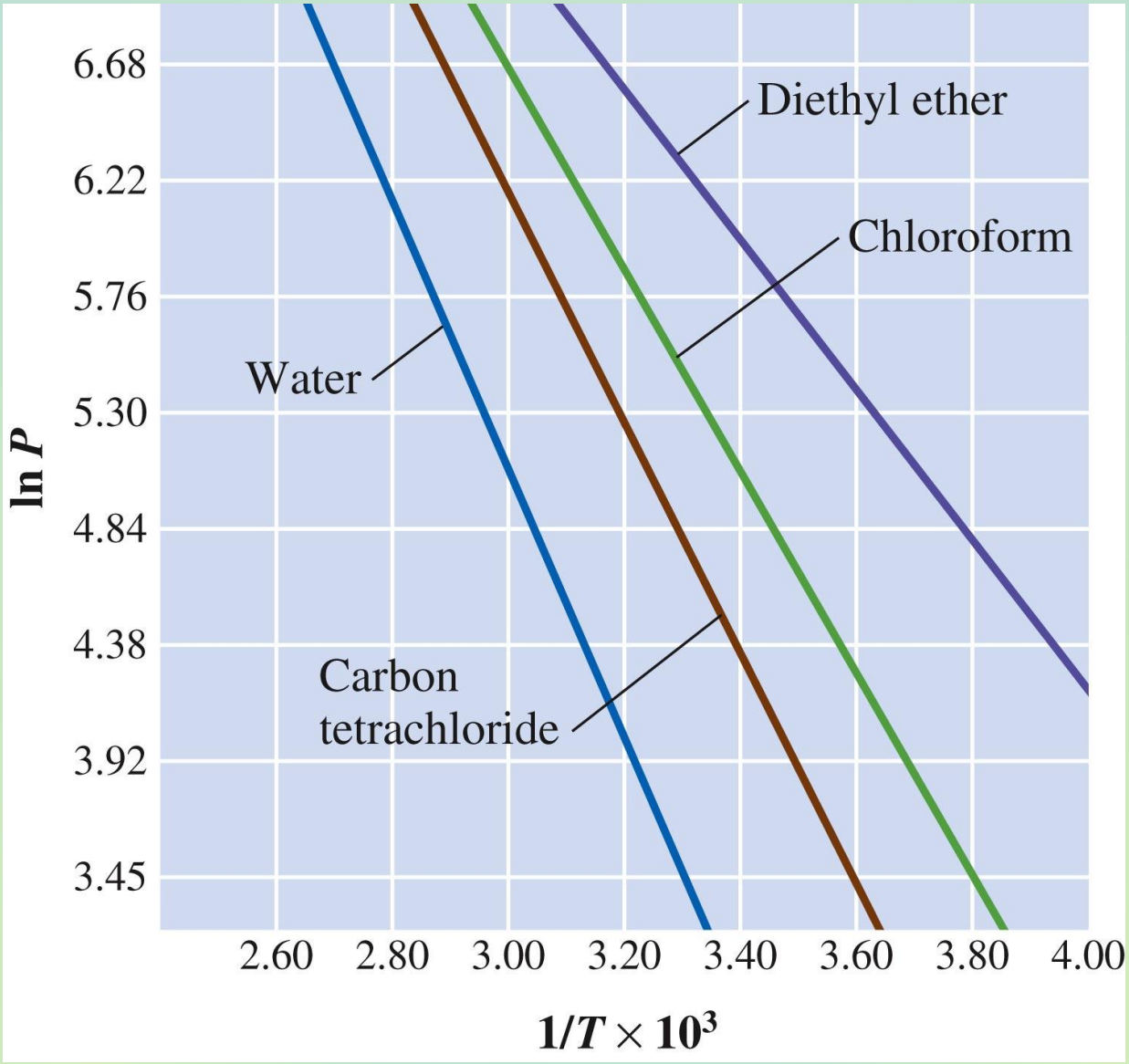
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When vapor pressure is plotted versus temperature, a curve is obtained.

When the natural log (ln P) of the vapor pressure is plotted against the reciprocal of temperature ($1/T$), a straight-line graph is obtained.

The next slide shows this graph for four liquids.

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According to the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This equation can be used to find the vapor pressure, the heat of vaporization, or the temperature.

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Estimate the vapor pressure of water at 85°C. Note that the normal boiling point of water is 100°C and that its heat of vaporization is 40.7 kJ/mol.

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Substitute the givens values in the Clausius-Clapeyron equation.

$$\ln\left(\frac{P_2}{760\ \text{mmHg}}\right) = \frac{40.7 \times 10^3\ \text{J/mol}}{8.31\ \text{J/(K}\cdot\text{mol)}}\left(\frac{1}{373\ \text{K}} - \frac{1}{358\ \text{K}}\right)$$

$$= (4898\ \text{K}) \times (-1.123 \times 10^{-4}\ \text{/K}) = -0.550$$

In order to solve the equation for P_2, take the antilogarithm of both sides of the equation.

$$\frac{P_2}{760\ \text{mmHg}} = \text{antiln}(-0.550)$$

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Therefore, the antilogarithm is $e^{-0.550} = 0.577$.

Thus,

$$\frac{P_2}{760\ \text{mmHg}} = 0.577$$

$$P_2 = 0.577 \times 760\ \text{mmHg} = \boxed{439\ \text{mmHg}}$$

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Calculate the heat of vaporization of diethyl ether, $C_4H_{10}O$, from 400 mmHg at 18° C

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Substitute the givens values in the Clausius-Clapeyron equation.

$$\ln\left(\frac{760\ \text{mmHg}}{400\ \text{mmHg}}\right) = \frac{\Delta H_{vap}}{8.31\ \text{J/(K}\cdot\text{mol)}} \times \left(\frac{1}{291\ \text{K}} - \frac{1}{308\ \text{K}}\right)$$

$$0.642 = (2.28 \times 10^{-5}) \times \Delta H_{vap}\ /\ (\text{J/mol})$$

Therefore

$$\Delta H_{vap} = 2.82 \times 10^{4}\ \text{J/mol}$$

(28.2 kJ/mol)

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A phase **diagram** is a graphical way to summarize the conditions under which the various states of a substance are stable.

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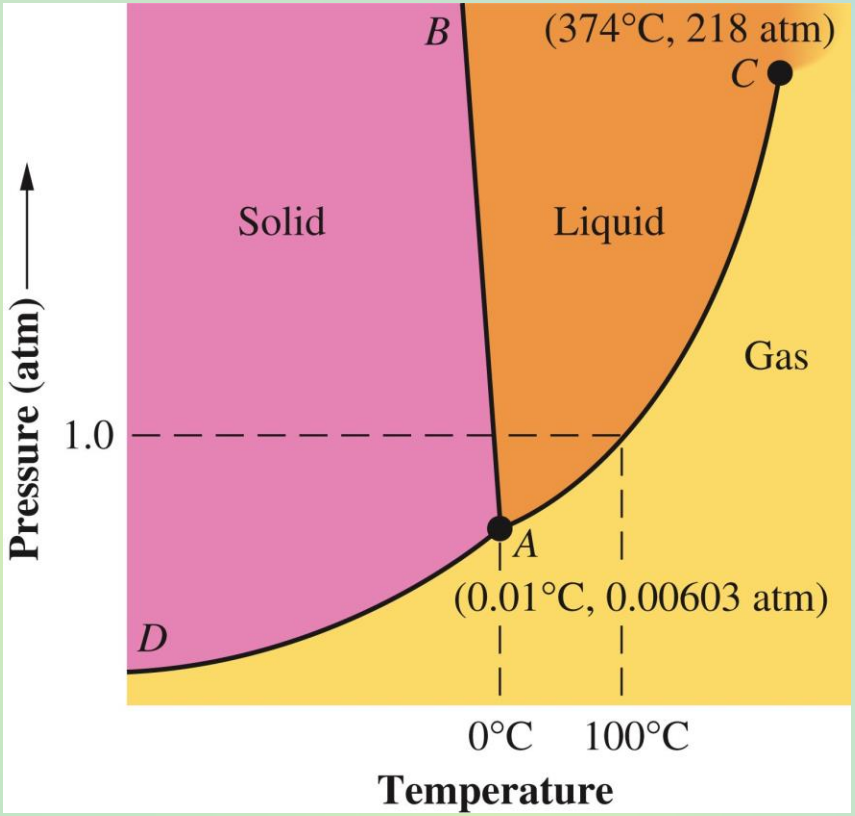
In a phase diagram, phases are separated by curves that represent equilibrium between those phases.

The triple point is the point where all three phases coexist in equilibrium.

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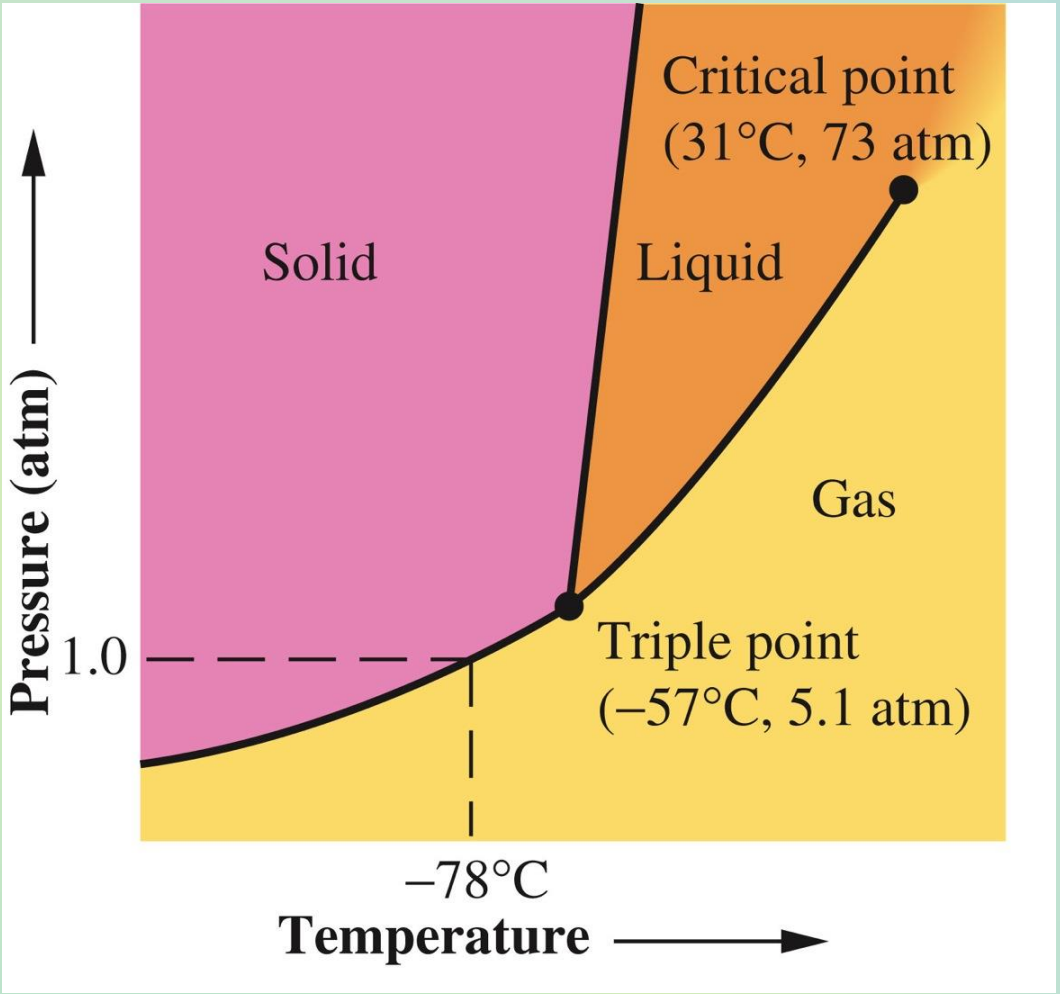
The phase diagram for water illustrates the components described on the previous slide.

The slope of the *AB* line, which shows the equilibrium between solid and liquid, slants to the left. This is because the density of the liquid is greater than the density of the solid.



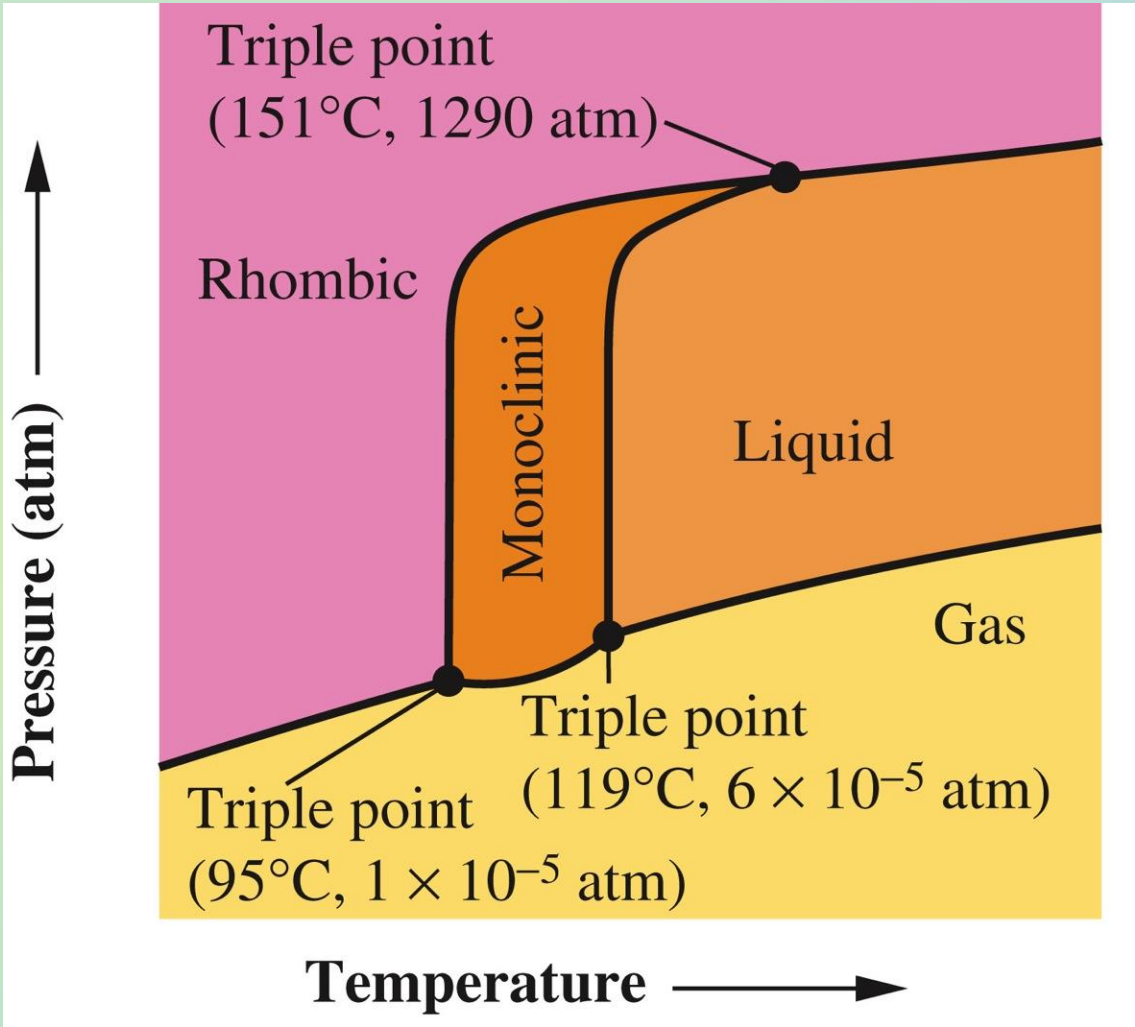
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Carbon dioxide undergoes sublimation when warmed at 1 atm.



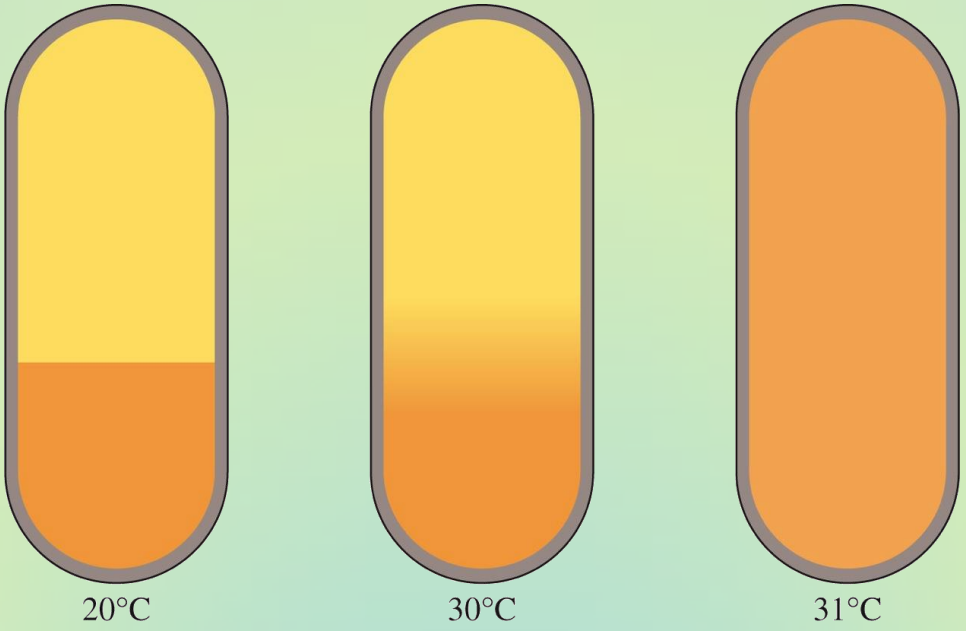
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The phase diagram of sulfur displays three triple points. One of them involve two different forms of sulfur as well as the vapor.



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The critical point gives the temperature (critical temperature, T_C) at which the liquid state can no longer exist and the pressure at that temperature (critical pressure). Above this temperature and pressure, there is only one state, a supercritical fluid. This is illustrated below for CO_2, for which $T_C = 31^\circ$ C.



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The critical temperatures of ammonia and nitrogen are 132°C and –147°C respectively. Explain why ammonia can be liquefied at room temperature by merely compressing the gas to a high enough pressure, whereas the compression of nitrogen requires lower temperatures for liquefaction to occur.

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The critical temperature of ammonia is well above room temperature. If compressed at room temperature, it will liquefy.

Nitrogen has a critical temperature well below room temperature. It cannot be liquefied by compression unless the temperature is below the critical temperature.

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When camping at high altitude, you need to pay particular attention to changes in cooking times for foods that are boiled in water. If you like eggs that are boiled for 10 minutes near sea level, would you have to cook them for a longer or a shorter time at 3200 m to get the egg you like? Be sure to explain your answer.

At 3200 m, the pressure on the liquid is less than at sea level, which means the boiling point is lower. The eggs will need to be cooked longer at the higher altitude.

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To explain the properties of liquids that we've just studied, we need to learn about **intermolecular forces**—the forces of interaction between molecules.

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Heat of vaporization is an indicator of intermolecular force.

Neon is normally a gas, but it liquefies at a temperature of –246° C at 1 atm of pressure. The heat of vaporization for liquid neon is 1.77 kJ/mol.

The ΔH_{vap} for neon is in part the energy needed to push back the atmosphere when the vapor forms (0.23 kJ/mol) and in part the energy needed to overcome intermolecular attractions (1.54 kJ/mol).

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Three types of intermolecular forces exist between neutral molecules or atoms: dipole-dipole forces, London forces, and hydrogen bonding forces.

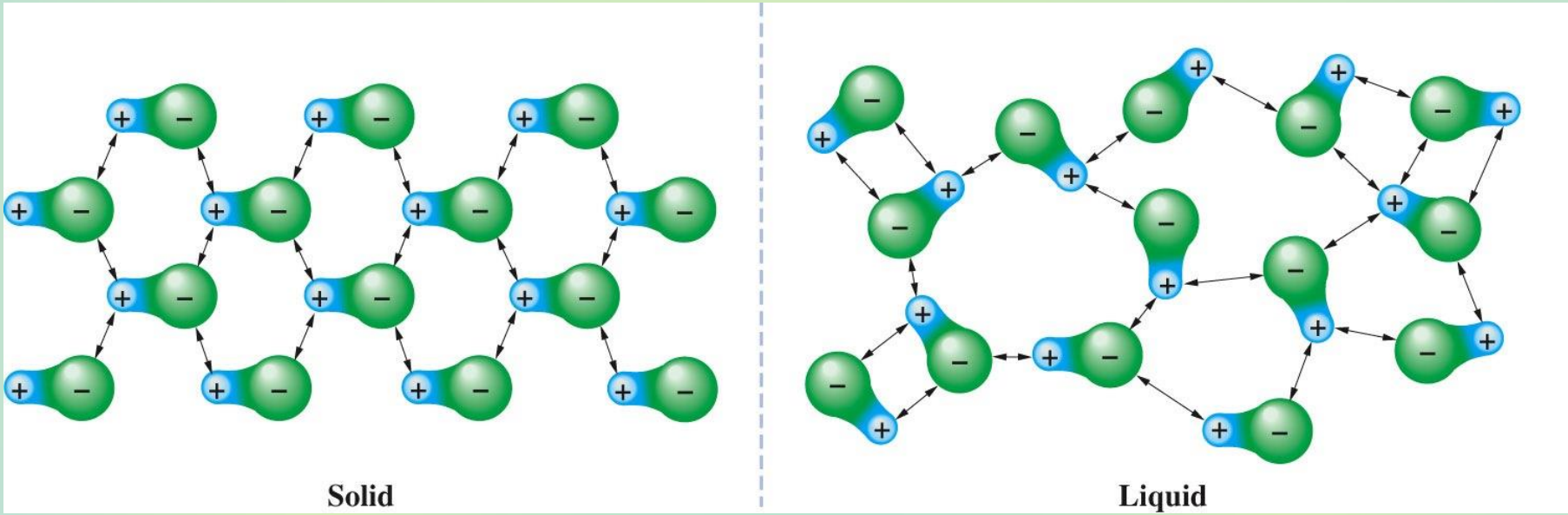
Table 11.3 Types of Intermolecular and Chemical Bonding Interactions

Type of Interaction	Approximate Energy (kJ/mol)
Intermolecular	
Van der Waals	
(dipole–dipole, London)	0.1 to 10
Hydrogen bonding	10 to 40
Chemical bonding	
Ionic	100 to 1000
Covalent	100 to 1000

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The term **van der Waals forces** is a general term that includes both dipole-dipole forces and London forces.

Polar molecules exhibit dipole-dipole forces that result in alignment of the molecules. This phenomenon is illustrated below for solid and liquid HCl.

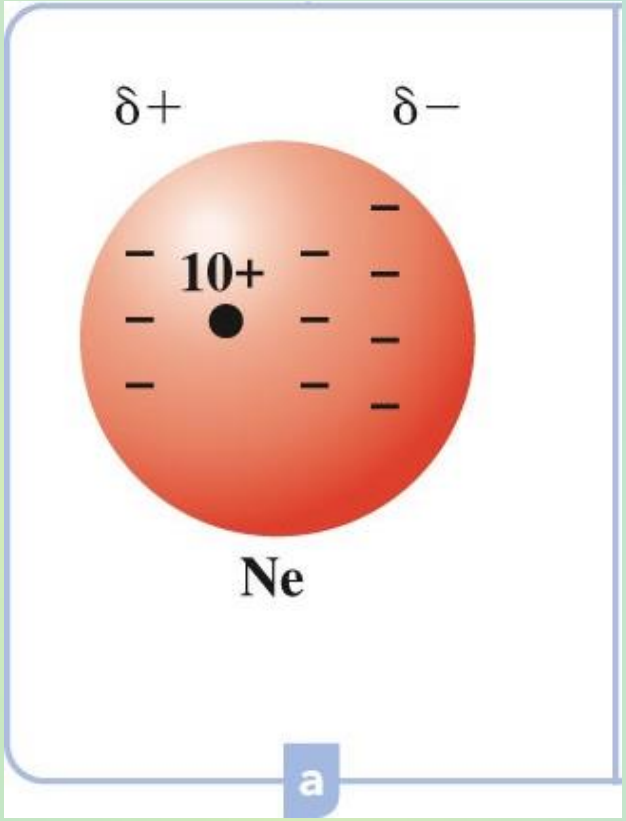


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In nonpolar molecules, there is no dipole-dipole force, yet there is still a force of attraction. In 1930, Fritz London explained this relationship with what we now call the London forces.

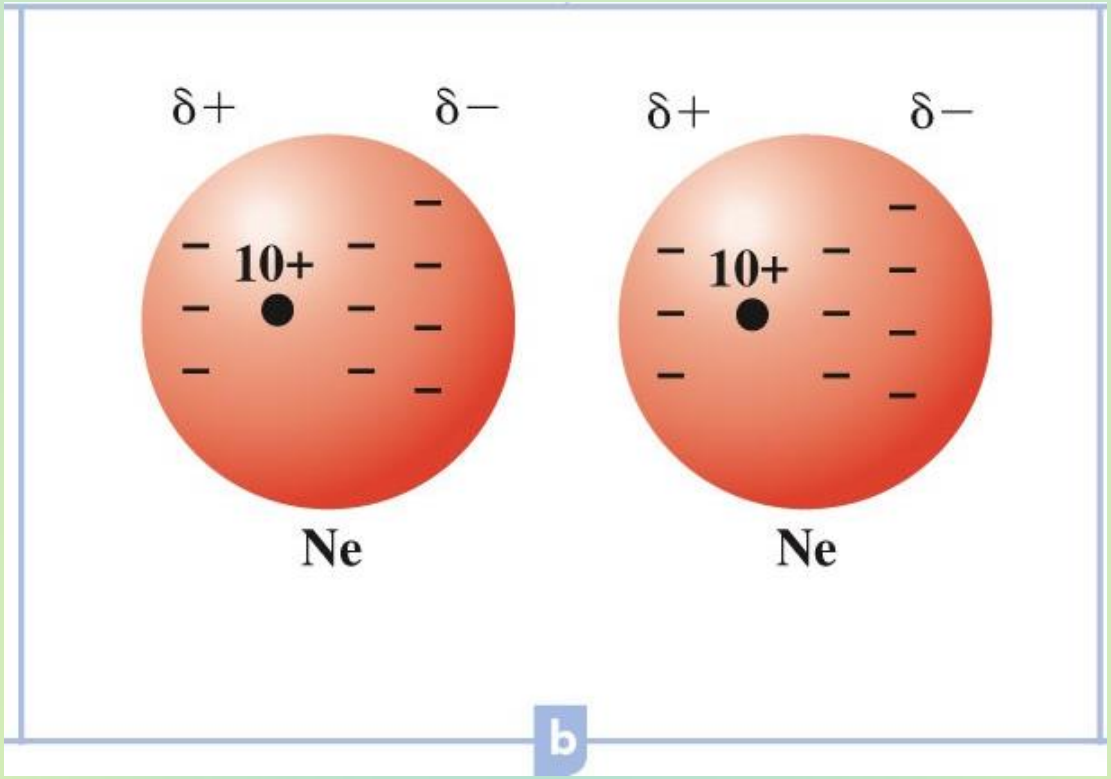
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In a neon atom, though the electrons are spherically distributed over time, at any instant, one side of the nucleus may posses a higher amount of electrons. The atom becomes a small, instantaneous dipole.



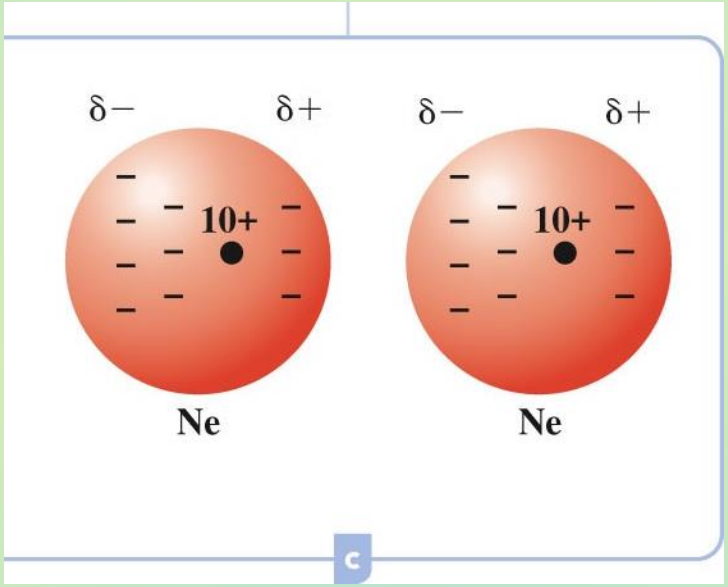
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The instantaneous dipole of the neon atom induces an instantaneous dipole in adjacent atoms, resulting in an attractive force between them.



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The motion of electrons in one atom affects the motion of electrons in another atom. This causes the instantaneous dipoles of the atoms change together, maintaining a net attractive force.



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London forces are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about the nuclei.

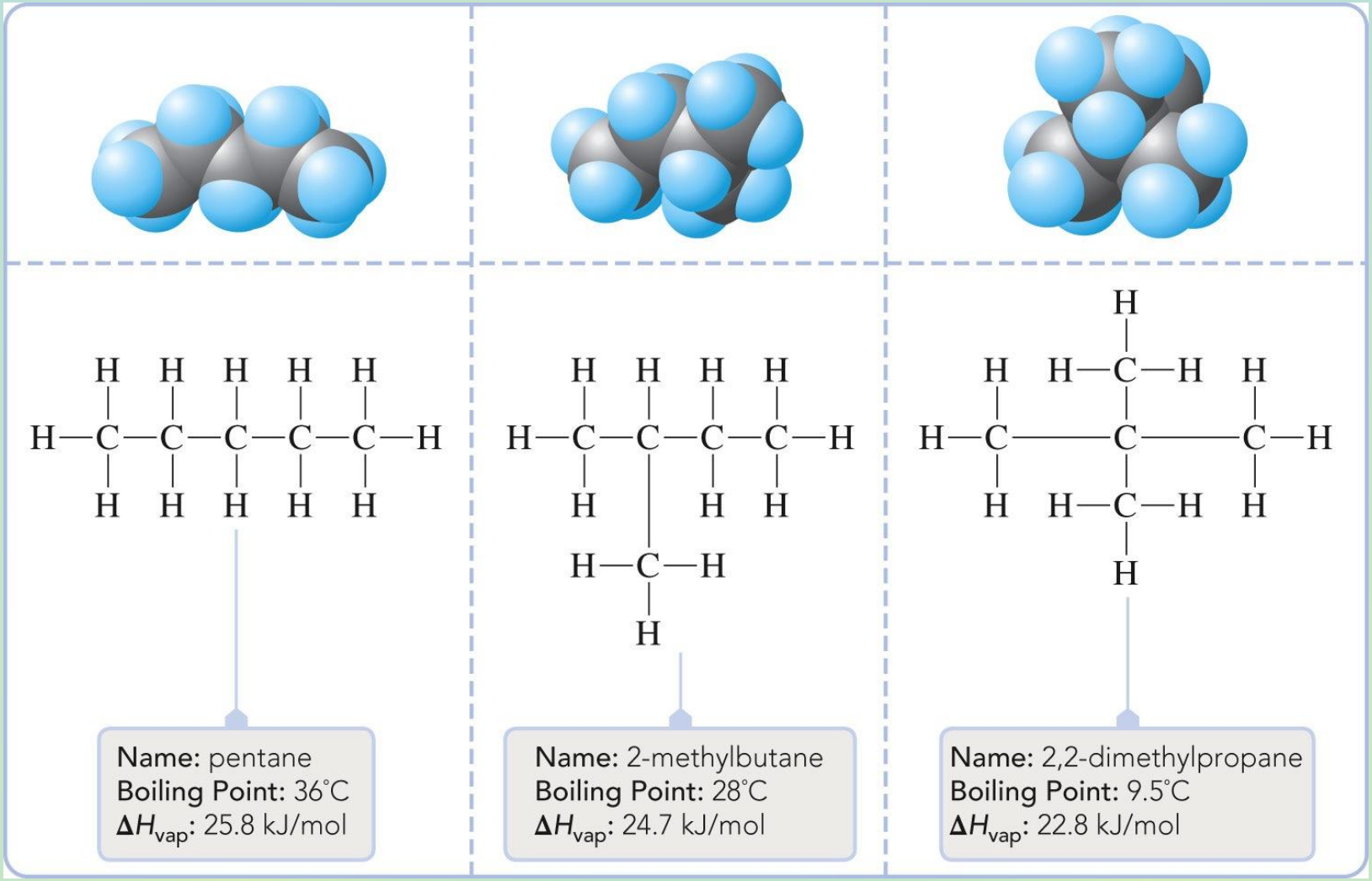
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London forces increase with molecular weight because molecules with larger molecular weight have more electrons, which generally means larger atoms that are more polarizable.

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On the next slide, each compound has the same chemical formula, C_5H_{12}. However, in each compound, the carbon atoms are bonded in a different structure. Note how the heats of vaporization differ for the molecules.

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Pentane is a long chain of carbon atoms to which hydrogen atoms are attached. 2-methylbutane and neopentane are more compact.

The most compact compound has the weakest intermolecular forces and the lowest heat of vaporization.

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We have just related heat of vaporization to the strength of intermolecular forces: The stronger the intermolecular forces, the higher the heat of vaporization.

We can do the same for vapor pressure, boiling point, surface tension, and viscosity.

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The stronger the intermolecular forces, the lower the vapor pressure at any given temperature.

The stronger the intermolecular forces, the higher the boiling point.

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The stronger the intermolecular forces, the higher the surface tension.

Viscosity depends in part on intermolecular forces: The stronger the intermolecular forces, the more viscous the liquid.

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Consider two liquids, labeled A and B, that are both pure substances. Liquid A has relatively strong intermolecular forces when compared to liquid B. The molecular structures of A and B are similar. Which one of the statements regarding liquids A and B is false?

a. Liquid A would have a higher boiling point than liquid B.
b. Liquid B would be more viscous than liquid A.
c. Liquid B would have a lower freezing point than liquid A.
d. Liquid A would have a lower vapor pressure than Liquid B.
e. Liquid A and B would melt at different temperatures.

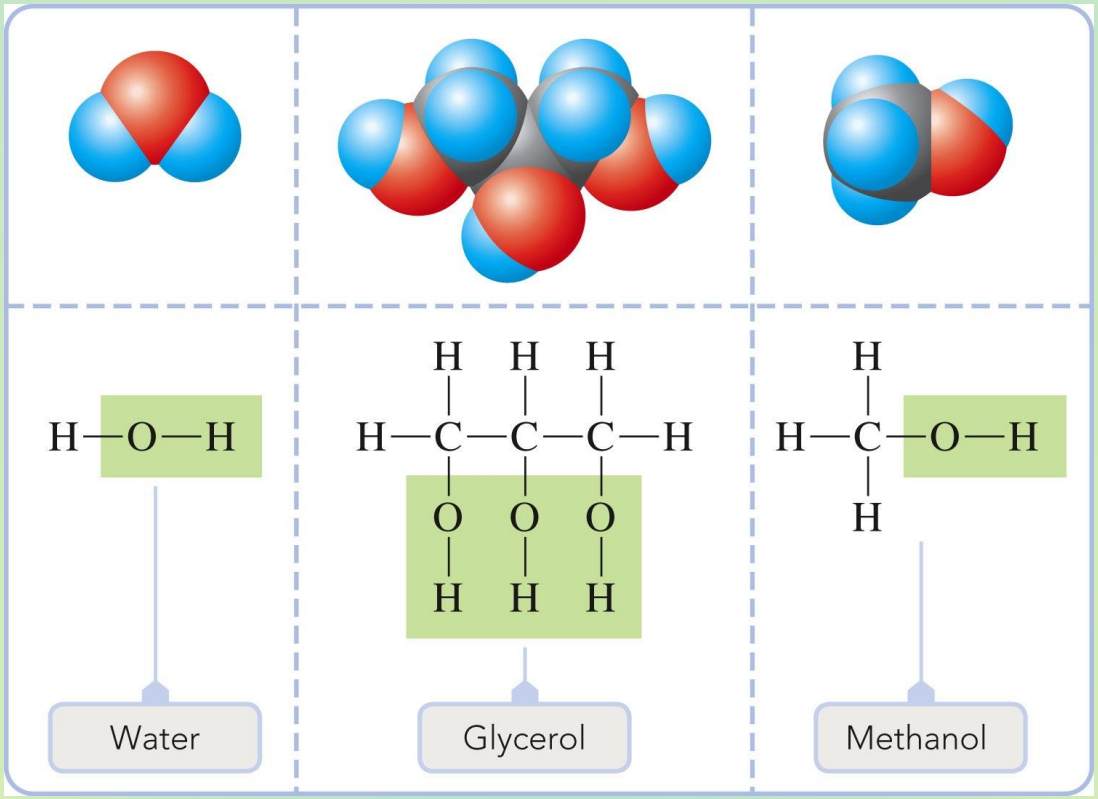
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Some compounds have about the same molecular weight and dipole moment. Yet they have different boiling points.

How can this be explained?

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Let's look at the structures of water, glycerol, and methanol. These compounds have unusually low vapor pressures and unusually high boiling points. What do these molecules have in common?



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Each molecule has one or more –OH group.

Molecules with this group have an additional force called the hydrogen bonding force.

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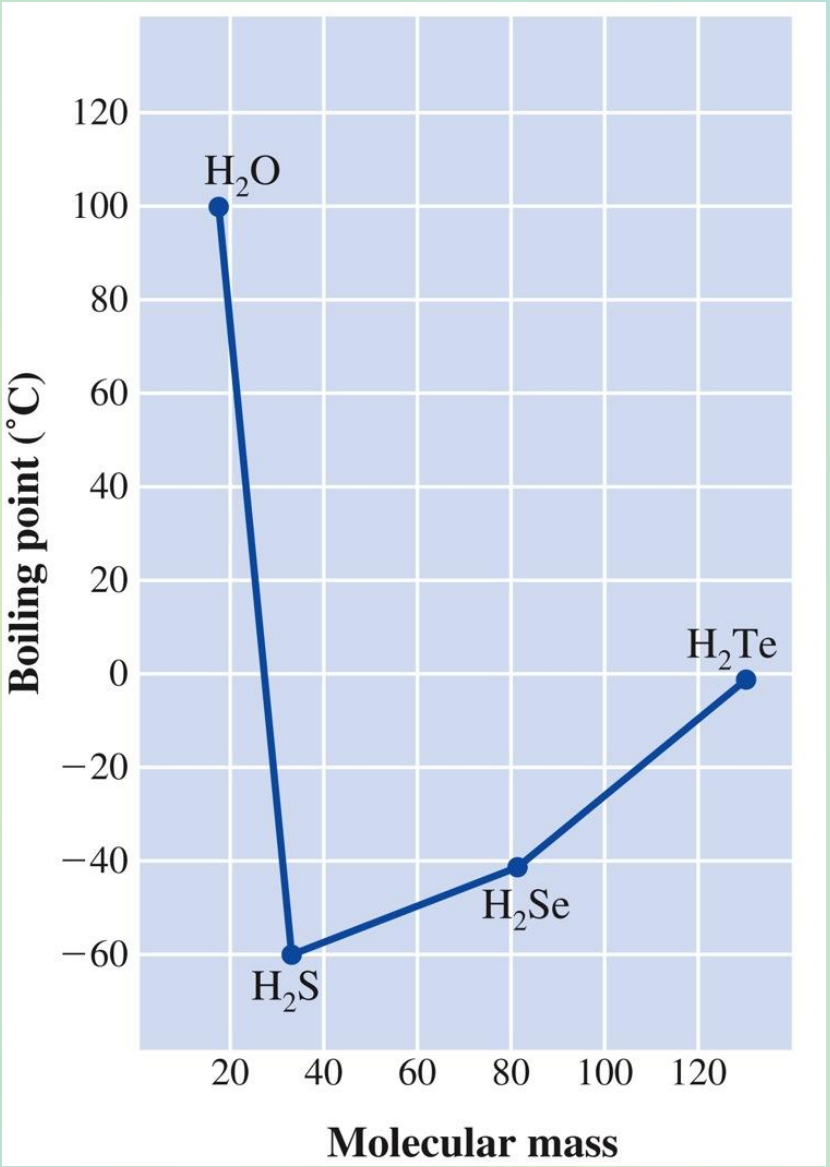
Hydrogen bonding is a weak attractive force that exists between hydrogen atoms bonded to a very electronegative atom, X, and a lone pair of electrons on another small, electronegative atom, Y.

—X—H ··· Y—

Hydrogen bonding is observed in cases where X and Y are the atoms F, O, or N.

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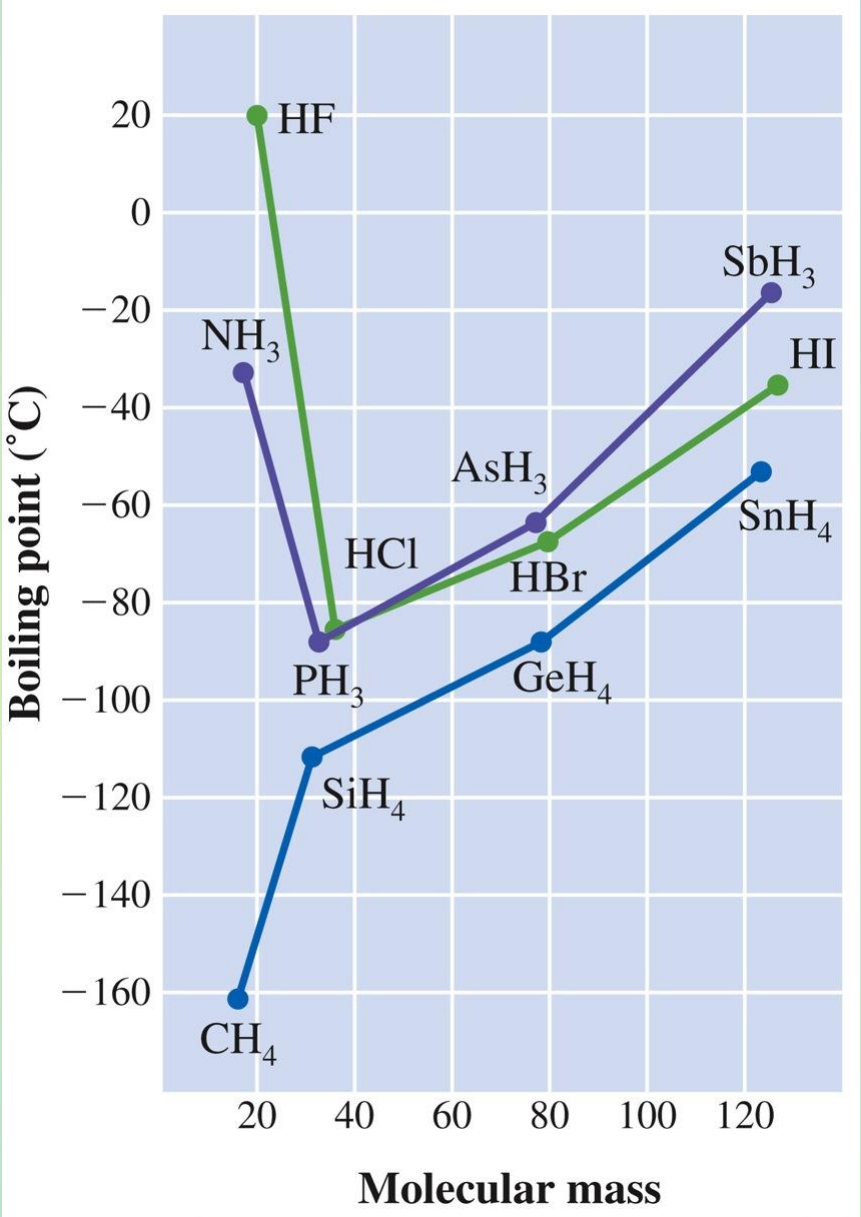
We can see the impact of adding hydrogen bonding forces on the boiling points of Group 6A elements.



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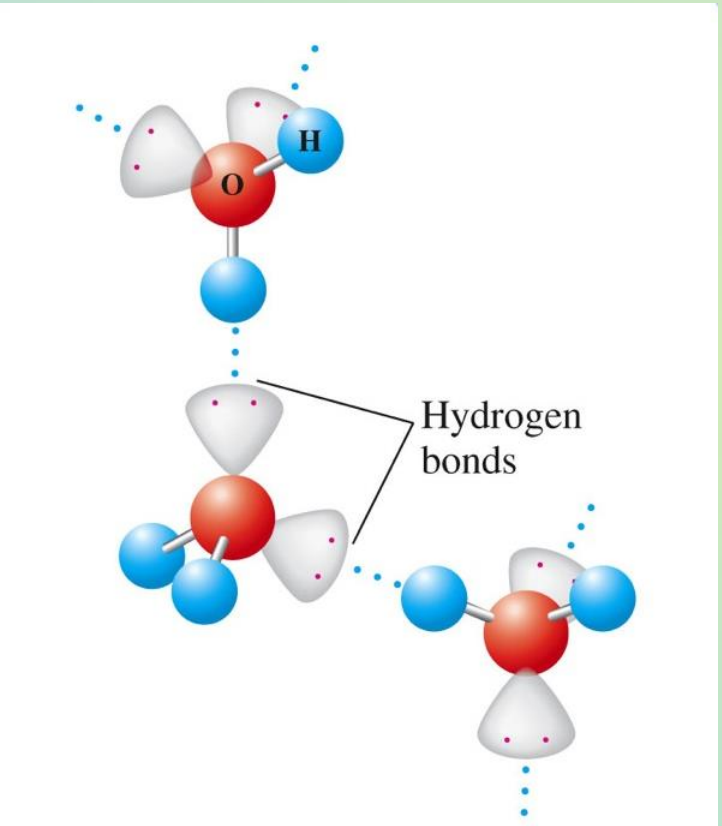
The boiling points for Group IVA, VA, and VIIA hydrides are graphed to the right.

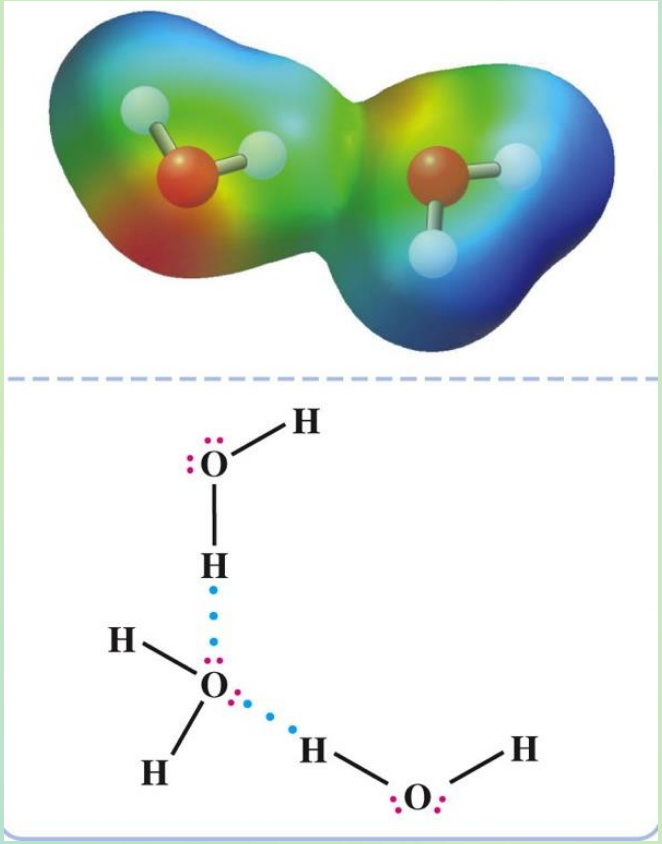
HF and NH_3 possess boiling points significantly higher than other hydrides of the corresponding periodic group.



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Hydrogen bonding in water is illustrated here in three different formats: ball-and-stick model, electrostatic map showing electron density distributions, and Lewis formula.





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A common misconception is that the following chemical reaction occurs when water is boiled:

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

instead of

$$H_2O(l) \longrightarrow H_2O(g)$$

a. What evidence do you have that the second reaction is correct?

b. How would the enthalpy of the wrong reaction compare with that of the correct reaction?

c. How could you calculate the enthalpy change for the wrong reaction (Chapter 6)?

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a. There are several ways to determine this.

First, the products in the first reaction form an explosive mix.

Second, the volume of gas from the first reaction is three times that of the second reaction.

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b. The first reaction requires breaking bonds. The second reaction is a phase change that involves disrupting intermolecular forces. Because chemical bonds are much stronger than intermolecular forces, the enthalpy of the first reaction would be much higher than that of the second reaction.

c. The enthalpy change for the first reaction could be calculated using standard enthalpy of formation values (Chapter 6) or bond energies (Chapter 9).

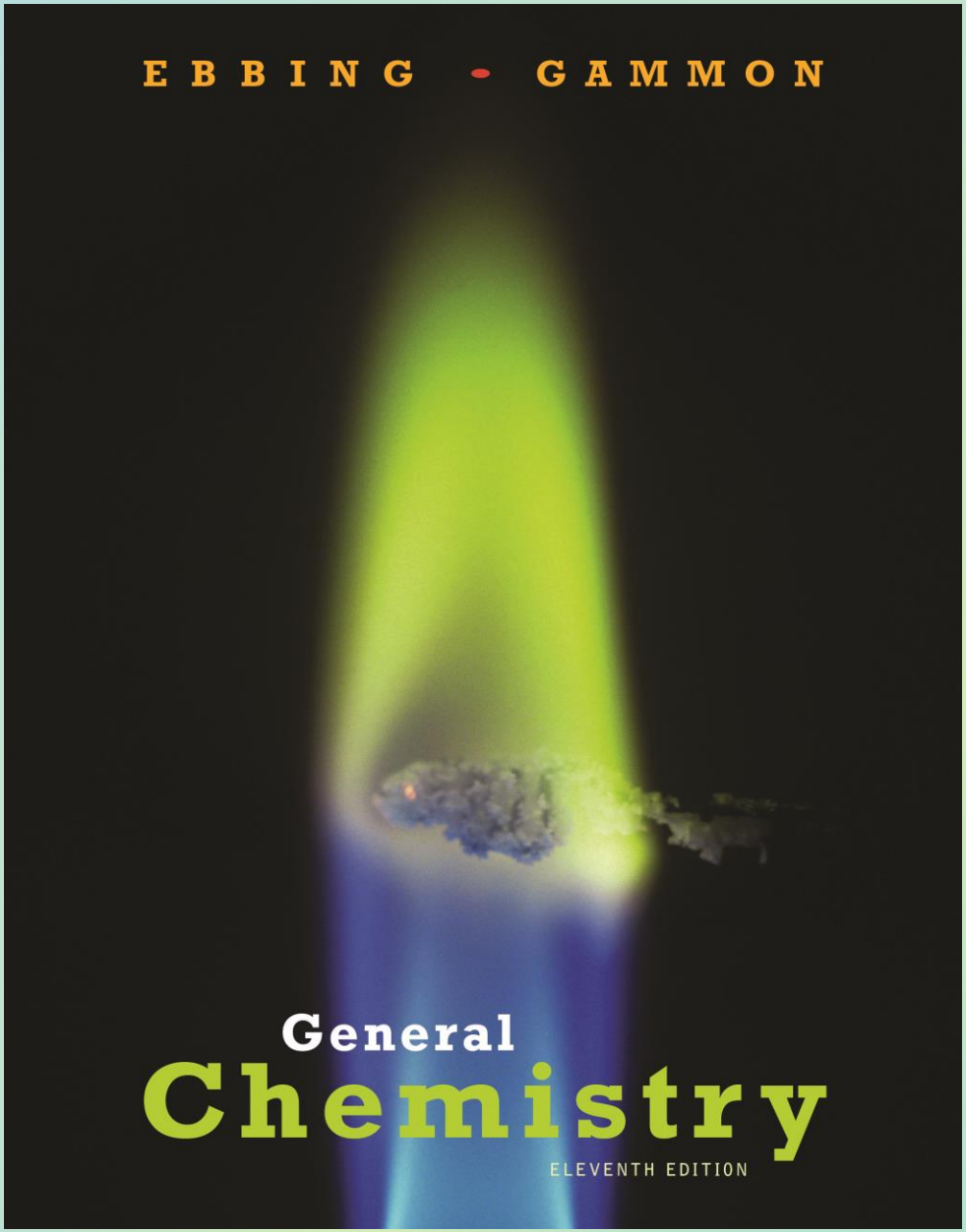
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Identify the intermolecular forces that expected for each of the following substances:

a. Methane
b. Trichloromethane
c. Butanol

a. Nonpolar molecule - London forces
b. Unsymmetrical bond - London forces, dipole-dipole forces, hydrogen bonding
c. H attached to O - London forces, dipole-dipole forces, hydrogen bonding

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Chapter 12
Solutions

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A solution is composed of two parts: the solute and the solvent.

Solute

The gas (or solid) in a solution of gases (or solids), or the component present in the smaller amount.

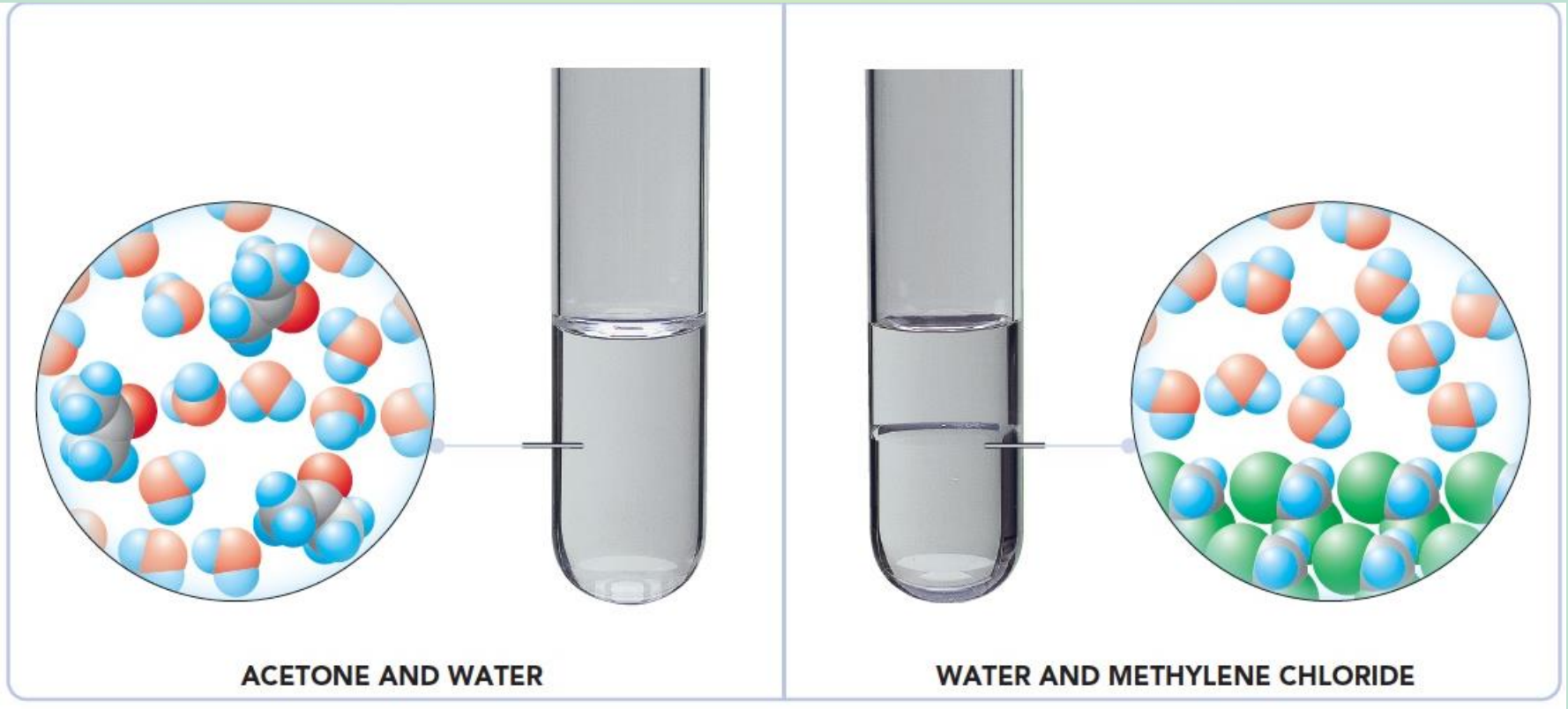
Solvent

The liquid in the case of a solution of gases or solids, or the component present in the larger amount.

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Fluids that mix with or dissolve in each other in all proportions are said to be **miscible** (left).

Fluids that do not dissolve in each other are said to be **immiscible** (right).



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Concept Check 12.1

Identify the solute(s) and solvent(s) in the following solutions.

a. 80 g of Cr and 5 g of Mo
b. 5 g of $MgCl_2$ dissolved in 1000 g of H_2O
c. 39% N_2, 41% Ar, and the rest O_2

a. The 5 g of Mo is the solute; the 80 g of Cr is the solvent.

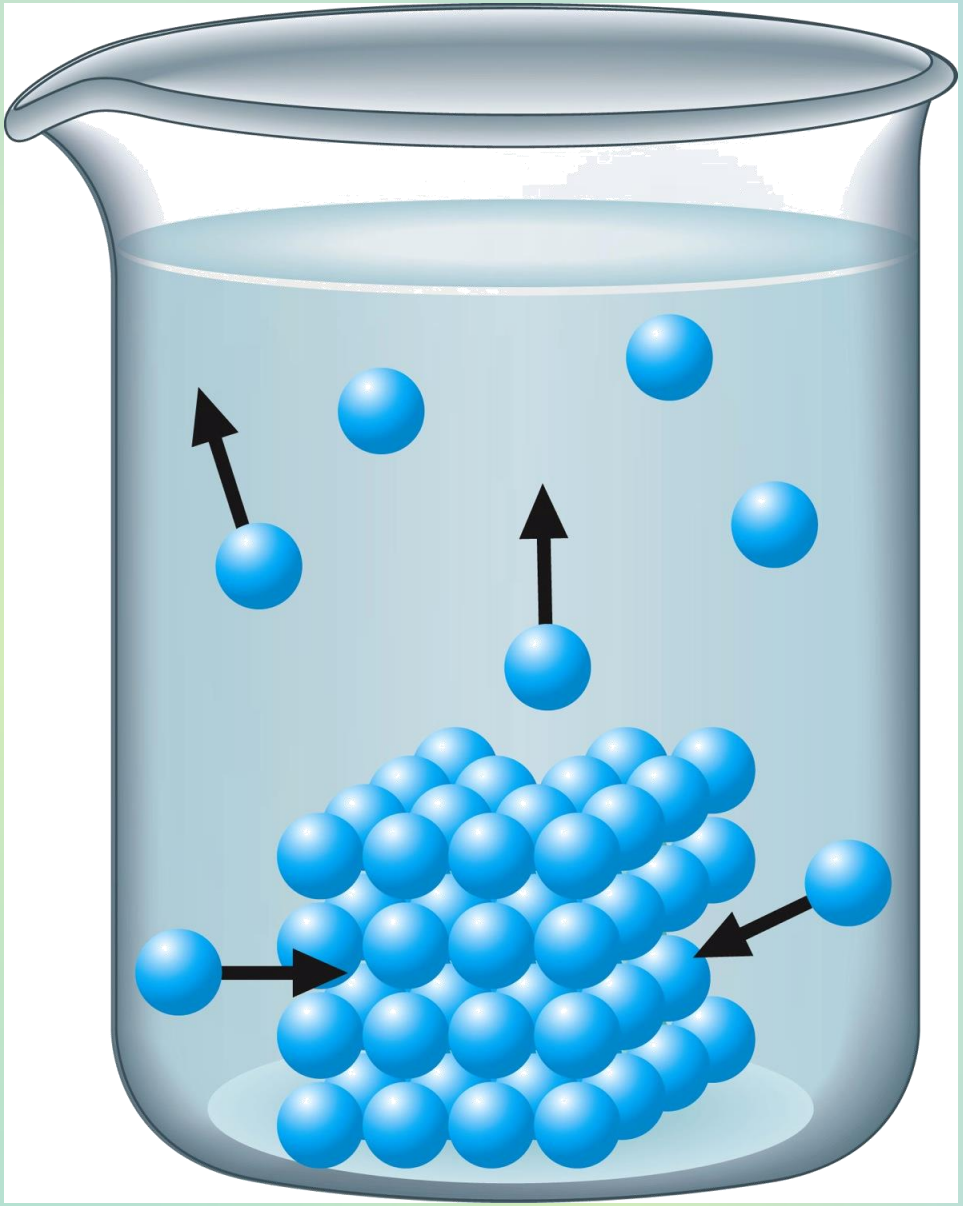
b. $MgCl_2$ is the solute; H_2O is the solvent.

c. O_2 and N_2 are the solutes; Ar is the solvent.

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Dynamic equilibrium is reached when the rate at which ions leave the crystals equals the rate at which ions return to crystals

A **saturated** solution is in equilibrium with respect to the amount of dissolved solute.

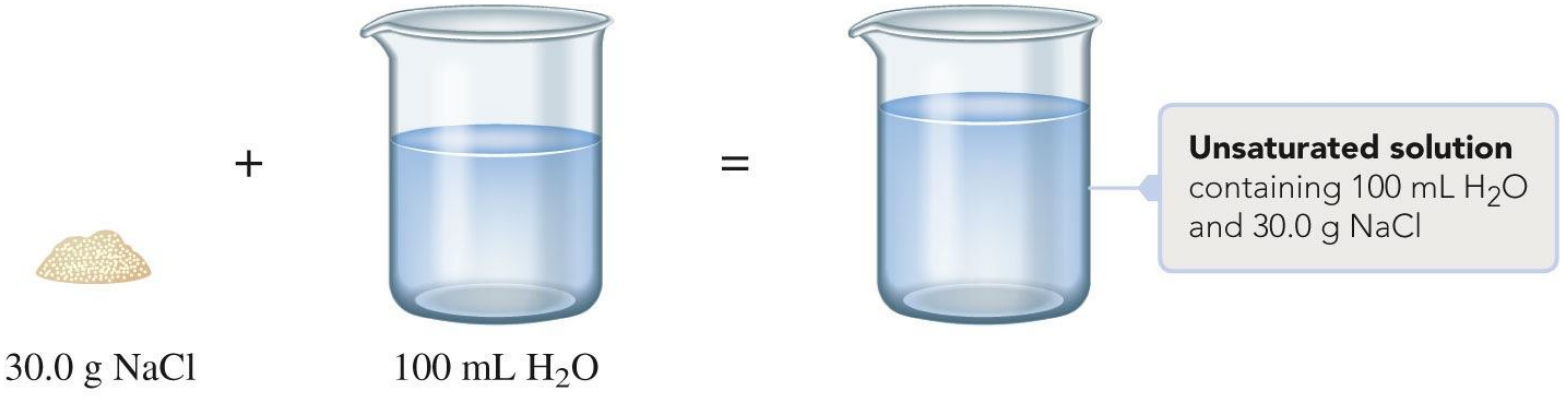


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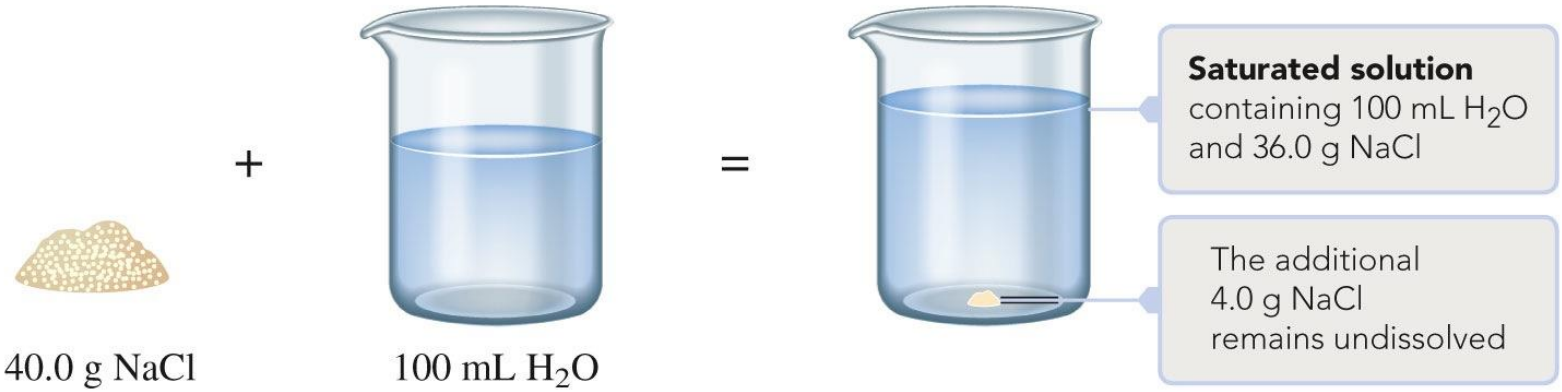
The **solubility** of a solute is the amount that dissolves in a given quantity of solvent at a given temperature.

An **unsaturated** solution is a solution not in equilibrium with respect to a given dissolved substance and in which more of the substance can be dissolved.

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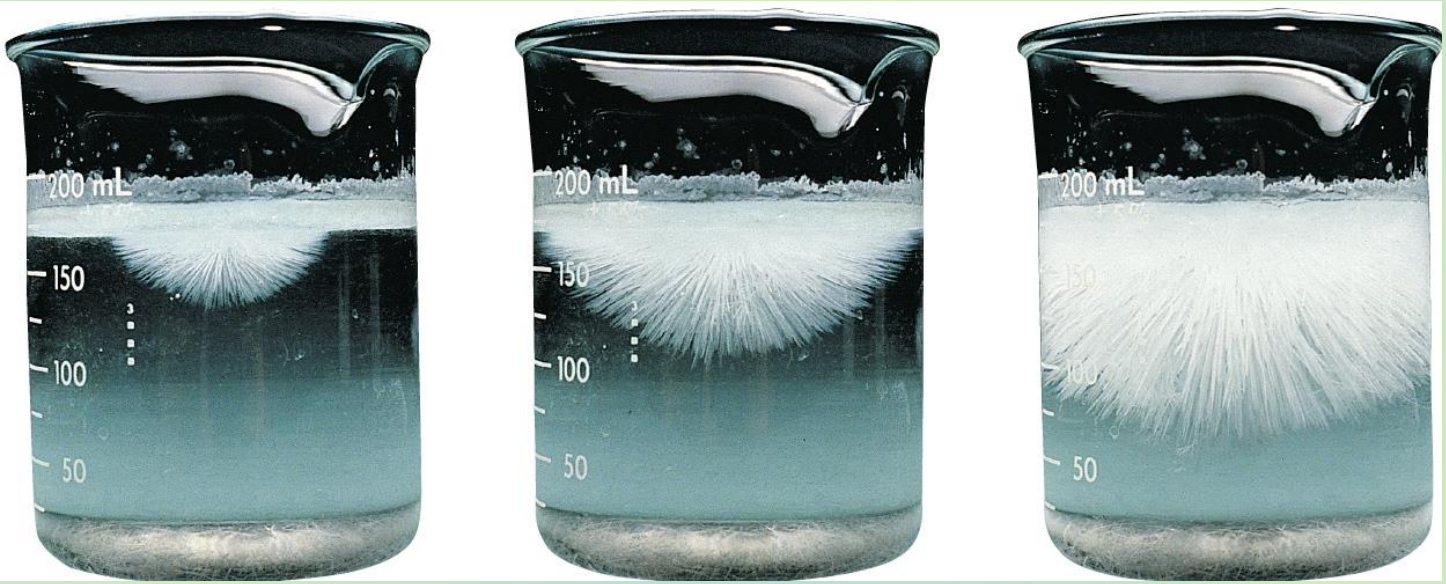
The 30.0-g pile of NaCl will dissolve completely in 100 mL of water at 20°C giving an unsaturated solution.



When 40.0 g NaCl is stirred into 100 mL H_2O, 36.0 g dissolves at 20°C, leaving 4.0 g of the crystalline solid on the bottom of the beaker. This solution is saturated.

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A **supersaturated** solution is a solution that contains more dissolved substance than a saturated solution does. This occurs when a solution is prepared at a higher temperature and is then slowly cooled. This is a very unstable situation, so any disturbance causes precipitation.



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Solubility can be understood in terms of two factors:

1. The natural tendency of substances to mix.
2. The relative forces between and within species must be considered.

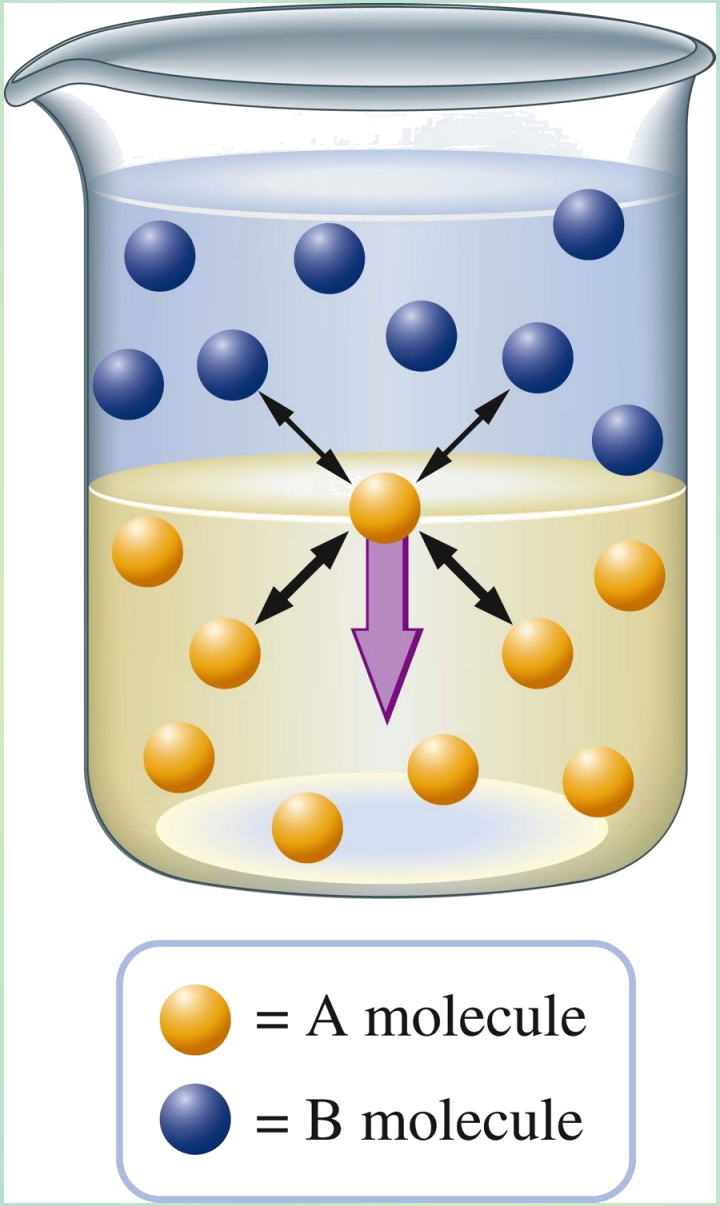
Stronger forces *within* solute species oppose dissolving.

Stronger forces *between* species favor dissolving.

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For molecular solutions, this can be summarized as “Like dissolves like.” In other words, solutes dissolve in solvents that have the same type of intermolecular forces.

An immiscible solute and solvent are illustrated at the right.



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You have two molecular compounds, X and Y. Compound X has stronger intermolecular forces than compound Y. X has no dipole-dipole bonding of any kind, and Y exhibits hydrogen bonding. Predict the relative solubility of compounds X and Y in water and in a nonpolar solvent. Explain your reasoning.

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Compound X is a large nonpolar molecule.
Compound Y is a molecule that exhibits hydrogen bonding.
Applying the like dissolves like concept, compound X will be more soluble in the nonpolar solvent and compound Y will be more soluble in a polar solvent.

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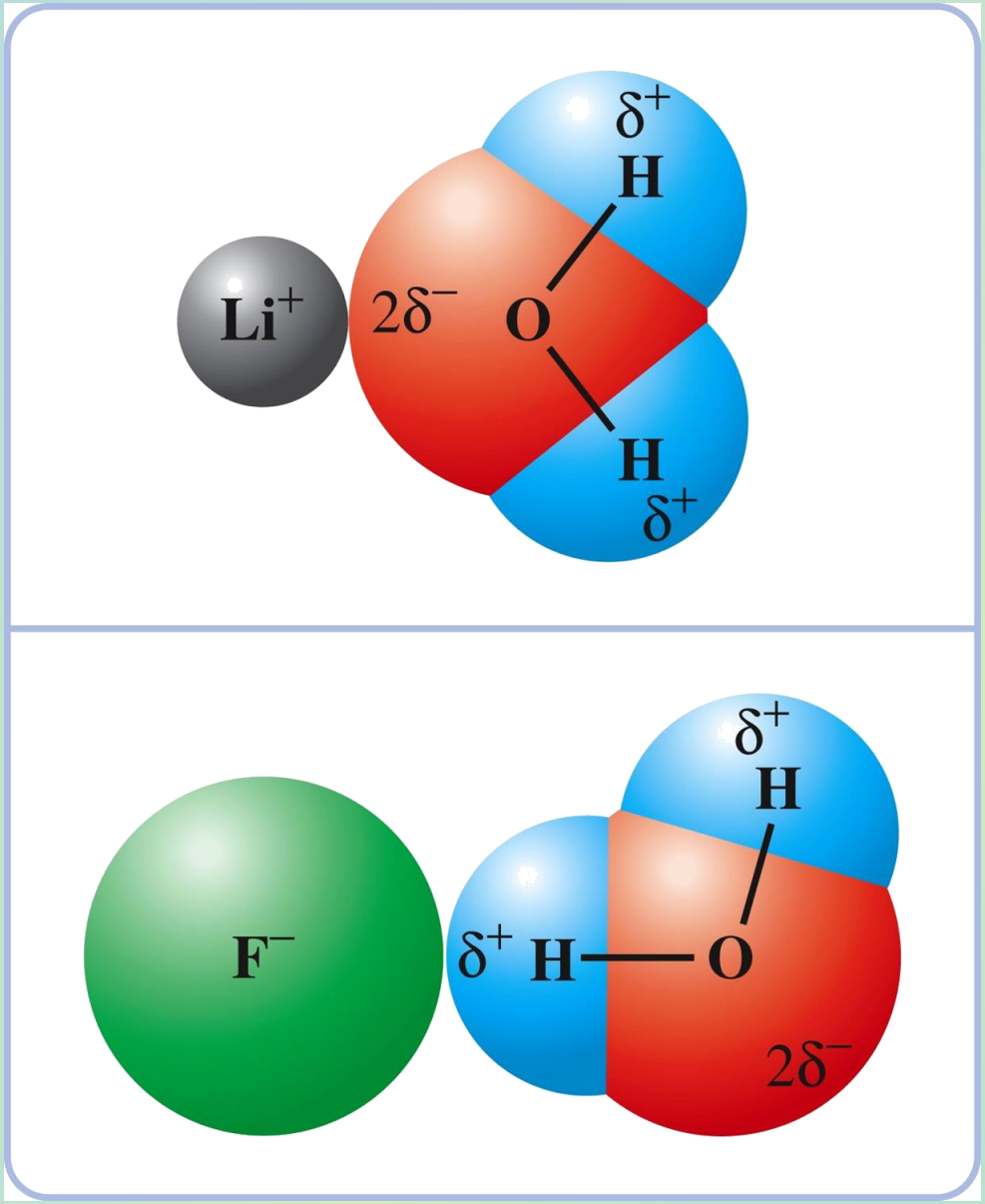
When considering ionic solutes in water, we need to examine hydration energy and lattice energy.

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Ion-dipole force is responsible for the energy of attraction between an ion and a water molecule.

Hydration is the attraction of ions for water molecules. It favors the dissolving of an ionic solid in water.

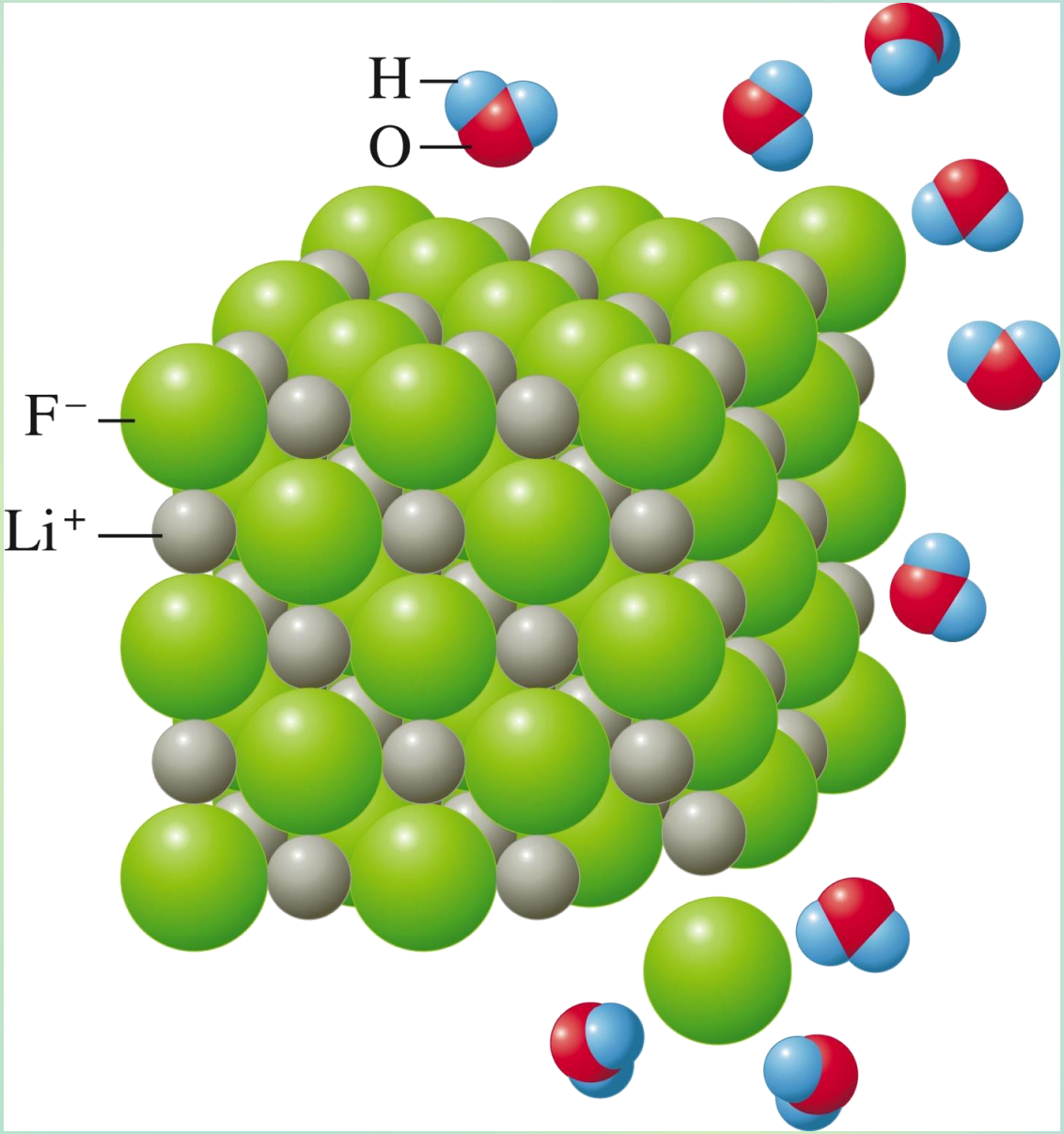
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The force of attraction between water and both a cation and an anion is illustrated on the left with lithium fluoride, LiF.

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The process of dissolving occurs at the surfaces of the solid. Here, we see water hydrating (dissolving) ions.



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Lattice energy and the energy of hydration influence the solubility of an ionic solid.

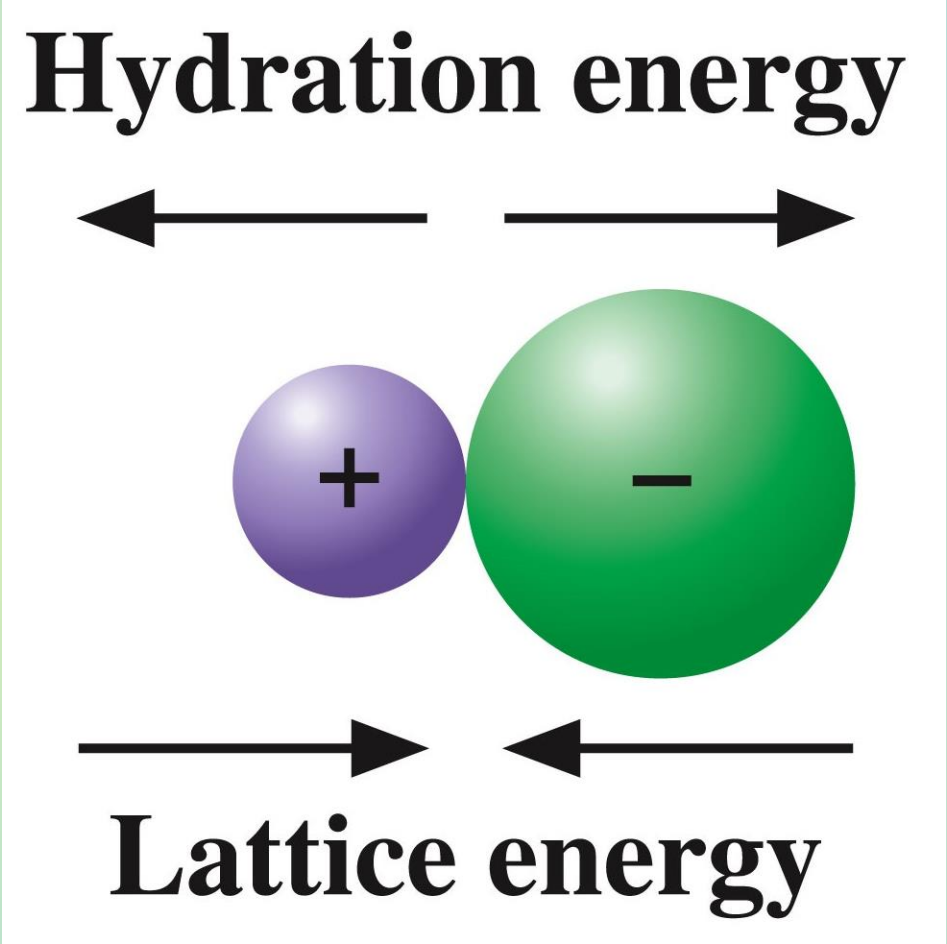
Lattice energy is the energy holding ions together in the crystal lattice.

Energy of hydration is the energy associated with the attraction between ions and water molecules.

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A stronger ion-dipole force between the ion and the solvent—that is, hydration energy—favors dissolving.

A stronger force between ions—that is, lattice energy—opposes dissolving.



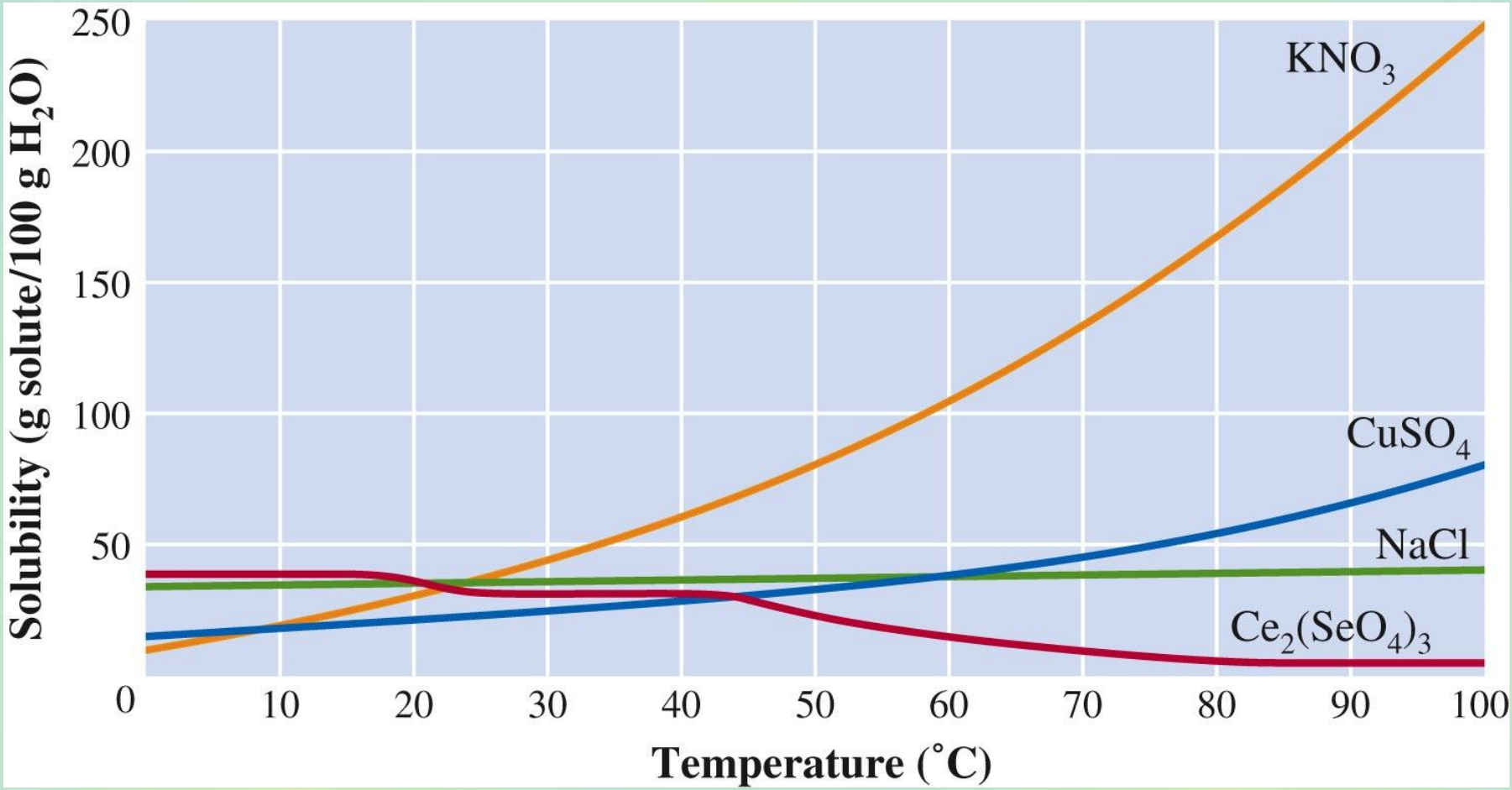
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The hypothetical ionic compound AB_2 is very soluble in water. Another hypothetical ionic compound, CB_2, is only slightly soluble in water. The lattice energies for these compounds are about the same. Provide an explanation for the solubility difference between these compounds.

The A^{2+} ion must be smaller, so it has a greater energy of hydration.

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In general, solubility depends on temperature.



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In most cases, solubility increases with increasing temperature. However, for a number of compounds, solubility *decreases* with increasing temperature.

The difference is explained by differences in the heat of solution.

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When dissolving absorbs heat (is endothermic), the temperature of the solution decreases as the solute dissolves. The solubility will increase as temperature increases.

When dissolving releases heat (is exothermic), the temperature of the solution increases as the solute dissolves. The solubility will decrease as temperature increases.

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Hot packs use an exothermic solution process.

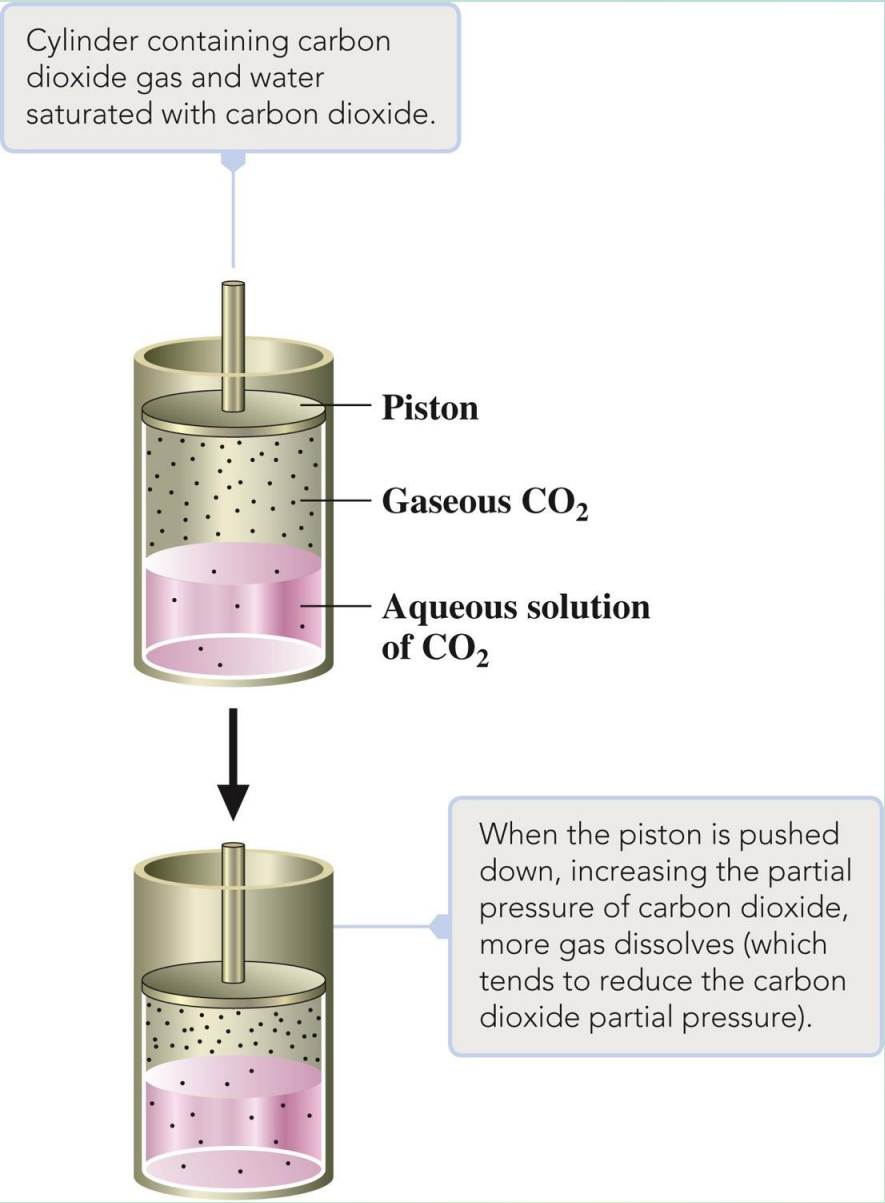
Cold packs use an endothermic solution process.



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In general, pressure has little or no effect on the solubility of solids or liquids in water.

The solubility of a gas increases as pressure increases, as illustrated on the right.



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Le Châtelier's Principle

When a system in equilibrium is disturbed by a change of temperature, pressure, or concentration variable, the system shifts in equilibrium composition in a way that tends to counteract this change of variable.

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Henry's law states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution.

This is expressed mathematically in the equation

$$S = k_H P$$

where

S = gas solubility

k_H = Henry's law constant for the gas

P = partial pressure of the gas over the solution

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27 g of acetylene, C_2H_2, dissolves in 1 L of acetone at 1.0 atm pressure. If the partial pressure of acetylene is increased to 12 atm, what is its solubility in acetone?

$P_1 = 1.0$ atm $\qquad P_2 = 12$ atm

$S_1 = 27$ g $\qquad S_2 = ?$

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Using the equation:

$$\frac{S_2}{S_1} = \frac{P_2}{P_1}$$

$$\frac{S_2}{27\ \text{g}\ C_2H_2/\text{L acetone}} = \frac{12\ \cancel{\text{atm}}}{1.0\ \cancel{\text{atm}}}$$

$$S_2 = \frac{27\ \text{g}\ C_2H_2}{\text{L acetone}} \times \frac{12}{1.0} = \frac{3.2 \times 10^2\ \text{g}\ C_2H_2}{\text{L acetone}}$$

At 12 atm partial pressure, 1L of acetone dissolves 3.2×10^2 g of acetylene

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Most fish have a very difficult time surviving at elevations above 3500 m. How can Henry's law be used to account for this fact?

At high elevations, the partial pressure of oxygen decreases, decreasing the solubility of oxygen in water. Fish require a certain minimum level of dissolved oxygen to survive.

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Colligative properties of solutions are properties that depend on the concentration of solute molecules or ions in solution but not on the chemical identity of the solute.

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The concentration of a solute can be quantitatively expressed in several ways:

1. Molarity
2. Mass percentage of solute
3. Molality
4. Mole fraction

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Molarity is the moles of solute per liter of solution. It is abbreviated as *M*.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

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Mass percentage of solute is the percentage by mass of solute in a solution.

$$\text{Mass percentage of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

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How would you prepare 425 g of an aqueous solution containing 2.40% by mass of sodium acetate, $NaC_2H_3O_2$?

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The mass of sodium acetate (solute) in 425 g of solution is:

$$\text{Mass of } NaC_2H_3O_2 = 425 \text{ g} \times 0.0240 = 10.2 \text{ g}$$

Consider the relationship:

$$\text{Mass of solution} = \text{mass } NaC_2H_3O_2 + \text{mass } H_2O$$

Therefore, the quantity of water in the solution is:

$$\text{Mass of } H_2O = \text{mass of solution} - \text{mass of } NaC_2H_3O_2$$

$$= 425 \text{ g} - 10.2 \text{ g} = 415 \text{ g}$$

The solution can be prepared by dissolving 10.2 g of sodium acetate in 415 g of water.

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Molality is the moles of solute per kilogram of solvent. It is abbreviated as *m*.

$$m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

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Determine the molality of a solution containing 5.67 g of glucose dissolved in 25.2 g of water.

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Calculate the moles of glucose (MM = 180.2 amu) in 5.67 g as shown below.

$$5.67\ \text{g}\ \cancel{C_6H_{12}O_6} \times \frac{1\ \text{mol}\ C_6H_{12}O_6}{180.2\ \text{g}\ \cancel{C_6H_{12}O_6}} = 0.0315\ \text{mol}\ C_6H_{12}O_6$$

The mass of water is 25.2 g, or 25.2×10^{-3} kg.

$$\text{Molality} = \frac{0.0315\ \text{mol}\ C_6H_{12}O_6}{25.2 \times 10^{-3}\ \text{kg solvent}} = 1.25\ m\ C_6H_{12}O_6$$

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Mole fraction is the moles of component over the total moles of solution. It is abbreviated as *X*.

$$X = \frac{\text{moles of solute}}{\text{total moles of solution}}$$

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Determine the mole fractions of glucose and water in a solution containing 5.67 g of glucose dissolved in 25.2 g of water.

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5.67 g of glucose = 0.0315 mol of glucose.

Calculate the total moles of solution.

$$25.2\ \text{g}\ \cancel{H_2O} \times \frac{1\ \text{mol}\ H_2O}{18.0\ \text{g}\ \cancel{H_2O}} = 1.40\ \text{mol}\ H_2O$$

The total moles of solution are:

$$1.40\ \text{mol} + 0.0315\ \text{mol} = 1.432\ \text{mol}$$

Therefore,

$$\text{Mole fraction glucose} = \frac{0.0315\ \text{mol}}{1.432\ \text{mol}} = 0.0220$$

$$\text{Mole fraction water} = \frac{1.40\ \text{mol}}{1.432\ \text{mol}} = 0.978$$

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Conversion of concentration units requires them to be expressed in terms of mass or moles of solute and solvent.

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A solution is 0.150 mole fraction glucose $C_6H_{12}O_6$ and 0.850 mole fraction water. Determine the molality of glucose in the solution.

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The mass of this amount of water is:

$$0.850 \text{ mol } \cancel{H_2O} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mol } \cancel{H_2O}} = 15.3 \text{ g } H_2O \; (= 0.0153 \text{ kg } H_2O)$$

The molality of glucose in the solution is:

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.150 \text{ mol } C_6H_{12}O_6}{0.0153 \text{ kg solvent}} = 9.80 \; m \; C_6H_{12}O_6$$

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Conversion of molarity to molality requires the density of the solution, as demonstrated in the next two examples.

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An aqueous solution is 0.273 *m* KCl. Determine the molar concentration of KCl. The density of the solution is 1.011×10^3 g/L.

Determine the mass of KCl in the given quantity of the solution.

$$0.273 \text{ mol KCl} \times \frac{74.6 \text{ g KCl}}{1 \text{ mol KCl}} = 20.4 \text{ g KCl}$$

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The total mass of the solution equals the mass of water plus the mass of KCl.

$$1.000 \times 10^3 \text{ g} + 20.4 \text{ g} = 1.020 \times 10^3 \text{ g}$$

Use the inverse of the density of the solution to determine its volume.

$$\text{Volume of solution} = 1.020 \times 10^3 \cancel{\text{g}} \times \frac{1 \text{ L}}{1.011 \times 10^3 \cancel{\text{g}}} = 1.009 \text{ L}$$

There is 0.273 mol KCl in every 1.009 L of solution. Hence,

$$\frac{0.273 \text{ mol KCl}}{1.009 \text{ L solution}} = 0.271 \, M \text{ KCl}$$

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An aqueous solution is 0.907 *M* $Pb(NO_3)_2$. Determine the molality of lead (II) nitrate, $Pb(NO_3)_2$. The density of the solution is 1.252 g/mL.

Assuming 1.000 L (1.000×10^3 mL) of solution,

$$\text{Mass of solution} = \text{density} \times \text{volume}$$

$$= 1.252\ \text{g/}\cancel{\text{mL}} \times 1.000 \times 10^3\ \cancel{\text{mL}}$$

$$= 1.252 \times 10^3\ \text{g}$$

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The mass of lead nitrate is:

$$0.907 \text{ mol } Pb(NO_3)_2 \times \frac{331.2 \text{ g } Pb(NO_3)_2}{1 \text{ mol } Pb(NO_3)_2} = 3.00 \times 10^2 \text{ g } Pb(NO_3)_2$$

The mass of water in 1.000 L of solution is:

$$\text{Mass of } H_2O = \text{mass of solution} - \text{mass of } Pb(NO_3)_2$$

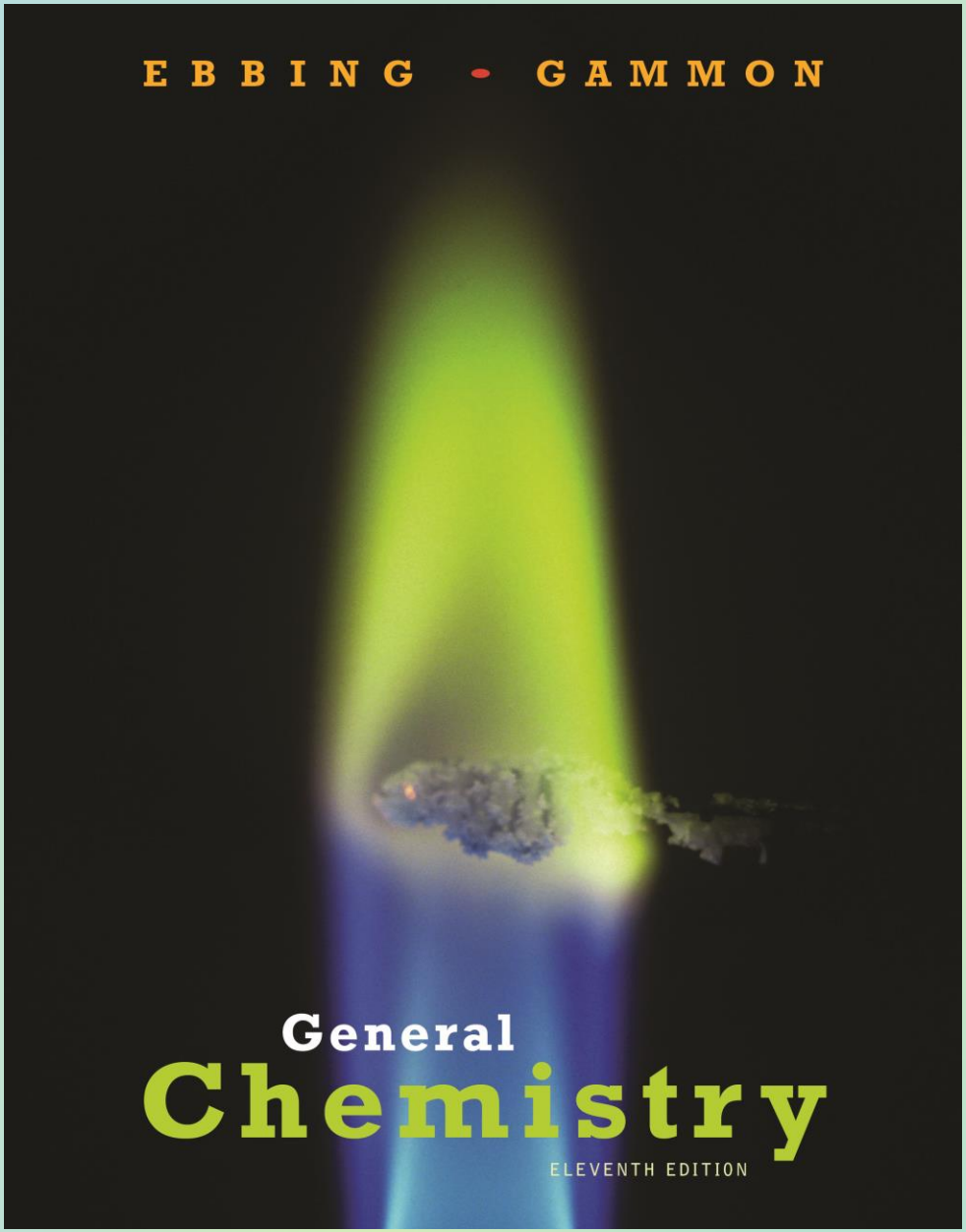
$$= 1.252 \times 10^3 \text{ g} - 3.00 \times 10^2 \text{ g}$$

$$= 9.52 \times 10^2 \text{ g } (= 0.952 \text{ kg } H_2O)$$

The molality of lead(II) nitrate is:

$$\frac{0.907 \text{ mol } Pb(NO_3)_2}{0.952 \text{ kg solvent}} = 0.953 \, m \, Pb(NO_3)_2$$

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Chapter 13
Rates of Reaction

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Chemical kinetics is the study of reaction rates, including how reaction rates change with varying conditions and which molecular events occur during the overall reaction.

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The following questions are explored in this chapter:

- How is the rate of a reaction measured?
- What conditions will affect the rate of a reaction?
- How do you express the relationship of rate to the variables affecting the rate?
- What happens on a molecular level during a chemical reaction?

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What conditions will affect the rate of a reaction?

Four variables affect the rate of reaction.

1. Concentrations of the reactant
2. Concentration of the catalyst
3. Temperature at which the reaction occurs
4. Surface area of the solid reactant or catalyst

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Concentrations of Reactants

In certain reactions the rate of reaction increases when the concentration of a reactant is increased. In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.

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Concentration of Catalyst

Hydrogen peroxide, H_2O_2, decomposes rapidly in the presence of HBr, giving oxygen and water. Some of the HBr is oxidized to Br_2, as can be seen above.

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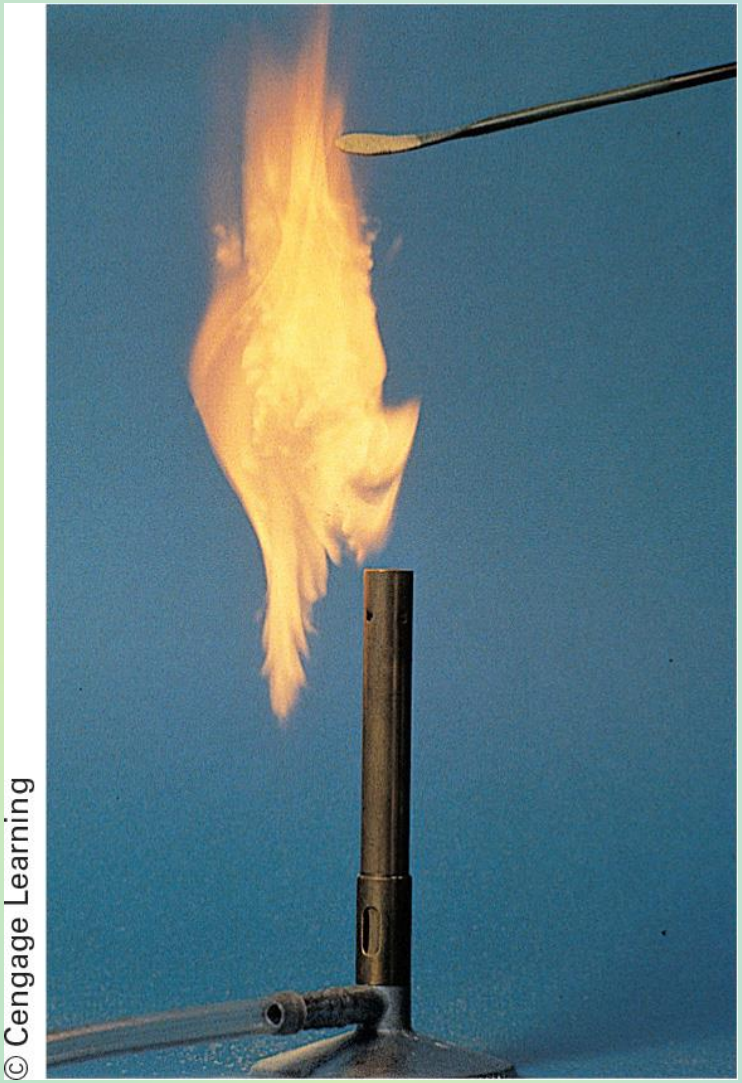
Temperature at Which Reaction Occurs

In most cases reactions speed up when the temperature increases. It takes less time to boil an egg at sea level than on a mountaintop, where water boils at a lower temperature. Reactions during cooking go faster at higher temperature.

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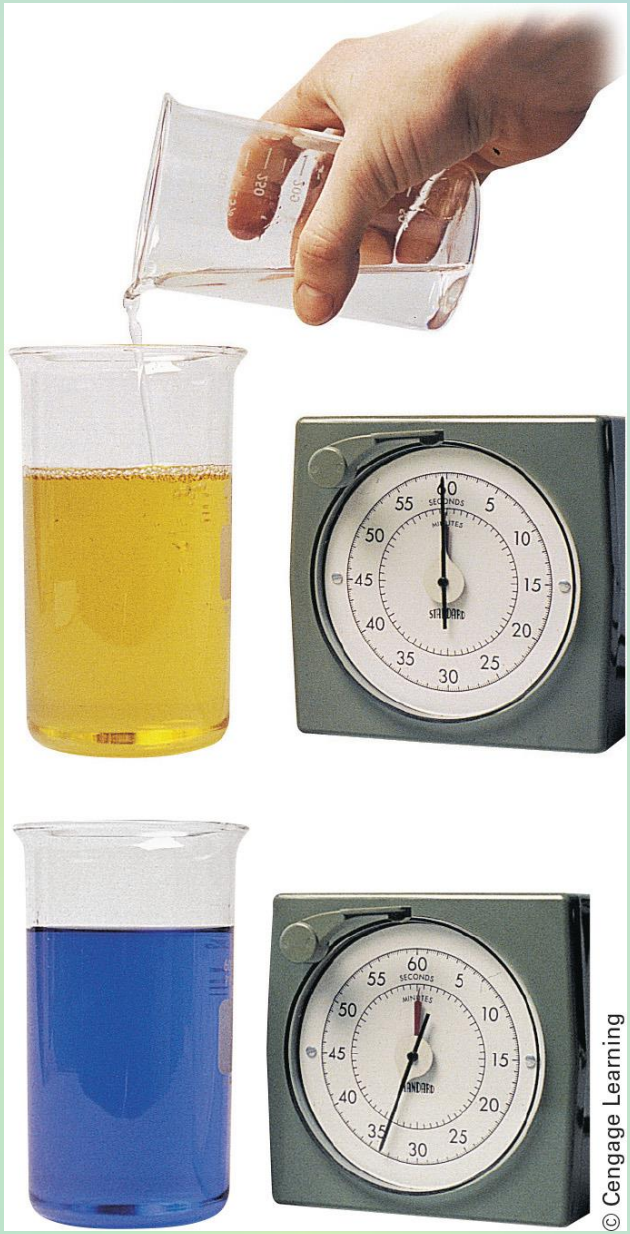
Surface Area of a Solid Reactant or Catalyst

If a reaction involves a solid with a gas or liquid, then the surface area of the solid affects the reaction rate. Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area. For example, a wood fire burns faster if the logs are chopped into smaller pieces. Similarly, the surface area of a solid catalyst is important to the rate of reaction.

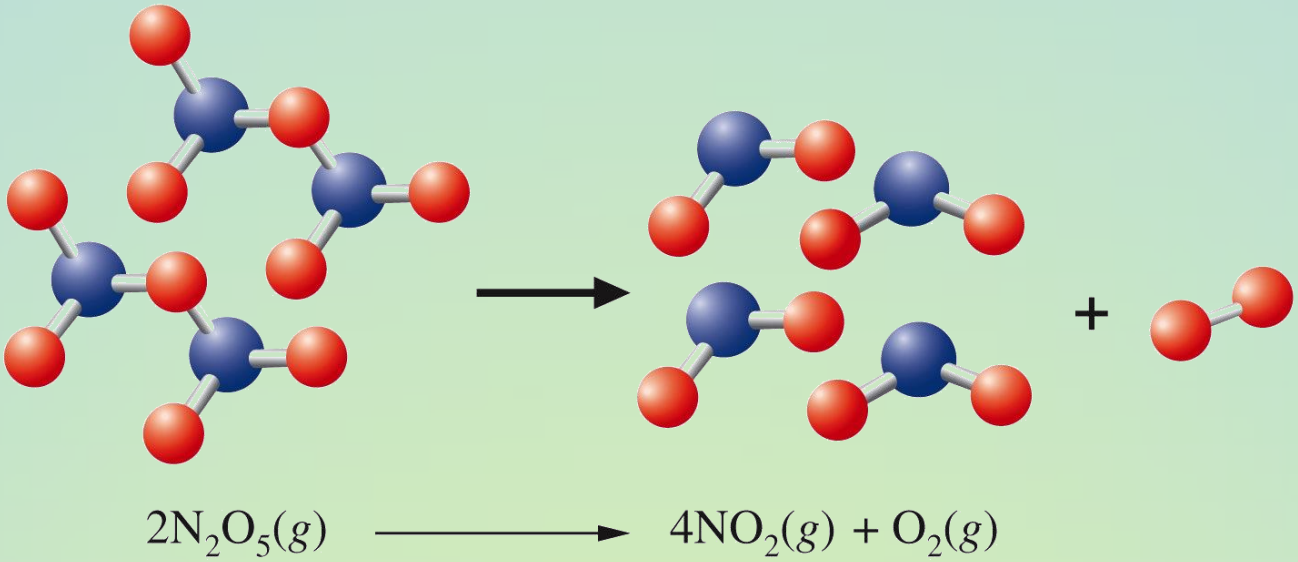


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Reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant per unit time. The unit is usually mol/(L·s) or *M*/s.



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The rate of this reaction can be found by measuring the concentration of O_2 at various times. Alternatively, the concentration of NO_2 could be measured. Both of these concentrations increase with time. The rate could also be determined by measuring the concentration of N_2O_5, which would decrease over time.

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$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Molar concentrations are denoted by enclosing the substance in square brackets.

Rate of formation of O_2 = $\dfrac{\Delta[O_2]}{\Delta t}$

Rate of formation of NO_2 = $\dfrac{\Delta[NO_2]}{\Delta t}$

Rate of decomposition of N_2O_5 = $-\dfrac{\Delta[N_2O_5]}{\Delta t}$

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We can relate these expressions by taking into account the reaction stoichiometry.

$$\text{Rate of decomposition of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t}$$

$$\text{Rate of formationof } O_2 = \frac{1}{2}(\text{rate of decomposition of } N_2O_5)$$

$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

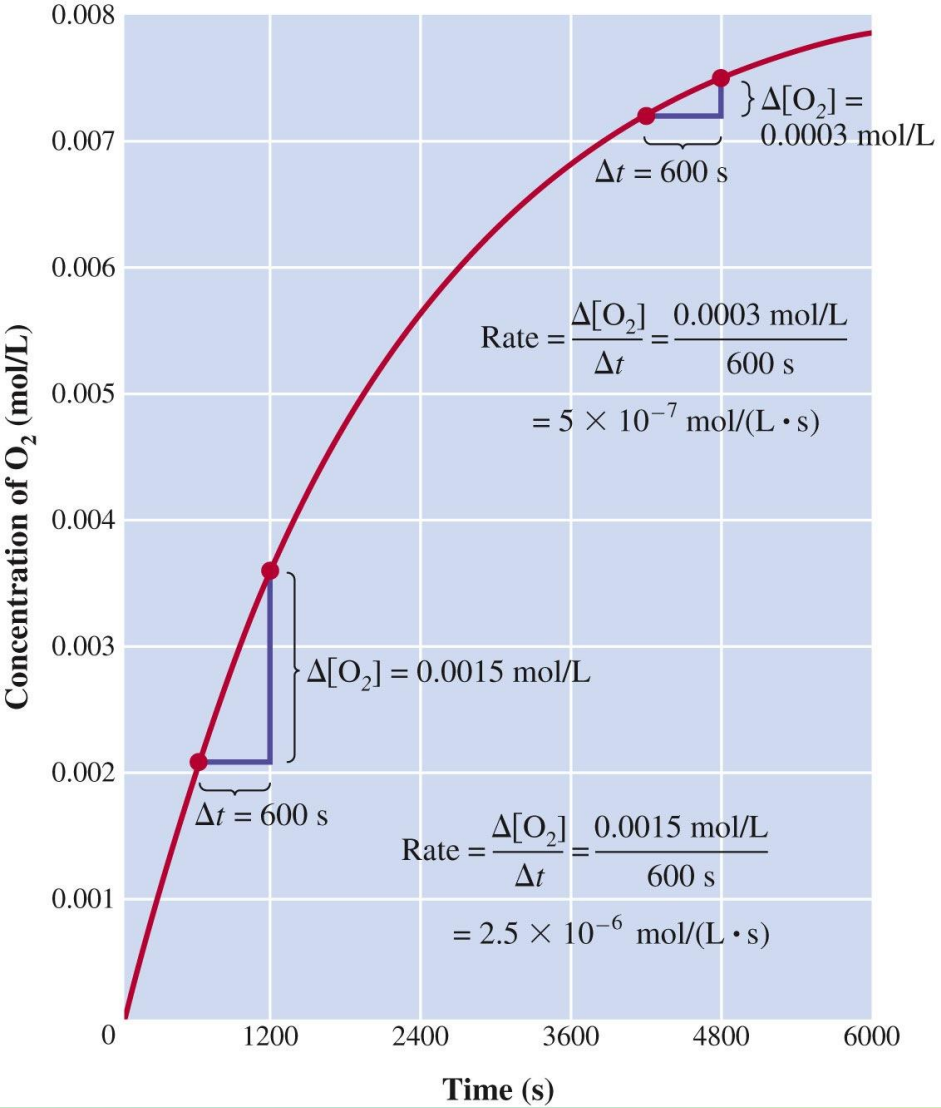
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These equations give the average rate over the time interval Δt. As Δt decreases and approaches zero, the equations give the instantaneous rate.

The next slides illustrate this relationship graphically for the increase in concentration of O_2.

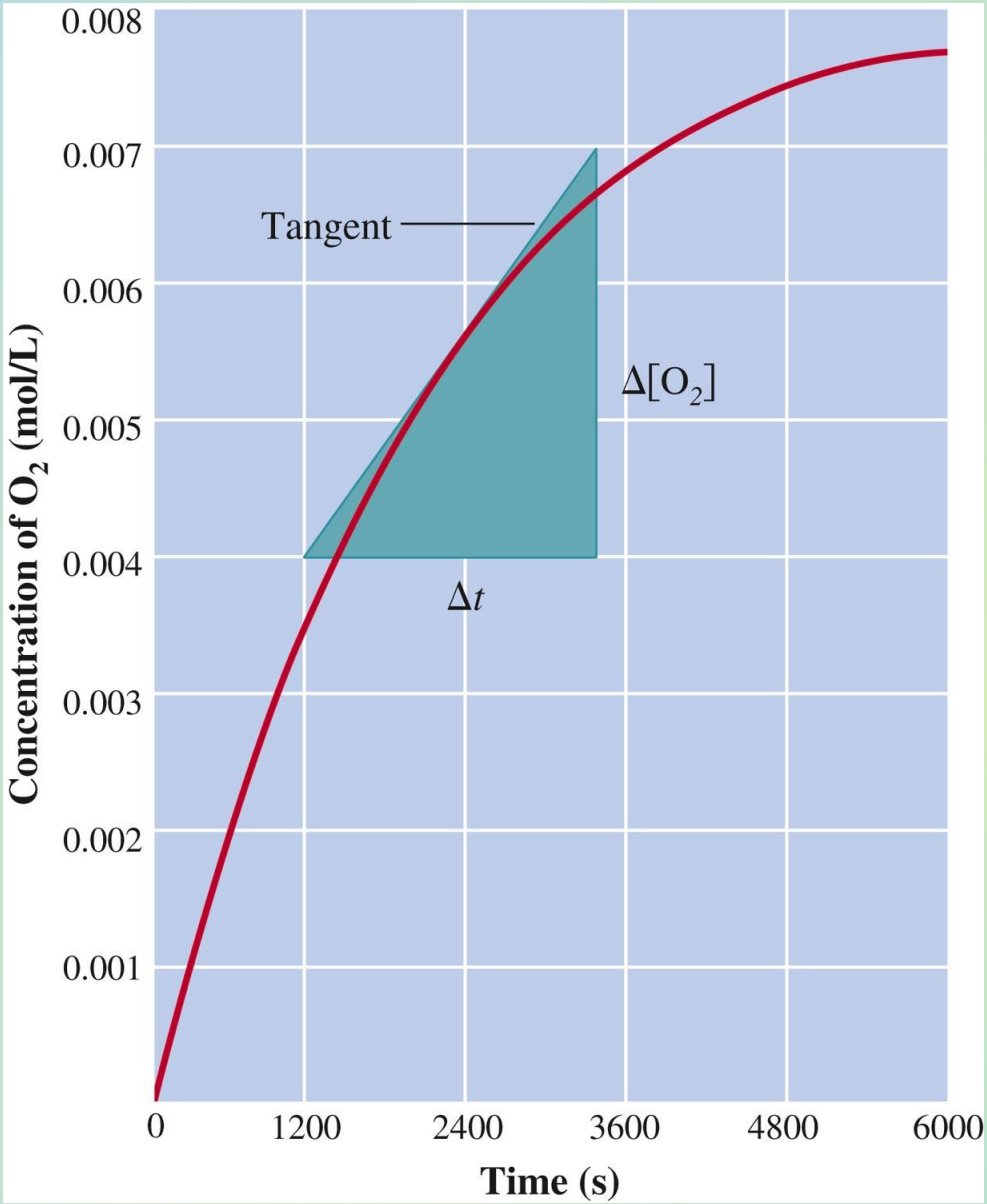
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The average rate is the slope of the hypotenuse of the triangle formed.



Time	$[O_2]$
0	0.0000
600	0.0021
1200	0.0036
1800	0.0048
2400	0.0057
3000	0.0063
3600	0.0068
4200	0.0072
4800	0.0075
5400	0.0077
6000	0.0078

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As Δt gets smaller and approaches zero, the hypotenuse becomes a tangent line at that point.

The slope of the tangent line equals the rate at that point.

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Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride, NO_2F.

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

How is the rate of formation of NO_2F related to the rate of reaction of fluorine?

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$$\text{Rate of formation of } NO_2F = \frac{\Delta[NO_2F]}{\Delta t}$$

$$\text{Rate of reaction of } F_2 = -\frac{\Delta[F_2]}{\Delta t}$$

Divide each rate by the corresponding coefficient and then equate them:

$$\frac{1}{2}\frac{\Delta[NO_2F]}{\Delta t} = -\frac{\Delta[F_2]}{\Delta t}$$

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Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

During the time interval from t = 600s to t = 1200s (regard all time figures as significant). Use the following data:

Time	$[N_2O_5]$
600s	$1.24 \times 10^{-2} M$
1200s	$0.93 \times 10^{-2} M$

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Solution

$$\text{Average rate of decomosition of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t}$$

$$= -\frac{(0.93 - 1.24) \times 10^{-2} M}{(1200 - 600)\,\text{s}}$$

$$= \frac{-0.31 \times 10^{-2} M}{600\,\text{s}}$$

$$= 5.2 \times 10^{-6} M / s$$

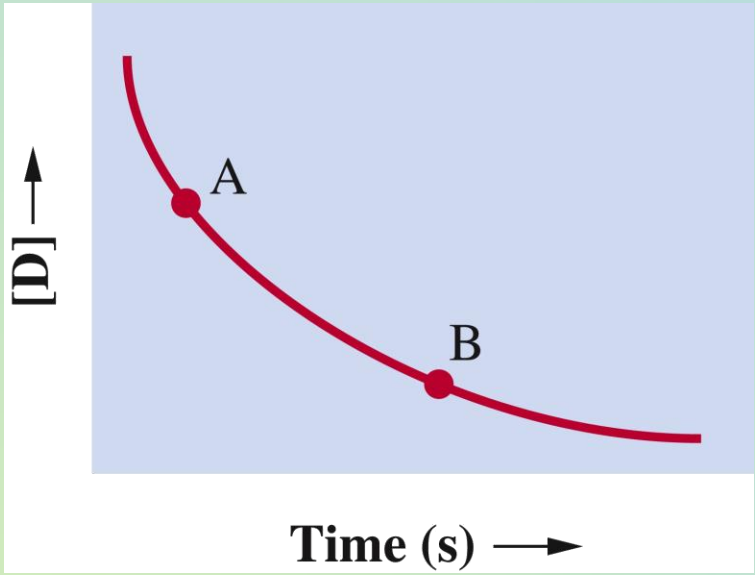
Note that this rate is twice the rate of formation of O_2 in the same time interval.

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Shown here is a plot of the concentration of a reactant D versus time.

a. How do the instantaneous rates at points A and B compare?

b. Is the rate for this reaction constant at all points in time?



a. The slope at point A is greater than the slope at point B, so the instantaneous rate at point A is greater than the instantaneous rate at point B.

b. No. If it were, the graph would be linear.

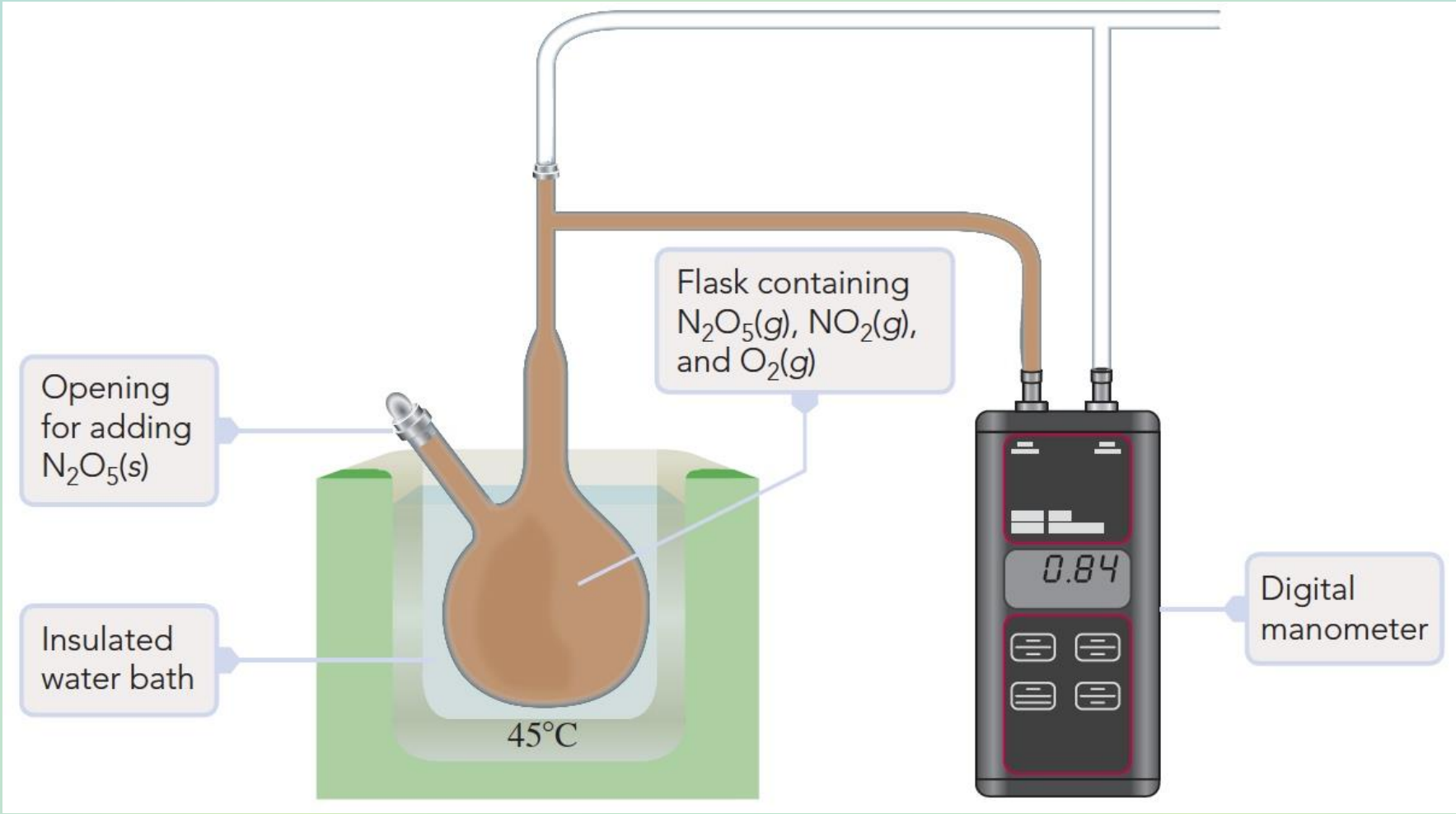
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Rates are determined experimentally in a variety of ways.

For slow reactions, samples can be taken and analyzed from the reaction at several different time intervals.

Continuously following the reaction is more convenient. This can be done by measuring pressure change, as shown on the next slide, or by measuring light absorbance and color change.

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Experimentally, it has been found that a reaction rate depends on the concentration of one or more reactants as well as the concentration of catalyst (if any).

This information is captured in the **rate law,** an equation that relates the rate of a reaction to the concentration of a reactant (and catalyst) raised to various powers. The proportionality constant, *k*, is the **rate constant**.

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For the generic reaction

$$aA + bB \xrightarrow{C} dD + eE \qquad C = \text{catalyst}$$

the rate law can be written in the following manner:

$$\text{Rate} = k[A]^m[B]^n[C]^p$$

The exponents *m*, *n*, and *p* are frequently integers and must be experimentally determined.

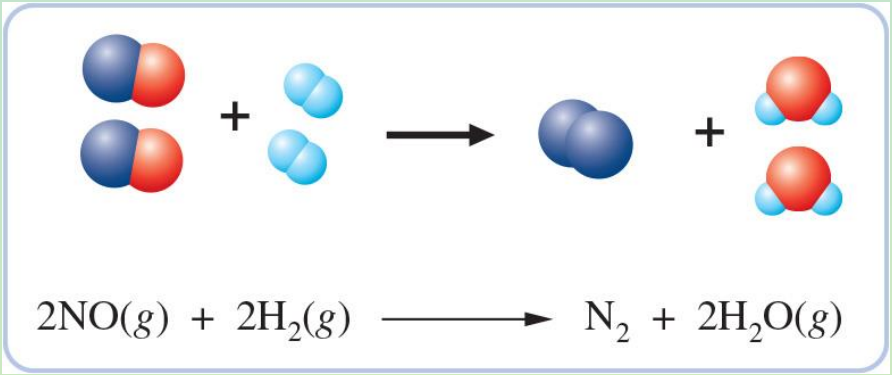
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The **reaction order** with respect to a specific reactant is the exponent of that species in the experimentally determined rate law.

The **overall order of a reaction** is the sum of the orders of the reactant species from the experimentally determined rate law.

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Nitrogen monoxide, NO, reacts with hydrogen according to the equation



The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

Thus, the reaction is second order in NO, first order in H_2, and third order overall.

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Bromide ion is oxidized by bromate ion in acidic solution.

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally determined rate law is

$$\text{Rate} = k\left[Br^-\right]\left[BrO_3^-\right]\left[H^+\right]^2$$

What is the order of reaction with respect to each reactant species?

What is the overall order of the reaction?

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Solution

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

$$\text{Rate} = k\left[Br^-\right]\left[BrO_3^-\right]\left[H^+\right]^2$$

a. The reaction is first order with respect to Br^-.

The reaction is first order with respect to BrO_3^-.

The reaction is second order with respect to H^+.

b. The reaction is fourth order overall (1+1+2).

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Consider the reaction

$$Q + R \rightarrow S + T$$

and the rate law for the reaction:

$$\text{Rate} = k[Q]^0[R]^2$$

a. You run the reaction three times, each time starting with [R] = 2.0 *M*. For each run you change the starting concentration of [Q]: run 1, [Q] = 0.0 *M*; run 2, [Q] = 1.0 *M*; run 3, [Q] = 2.0 *M*. Rank the rate of the three reactions using each of these concentrations.

a. The way the rate law is written in this problem is not typical for expressions containing reactants that are zero order in the rate law. Write the rate law in the more typical fashion.

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a. [Q] = 0.0 *M* is the slowest (no reaction).

The other two have equal rates because they are zero order with respect to [Q].

b. $\text{Rate} = k[\text{R}]^2$

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The rate law for a reaction must be determined experimentally.

We will study the initial rates method of determining the rate law. This method measures the initial rate of reaction using various starting concentrations, all measured at the same temperature.

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Returning to the decomposition of N_2O_5, we have the following data:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

	Initial N_2O_5 Concentration	Initial Rate of Disappearance of N_2O_5
Experiment 1	1.0×10^{-2} mol/L	4.8×10^{-6} mol/(L·s)
Experiment 2	2.0×10^{-2} mol/L	9.6×10^{-6} mol/(L·s)

Note that when the concentration doubles from experiment 1 to 2, the rate doubles.

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Examining the effect of doubling the initial concentration gives us the order in that reactant.

Table 13.1 Effect on Rate of Doubling the Initial Concentration of Reactant

m	Rate Is Multiplied by:
−1	$\frac{1}{2}$
0	1
1	2
2	4

In this case, when the concentration doubles, the rate doubles, so $m = 1$.

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Iodide ion is oxidized in acidic solution to triiodide ion, I_3^-, by hydrogen peroxide.

$$H_2O_2(aq) + 3\,I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$$

A series of four experiments was run at different concentrations, and the initial rates of I_3^- formation were determined. (see table in the next slide)

a. From these data, obtain the reaction orders with respect to H_2O_2, I^-, and H^+.

b. Find the rate constant.

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	Initial Concentrations (mol/L)			*Initial Rate*
	H_2O_2	I^-	H^+	[mol/(L·s)]
Exp.1	0.010	0.010	0.00050	1.15×10^{-6}
Exp.2	0.020	0.010	0.00050	2.30×10^{-6}
Exp.3	0.010	0.020	0.00050	2.30×10^{-6}
Exp.4	0.010	0.010	0.00100	1.15×10^{-6}

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To find the reaction orders of the reactants, know the rate law. Using the reactants in the chemical equation, assume that the rate law has the following form:

$$\text{Rate} = k\left[H_2O_2\right]^m\left[I^-\right]^n\left[H^+\right]^p$$

Each of the reaction orders can be determined by choosing experiments in which all concentrations of reactants, except one, are held constant.

To determine the rate constant, use data from one of the experiments and substitute them into the rate law.

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Solution

Write the rate law for two experiments (the subscript denotes the experiments).

$$(\text{Rate})_1 = k[\text{H}_2\text{O}_2]_1^m[\text{I}^-]_1^n[\text{H}^+]_1^p$$

$$(\text{Rate})_2 = k[\text{H}_2\text{O}_2]_2^m[\text{I}^-]_2^n[\text{H}^+]_2^p$$

Divide the second equation by the first.

$$\frac{(\text{Rate})_2 = \cancel{k}[\text{H}_2\text{O}_2]_2^m[\text{I}^-]_2^n[\text{H}^+]_2^p}{(\text{Rate})_1 = \cancel{k}[\text{H}_2\text{O}_2]_1^m[\text{I}^-]_1^n[\text{H}^+]_1^p}$$

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Group the terms.

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \left(\frac{[H_2O_2]_2}{[H_2O_2]_1}\right)^m \left(\frac{[I^-]_2}{[I^-]_1}\right)^n \left(\frac{[H^+]_2}{[H^+]_1}\right)^p$$

Substitute the values from Experiments 1 and 2.

$$\frac{2.30 \times 10^{-6}}{1.15 \times 10^{-6}} = \left[\frac{0.020}{0.010}\right]^m \left[\frac{0.010}{0.010}\right]^n \left[\frac{0.00050}{0.00050}\right]^p$$

$$2 = 2^m$$

$$m = 1$$

The reaction is first order in H_2O_2.

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Comparing Experiments 1 and 3, it is clear that with the doubling of the I^- concentration, the rate doubles.

$n=1$

Comparing Experiments 1 and 4, it is clear that with the doubling of the H^+ concentration, the rate is not affected.

$p=0$

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Since $[H^+]^0 = 1$, the rate law is:

$$\text{Rate} = k[H_2O_2][I^-]$$

The reaction orders with respect to H_2O_2, I^-, and H^+ are **1, 1, and 0,** respectively.

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The rate constant can be calculated by substituting values from any of the experiments into the rate law. By using Experiment 1:

$$1.15\times10^{-6}\,\frac{\cancel{\text{mol}}}{\text{L}\cdot\text{s}} = k\times0.010\,\frac{\cancel{\text{mol}}}{\cancel{\text{L}}}\times0.010\,\frac{\text{mol}}{\text{L}}$$

$$k = \frac{1.15\times10^{-6}\ /\ \text{s}}{0.010\times0.010\times\text{mol}/\text{L}}$$

$$k = 1.2\times10^{-2}\ \text{L}/(\text{mol}\cdot\text{s})$$

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Note that the units on the rate constant are specific to the overall order of the reaction.

- For a zero-order reaction, the unit is *M*/s or mol/(L · s).
- For a first-order reaction, the unit is 1/s or s^{-1}.
- For a second-order reaction, the unit is 1/(*M* · s) or L/(mol · s).

If you know the rate constant, you can deduce the overall rate of reaction.

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Rate laws are not restricted to chemical systems; they are used to help describe many "everyday" events. For example, a rate law for tree growth might look something like this:

$$\text{Rate of growth} = (\text{soil type})^{w}\,(\text{temperature})^{x}\,(\text{light})^{y}\,(\text{fertilizer})^{z}$$

In this equation, like chemical rate equations, the exponents need to be determined by experiment. (Can you think of some other factors?)

a. Say you are a famous physician trying to determine the factors that influence the rate of aging in humans. Develop a rate law, like the one above, that would take into account at least four factors that affect the rate of aging.

b. Explain what you would need to do in order to determine the exponents in your rate law.

c. Consider smoking to be one of the factors in your rate law. You conduct an experiment and find that a person smoking two packs of cigarettes a day quadruples (4×) the rate of aging over that of a one-pack-a-day smoker. Assuming that you could hold all other factors in your rate law constant, what would be the exponent of the smoking term in your rate law?

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a. $\text{Rate of aging} = (\text{diet})^{w}\,(\text{exercise})^{x}\,(\text{sex})^{y}\,(\text{occupation})^{z}$

b. You would need to run controlled studies quantifying each of the factors and measures of aging.

c. When smoking doubles, aging increases fourfold. That is a second-order reaction. Therefore, $m = 2$.

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The rate law tells us the relationship between the rate and the concentrations of reactants and catalysts.

To find concentrations at various times, we need to use the **integrated rate law**, the mathematical relationship between concentration and time.

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First-Order Rate Law

Consider the equation where A is the substance that reacts to give products.

$$a\mathrm{A} \rightarrow \text{products}$$

If this equation has a first-order rate law,

$$\text{Rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]$$

Using calculus, you derive the following integrated rate law equation:

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt \quad (\text{first - order integrated rate law})$$

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Second-Order Rate Law

Consider the following reaction:

$$aA \rightarrow \text{products}$$

Suppose it has the second-order rate law.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

Using calculus, you can obtain the following relationship between the concentrations of A and the time.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \left(\text{second - order integrated rate law}\right)$$

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Zero-Order Reactions

Consider the following reaction:

$$A \rightarrow B + C$$

Suppose it has a zero-order rate law of

$$\text{Rate} = k$$

Relationship between concentration and time would be:

$$[A]_t = -kt + [A]_0 \ (\text{zero - order integrated rate law})$$

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The decomposition of N_2O_5 to NO_2 and O_2 is first order, with a rate constant of 4.80×10^{-4}/s at 45° C.

a. If the initial concentration is 1.65×10^{-2} mol/L, what is the concentration after 825 s?
b. How long would it take for a concentration of N_2O_5 to decrease to is 1.00×10^{-2} mol/L from its initial value, given in a?

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Solution

a. The equation for first order reaction is $\ln \frac{[A]_t}{[A]_0} = -kt$

Substituting the appropriate values:

$$\ln \frac{[N_2O_5]_t}{1.65 \times 10^{-2} \text{ mol/L}} = -4.80 \times 10^{-4}/\text{s} \times 825 \text{ s} = -0.396$$

To solve for $[N_2O_5]_t$, take the antilongarithm (antiln) of both sides. This removes the ln from the left and gives the antiln(–0.396), or $e^{-0.396}$, on the right which equals 0.673.

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$$\frac{[N_2O_5]_t}{1.65\times10^{-2}\,mol/L} = 0.673$$

Hence,

$$[N_2O_5]_t = 1.65\times10^{-2}\,mol/L \times 0.673$$

$$[N_2O_5]_t = 0.0111\,mol/L$$

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b. Substitute into the same first-order equation relating concentration to time.

$$\ln\frac{1.00\times10^{-2}\,\text{mol/L}}{1.65\times10^{-2}\,\text{mol/L}} = -4.80\times10^{-4}\,/\,\text{s}\times t$$

$$0.501 = 4.80\times10^{-4}\,/\,\text{s}\times t$$

$$t = 1.04\times10^{3}\,\text{s}\ \left(17.4\,\text{min}\right)$$

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The **half-life** of a reaction, $t_{½}$, is the time it takes for the reactant concentration to decrease to one-half of its initial value.

By substituting $½[A]_0$ for $[A]_t$, we solve the integrated rate law for the special case of $t = t_{½}$.

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Table 13.2 Relationships for Zero-Order, First-Order, and Second-Order Reactions

Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	$\text{Rate} = k$	$[\text{A}]_t = -kt + [\text{A}]_0$	$\frac{[\text{A}]_0}{2k}$	[A] vs t
1	$\text{Rate} = k[\text{A}]$	$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$	$0.693/k$	ln[A] vs t
2	$\text{Rate} = k[\text{A}]^2$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$	$1/(k[\text{A}]_0)$	$\frac{1}{[\text{A}]}$ vs t

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Sulfuryl chloride, SO_2Cl_2, is a colorless, corrosive liquid whose vapor decomposes in a first-order reaction to sulfur dioxide and chlorine.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

At 320° C, the rate constant is 2.20×10^{-5}/s.

a. What is the half-life of SO_2Cl_2 vapor at this temperature?

b. How long (in hours) would it take for 50.0% of the SO_2Cl_2 to decompose?

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Solution

a. $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.20 \times 10^{-5}\ /\ \text{s}}$$

$$t_{1/2} = 3.15 \times 10^{4}\ \text{s}$$

b. The half-life time required to decompose one half of SO_2Cl_2 is 3.15×10^4 s or 8.75 hours.

The time required for two half-lives is

$$2 \times 8.75\ \text{hours} = 17.5\ \text{hours}$$

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Let's look again at the integrated rate laws.

Order	Rate Law	Integrated Rate Law	
0	$\text{Rate} = k$	$[\text{A}]_t = -kt + [\text{A}]_0$	$y = mx + b$
1	$\text{Rate} = k[\text{A}]$	$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$	$y = mx + b$
2	$\text{Rate} = k[\text{A}]^2$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$	$y = mx + b$

In each case, the rate law is in the form of $y = mx + b$, allowing us to use the slope and intercept to obtain the rate constant for a reaction.

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$$\textbf{Zero Order : } [A]_t = -kt + [A]_0$$

For a zero-order reaction, a plot of $[A]_t$ versus t is linear. The y-intercept is $[A]_0$.

$$\textbf{First Order : } \ln[A]_t = -kt + \ln[A]_0$$

For a first-order reaction, a plot of $\ln[A]_t$ versus t is linear. The graph crosses the origin ($b = 0$).

$$\textbf{Second Order : } \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

For a second-order reaction, a plot of $1/[A]_t$ versus t is linear. The y-intercept is $1/[A]_0$.

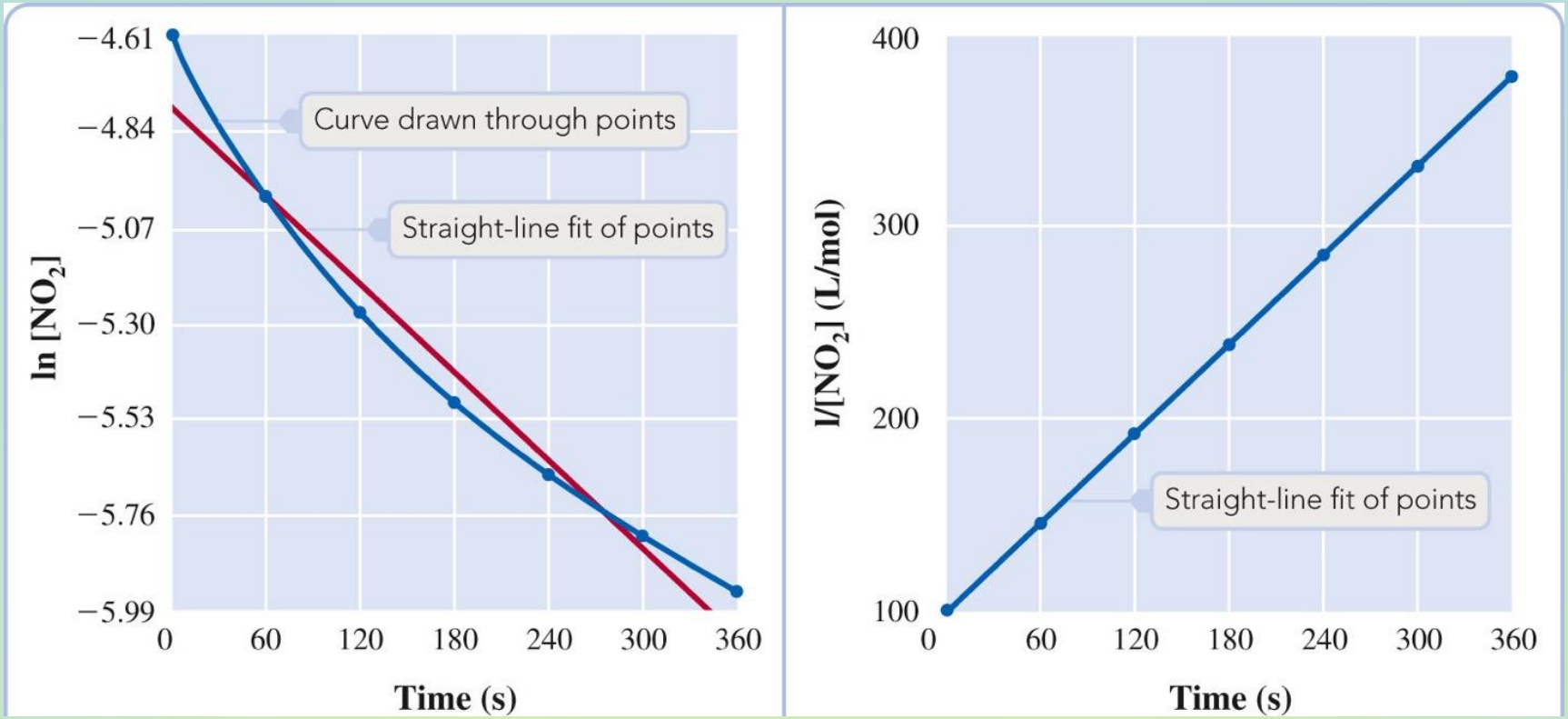
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Graphs of concentration and time can also be used to determine the order of reaction in that reactant.

- For zero-order reactions, [A] versus *t* is linear.
- For first-order reactions, ln[A] versus *t* is linear.
- For second order reactions, 1/[A] versus *t* is linear.

This is illustrated on the next slide for the decomposition of NO_2.

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Left: The plot of $\ln[NO_2]$ versus *t* is not linear, so the reaction is not first order.

Right: The plot of $1/[NO_2]$ versus *t* is linear, so the reaction is second order in NO_2.

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A reaction believed to be either first or second order has a half-life of 20 s at the beginning of the reaction but a half-life of 40 s sometime later. What is the order of the reaction?

$$\text{Zero Order}: \; t_{1/2} = \frac{[\text{A}]_0}{2k}$$

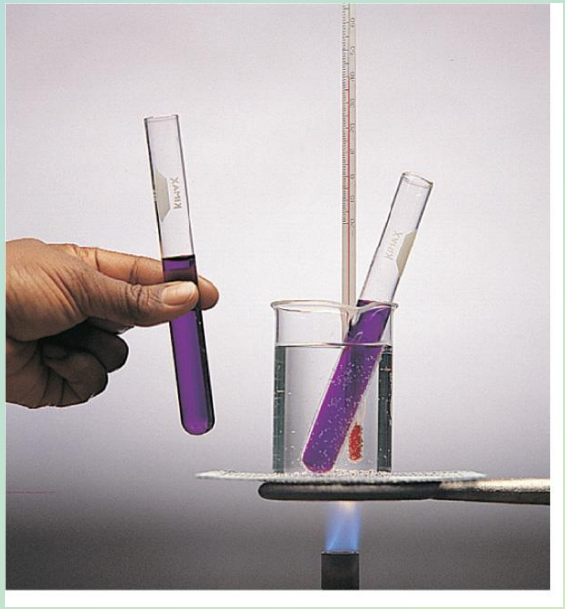
$$\text{First Order}: \; t_{1/2} = \frac{0.693}{k}$$

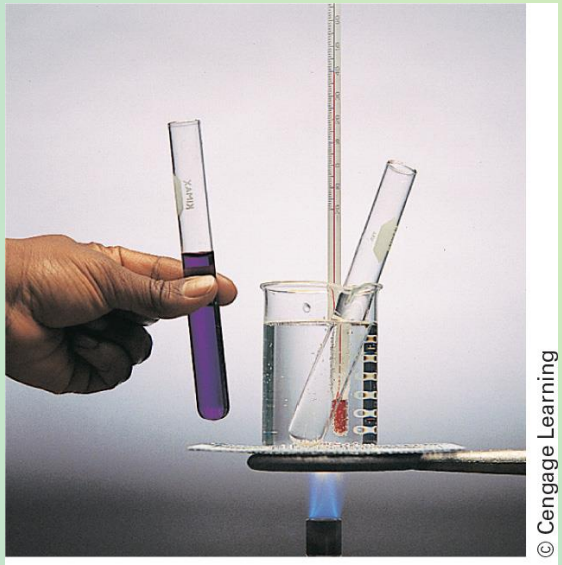
$$\text{Second Order}: \; t_{1/2} = \frac{1}{k[\text{A}]_t}$$

The initial concentration decreases in each time interval. The only equation that results in a larger value for $t_{1/2}$ is the second-order equation.

The reaction is second order.

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Each test tube contains potassium permanganate, $KMnO_4$, and oxalic acid, $H_2C_2O_4$, at the same concentrations. Permanganate ion oxidizes oxalic acid to CO_2 and H_2O.

Top: One test tube was placed in a beaker of warm water (40° C); the other was kept at room temperature (20° C).
Bottom: After 10 minutes, the test tube at 40° C showed a noticeable reaction, whereas the other did not.

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Rate Constant and Temperature

The rate constant depends strongly on temperature. How can we explain this relationship?

Collision theory assumes that reactant molecules must collide with an energy greater than some minimum value and with the proper orientation.

The minimum energy is called the **activation energy,** E_a.

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We will now explore the effect of a temperature increase on each of the three requirements for a reaction to occur.

The rate constant can be given by the equation

$$k = Zfp$$

Where

Z = collision frequency

f = fraction of collisions with the minimum energy

p = orientation factor

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Certainly, Z will increase with temperature, as the average velocity of the molecules increases with temperature.

However, this factor alone cannot explain the dramatic effect of temperature changes on reaction rates.

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The fraction of molecular collisions having the minimum energy required is given by *f.*

$$f = e^{-E_a/RT}$$

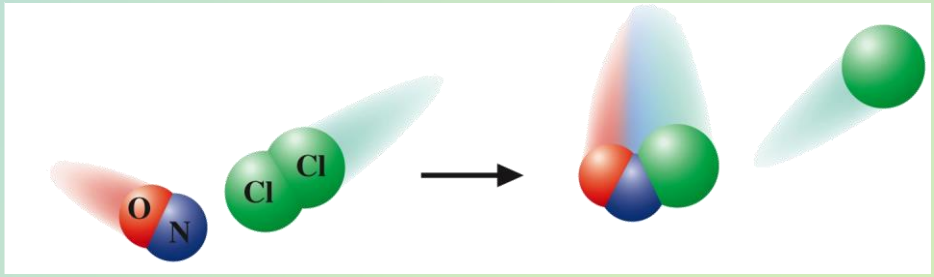
Now we can explain the dramatic impact of temperature. *f* decreases with increasing values of E_a. Since *k* depends on *f*, reactions with larger activation energies have small rate constants and vice versa.

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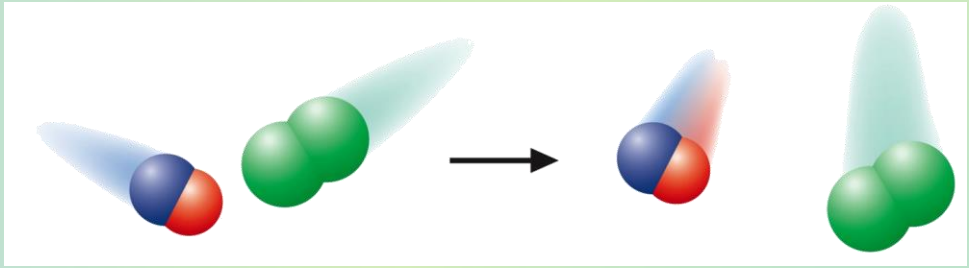
The reaction rate also depends on *p*, the proper orientation for the collision. This factor is independent of temperature changes.

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Importance of Molecular Orientation in the Reaction of NO and Cl_2



a. NO approaches with its N atom toward Cl_2, and an N–Cl bond forms. Also, the angle of approach is close to that in the product NOCl.



b. NO approaches with its O atom toward Cl_2. No N–Cl bond can form, so NO and Cl_2 collide and then fly apart.

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Transition-state theory explains the reaction resulting from the collision of two molecules in terms of an **activated complex** (transition state), an unstable grouping of atoms that can break up to form products.

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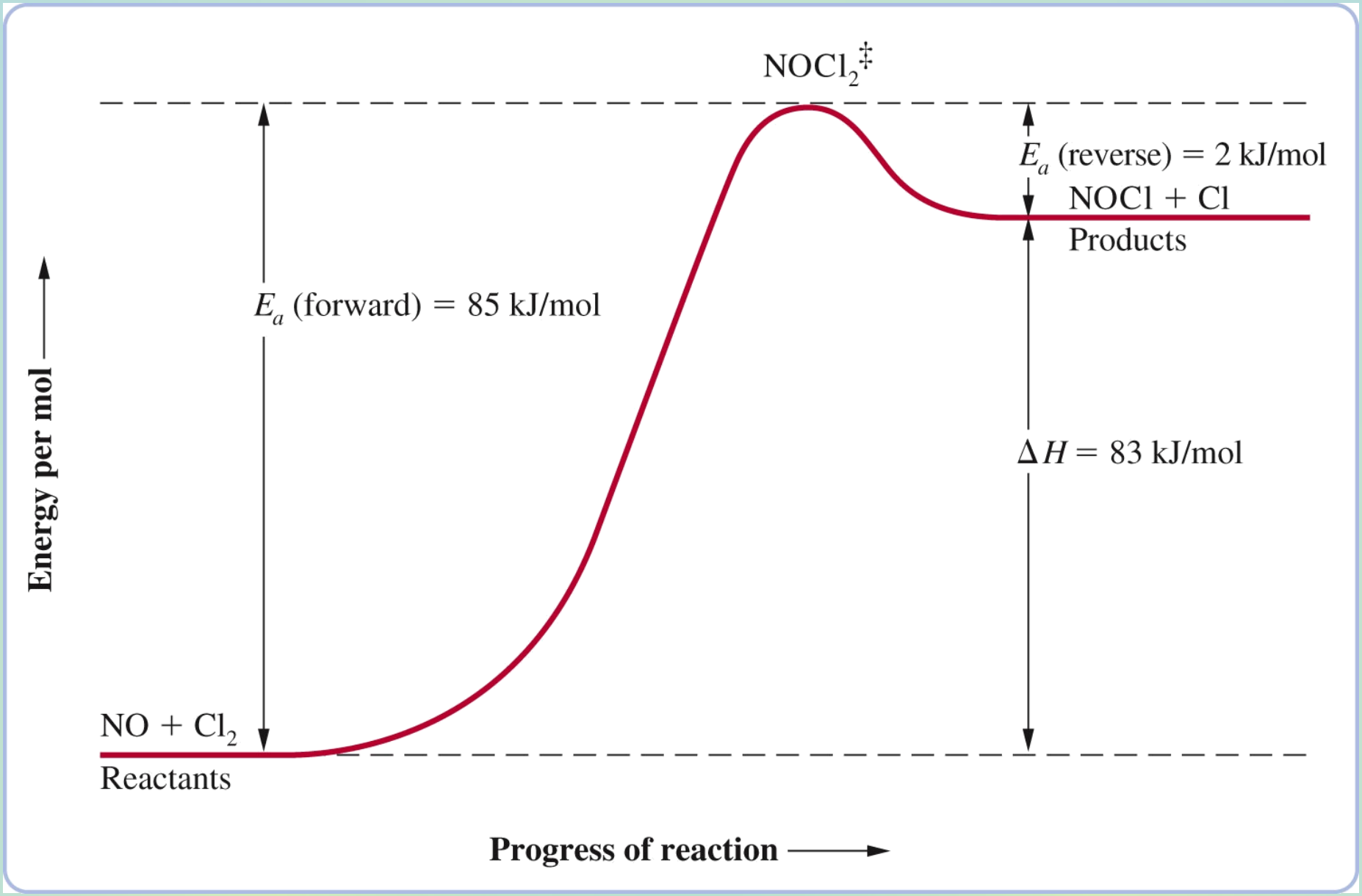
The potential energy diagram for a reaction visually illustrates the changes in energy that occur.

The next slide shows the diagram for the reaction

$$NO + Cl_2 \rightarrow NOCl_2^{\ddagger} \rightarrow NOCl + Cl$$

where $NOCl_2^{\ddagger}$ indicates the activated complex.

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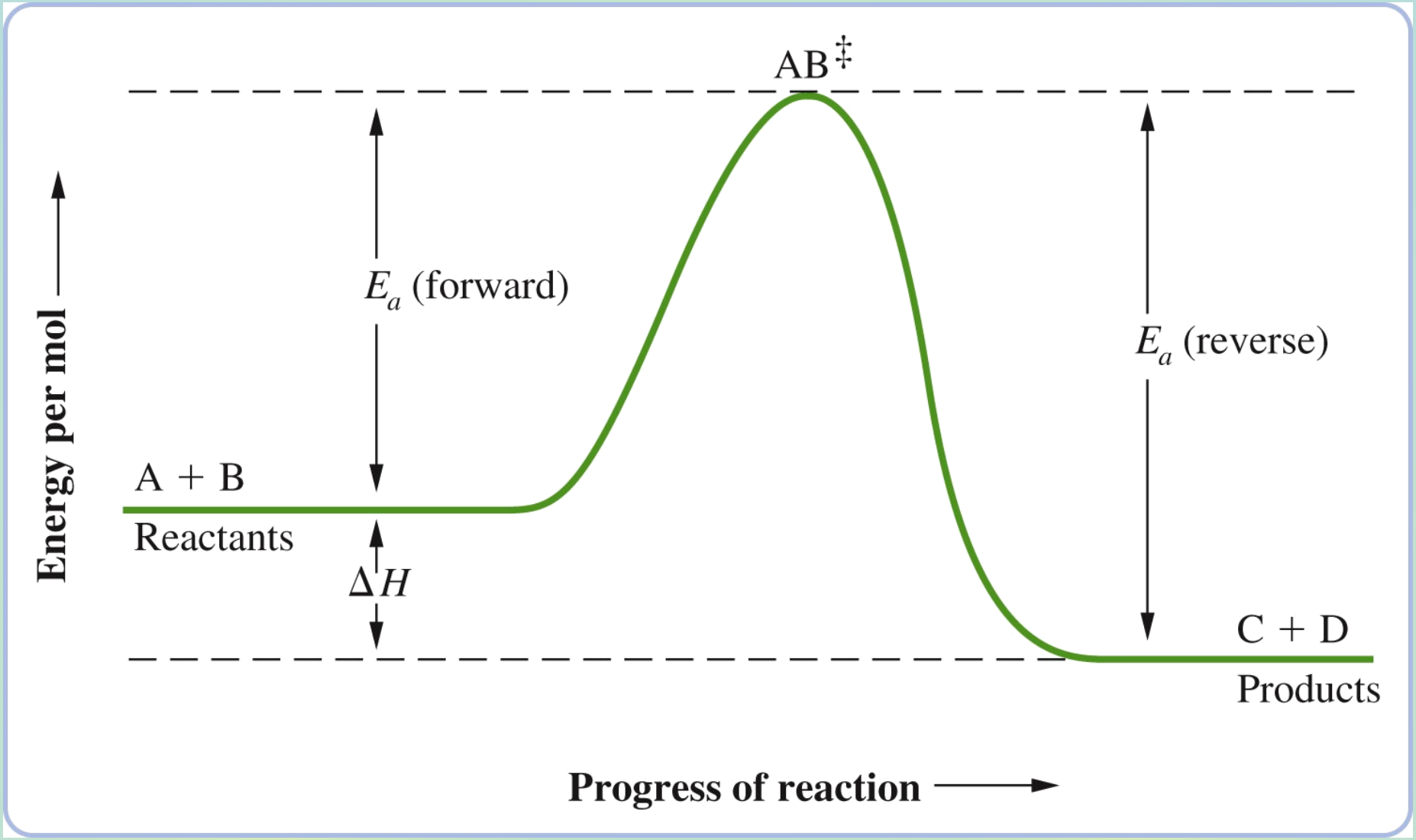


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The reaction of NO with Cl_2 is an endothermic reaction.

The next slide shows the curve for a generic exothermic reaction.

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Rate constants for most chemical reactions closely follow an equation in the following form:

$$k = Ae^{-E_a/RT}$$

This is called the Arrhenius equation, where

e is the base of natural logarithms.

E_a is the activation energy.

R is the gas constant, 8.31 J/(K·mol).

T is the absolute temperature.

A is the **frequency factor**, a constant.

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A more useful form of the Arrhenius equation is its two-point form.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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The rate constant for the formation of hydrogen iodide from the elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.27×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K.

a. Find the activation energy E_a.
b. Calculate the rate constant at 700 K.

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Solution

a. $$\ln\frac{3.5\times10^{-3}}{2.7\times10^{-4}} = \frac{E_a}{8.31\,\text{J}/(\text{mol}\cdot\text{K})}\left(\frac{1}{600\,\text{K}} - \frac{1}{650\,\text{K}}\right)$$

$$\ln 1.30\times10^{1} = 2.56 = \frac{E_a}{8.31\,\text{J/mol}}\times\left(1.28\times10^{-4}\right)$$

$$E_a = \frac{2.56\times8.31\,\text{J/mol}}{1.28\times10^{-4}}$$

$$E_a = 1.66\times10^{5}\,\text{J/mol}$$

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b. Substitute $E_a = 1.66 \times 10^5$ J/mol.

$k_1 = 2.7 \times 10^{-4}$ L/(mol·s) ($T_1 = 600$ K)

k_2 = unknown as yet ($T_2 = 700$ K)

$$\ln \frac{k_2}{2.7\times10^{-4}\,\mathrm{L/(mol\cdot s)}} = \frac{1.66\times10^5\,\mathrm{J/mol}}{8.31\,\mathrm{J/(mol\cdot K)}} \times \left(\frac{1}{600\,\mathrm{K}} - \frac{1}{700\,\mathrm{K}} \right) = 4.77$$

$$\frac{k_2}{2.7\times10^{-4}\,\mathrm{L/(mol\cdot s)}} = e^{4.77} = 1.2\times10^2$$

Taking antilogarithms:

$$k_2 = \left(1.2\times10^2\right) \times \left(2.7\times10^{-4}\right) \mathrm{L/(mol\cdot s)}$$

$$\boxed{k_2 = 3.2\times10^{-2}\,\mathrm{L/(mol\cdot s)}}$$

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Catalysis

It is an increase in the rate of reaction that results from the addition of a catalyst.

Enzymes are marvelously selective biological catalysts.

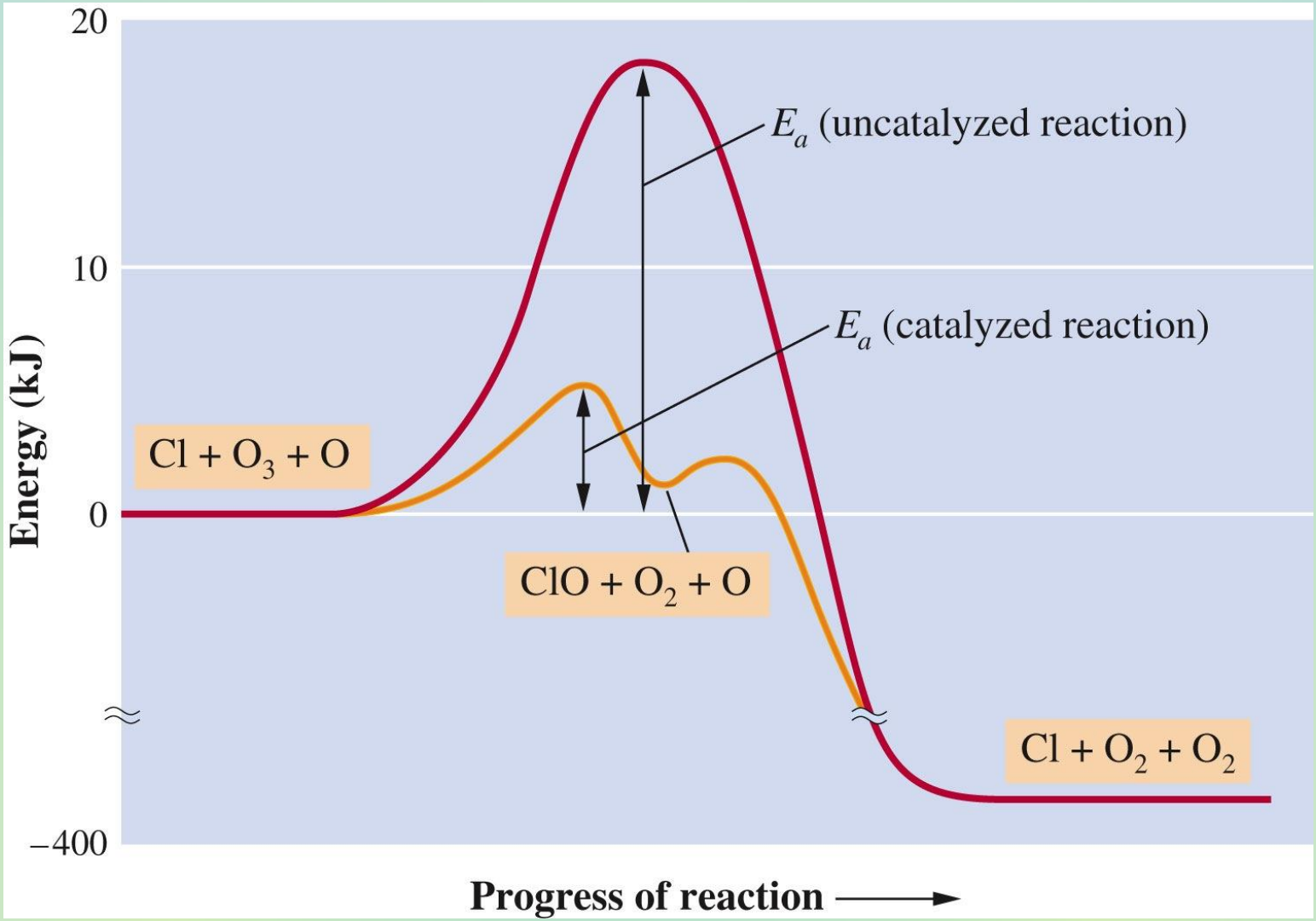
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A **catalyst** is not consumed in a reaction. Rather, it is present in the beginning, is used in one step, and is produced again in a subsequent step. As a result, the catalyst does not appear in the overall reaction equation.

A catalyst increases the reaction rate by either increasing the frequency factor *A*, or providing an alternative reaction path with a lower activation energy. When E_a is reduced, *k* increases exponentially.

This relationship is illustrated on the potential energy diagram for the decomposition of ozone.

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Homogenous Catalysis

It is the process which uses the catalyst in the same phase as the reacting species.

Consider the decomposition of aqueous hydrogen peroxide to form water and oxygen.

$$2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$$

Proposed mechanism is:

$$\text{Step 1: } H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(l) \quad \text{(slow)}$$

$$\text{Step 2: } IO^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq) \quad \text{(fast)}$$

$$\text{Overall: } 2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$$

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Heterogeneous Catalysis

Applied in most industrial reactions, it uses a catalyst that exists in a different phase from the reacting species, usually a solid catalyst in contact with a gaseous or liquid solution of reactants.

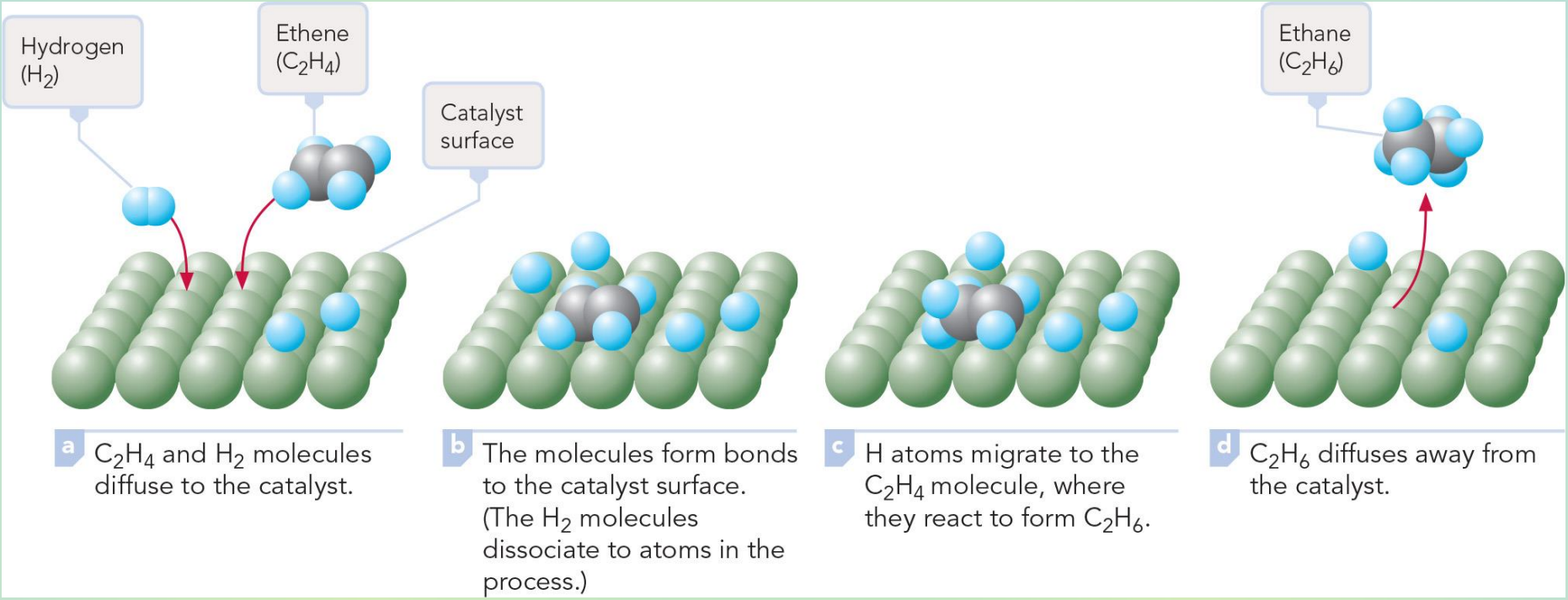
This occurs via chemical *adsorption* of reactants onto the catalyst surface.

Chemisorption

It is the binding of a species to the surface by chemical bonding forces that break the bonds in the species.

The best example is catalytic hydrogenation, illustrated in the following slide.

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Enzyme Catalysis

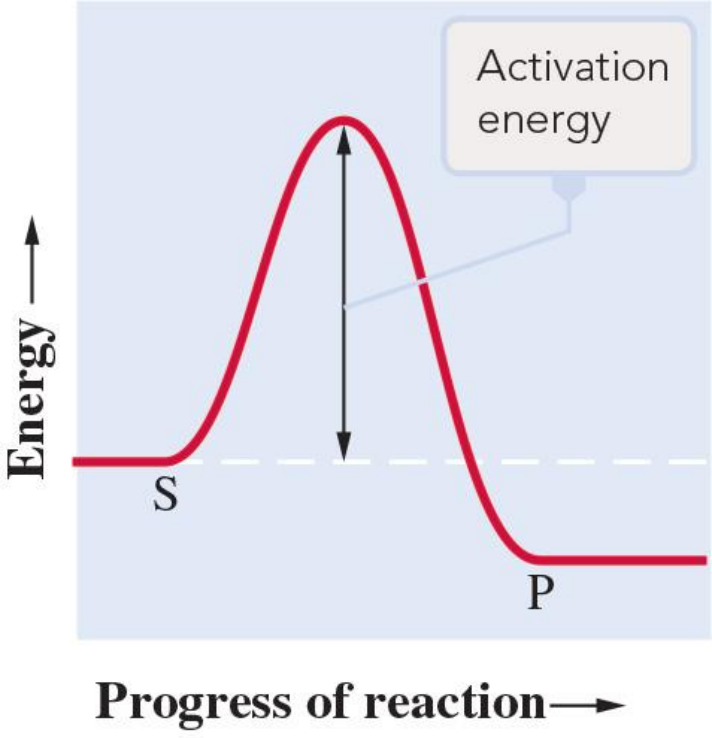
Enzymes have enormous catalytic activity and are highly specific. The substance whose reaction the enzyme catalyzes is called the **substrate**.

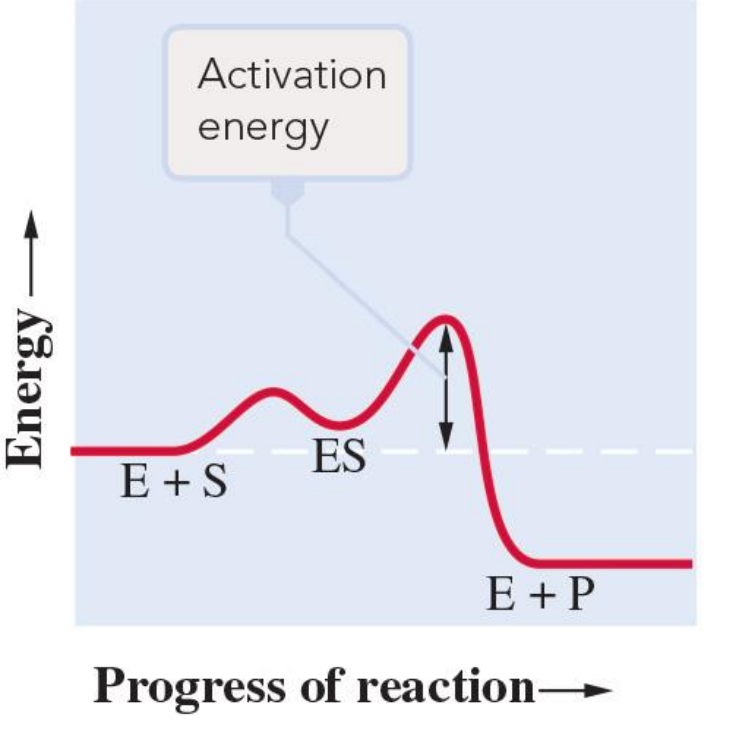
When a substrate fits into the active site where catalysis occurs, an enzyme-substrate (ES) complex is formed. On binding, the bonds in the substrate may weaken or new bonds may form. This helps yield a product, P.

$$E + S \rightarrow ES \rightarrow E + P$$

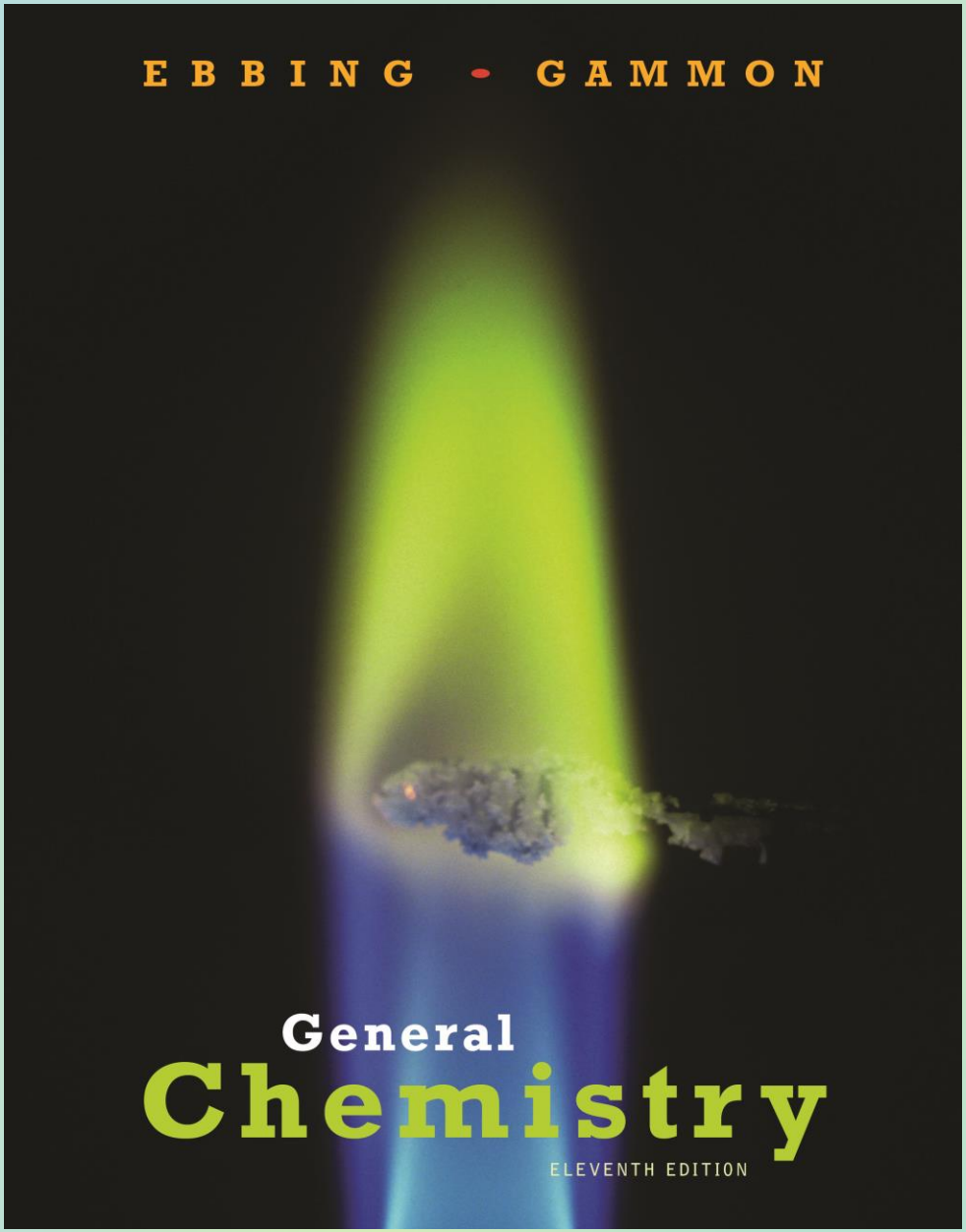
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Notice that the formation of the ES complex provides a new pathway for products with lower E_a, as mentioned below in the illustration.





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Chapter 14 Chemical Equilibrium

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Chemical reactions often seem to stop before they are complete.

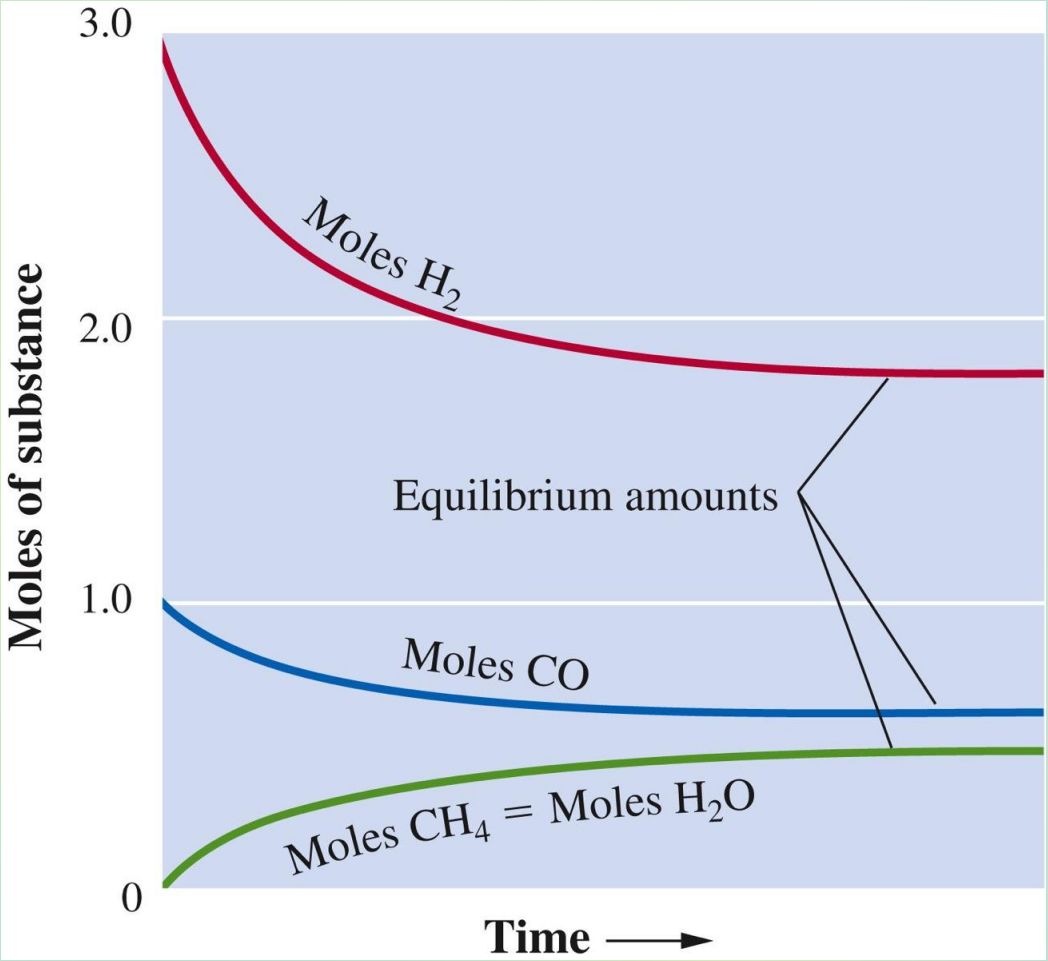
Actually, such reactions are *reversible*. That is, the original reactants form products, but then the products react with themselves to give back the original reactants.

When these two reactions—forward and reverse—occur at the same rate, a chemical equilibrium exists.

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$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

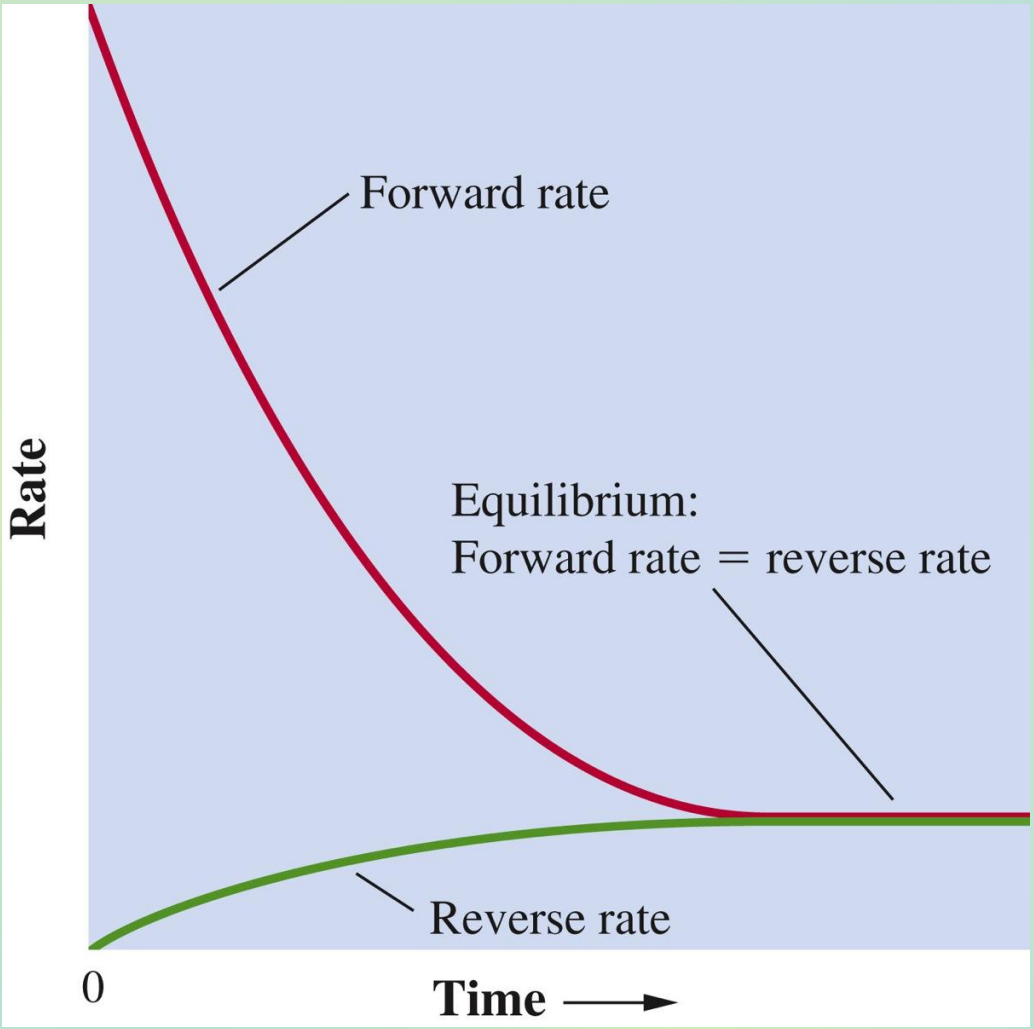
The graph shows how the amounts of reactants and products change as the reaction approaches equilibrium.



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$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

This graph shows how the rates of the forward reaction and the reverse reaction change as the reaction approaches equilibrium.



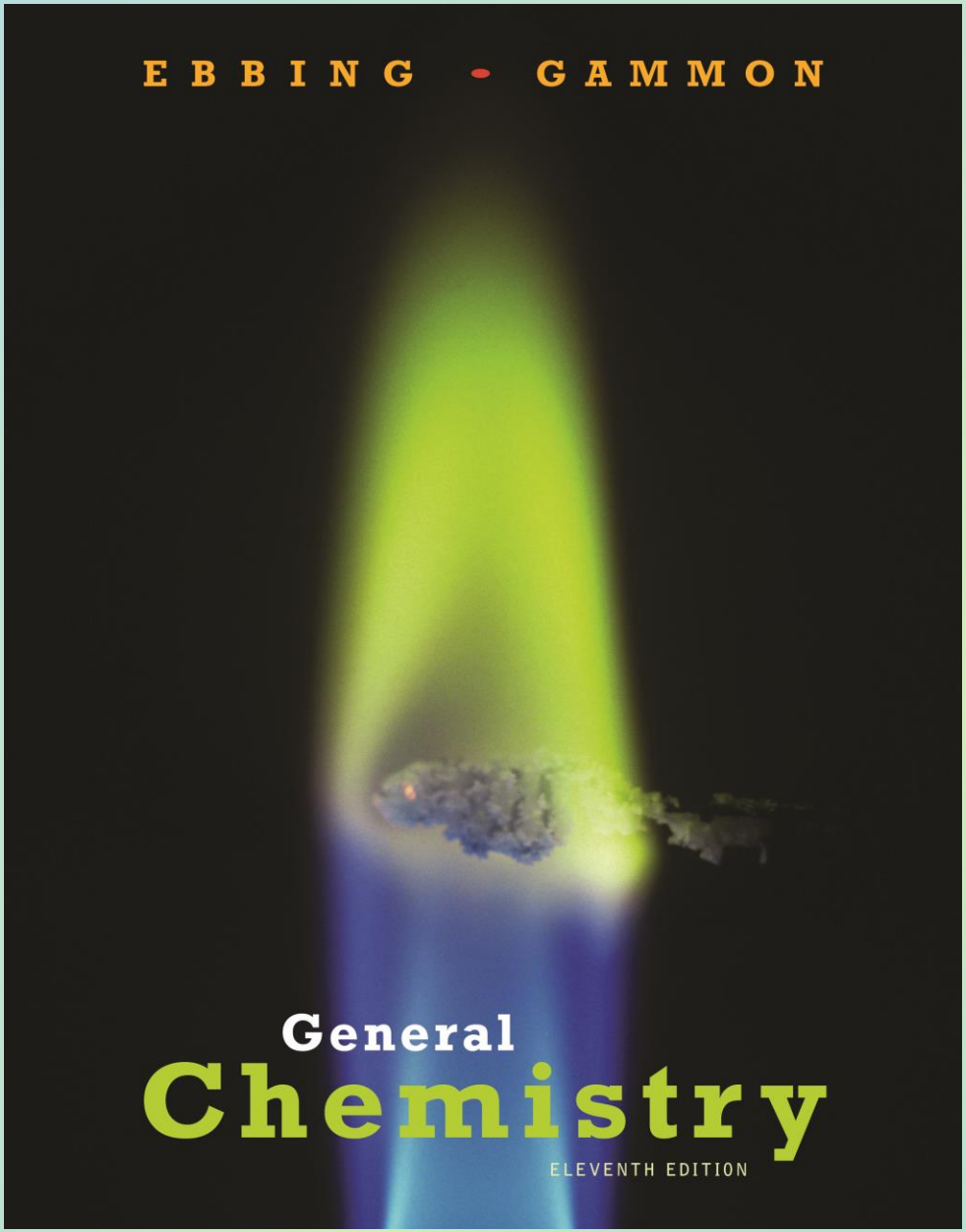
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Chemical equilibrium is the state reached by a reaction mixture when the rates of the forward and reverse reactions have become equal.

Continuous forward and reverse reactions make the equilibrium a *dynamic* process.

We can apply stoichiometry to compute the content of the reaction mixture at equilibrium.

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Chapter 15
Acids and Bases

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When gaseous hydrogen chloride meets gaseous ammonia, white fumes composed of ammonium chloride are formed.

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

This is an acid–base reaction.

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We will examine three ways to explain acid–base behavior:

1. Arrhenius Concept
2. Brønsted–Lowry Concept
3. Lewis Concept

Note: H^+ in water is H_3O^+.

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Arrhenius Concept of Acids and Bases

An Arrhenius acid is a substance that, when dissolved in water, increases the concentration of hydronium ion, $H_3O^+(aq)$.

An Arrhenius base is a substance that, when dissolved in water, increases the concentration of hydroxide ion, $OH^-(aq)$.

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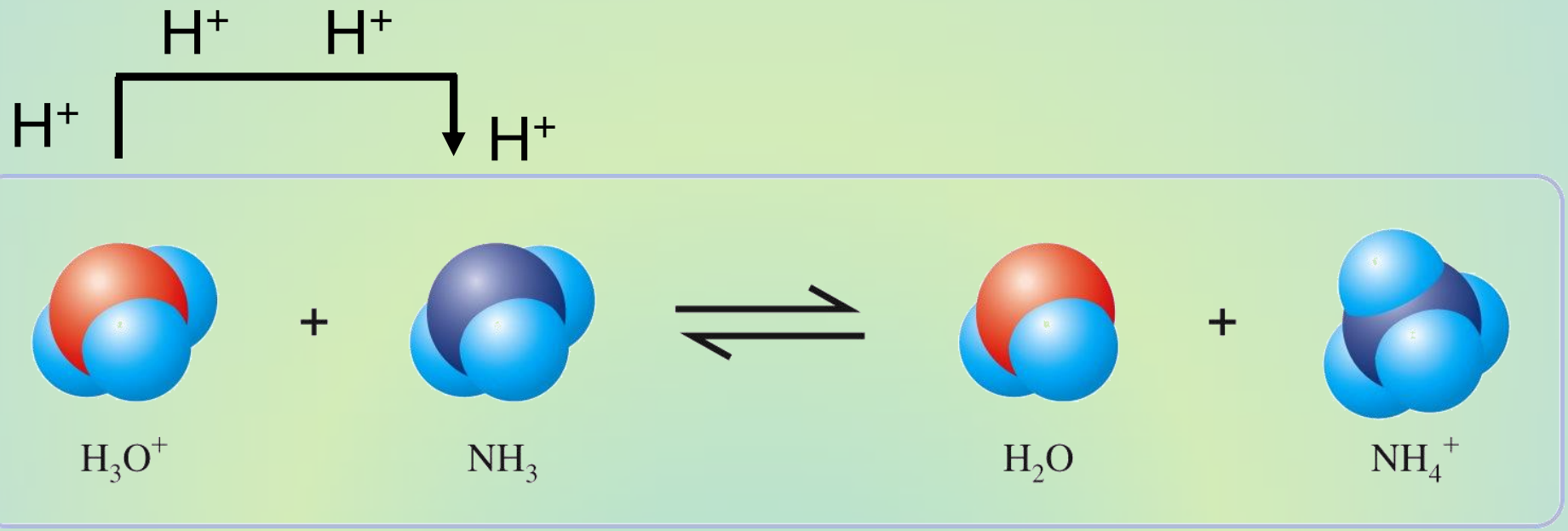
The Arrhenius concept is limited. It considers acid–base reactions only in aqueous solutions and limits bases to compounds that contain the hydroxide ion.

The Brønsted–Lowry concept provides broader definitions of acids and bases.

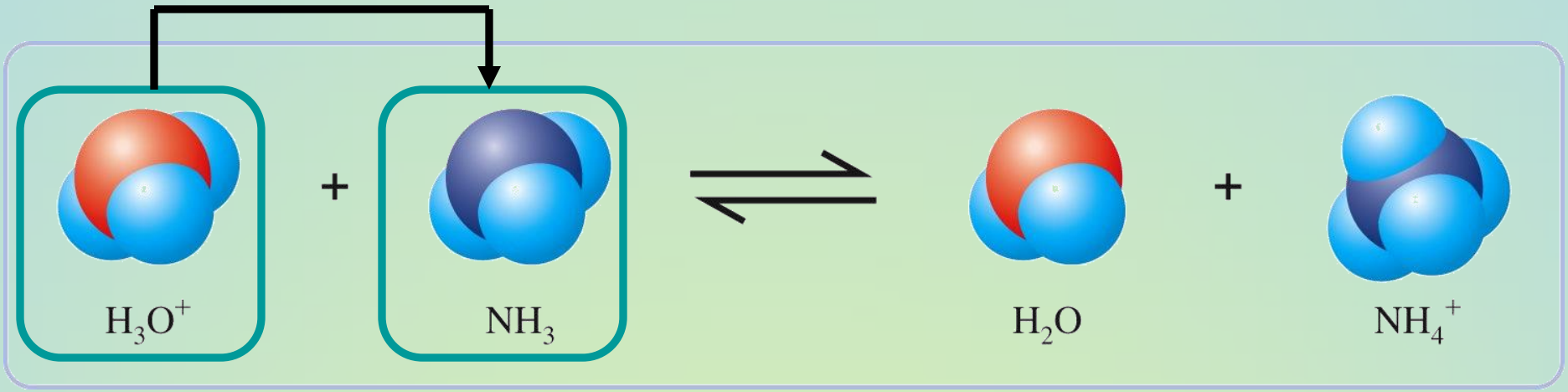
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Brønsted–Lowry Concept of Acids and Bases

An acid–base reaction is considered a proton (H^+) transfer reaction.



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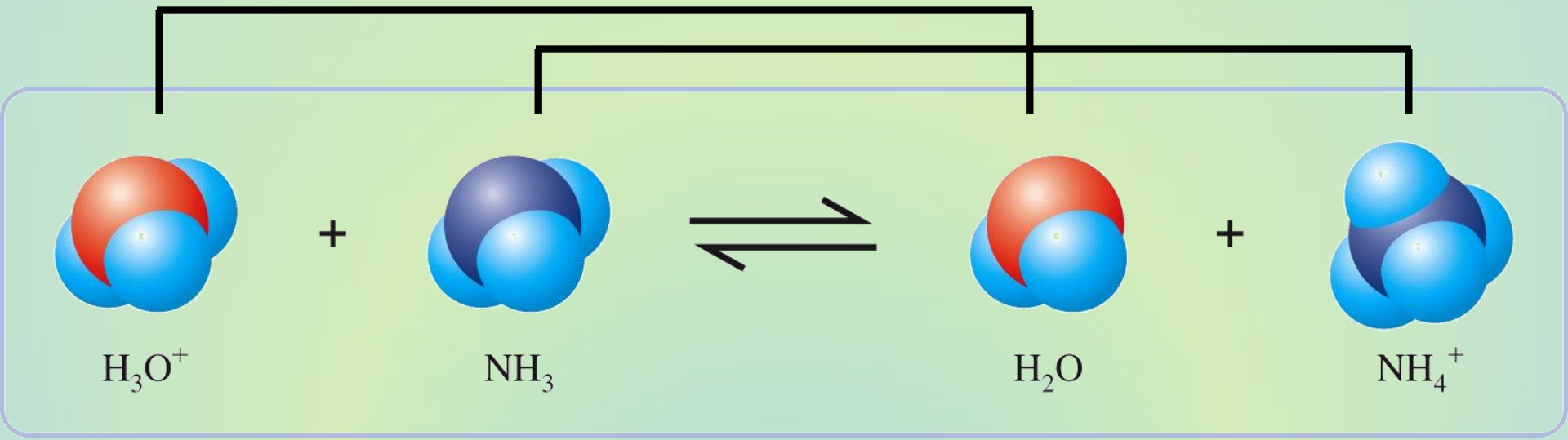


A Brønsted–Lowry **acid** is the species donating a proton in a proton-transfer reaction; it is a proton donor.

A Brønsted–Lowry **base** is the species accepting a proton in a proton-transfer reaction; it is a proton acceptor.

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Substances in the acid–base reaction that differ by the gain or loss of a proton, H^+, are called a conjugate **acid–base pair**. The acid is called the conjugate acid; the base is called a conjugate base.



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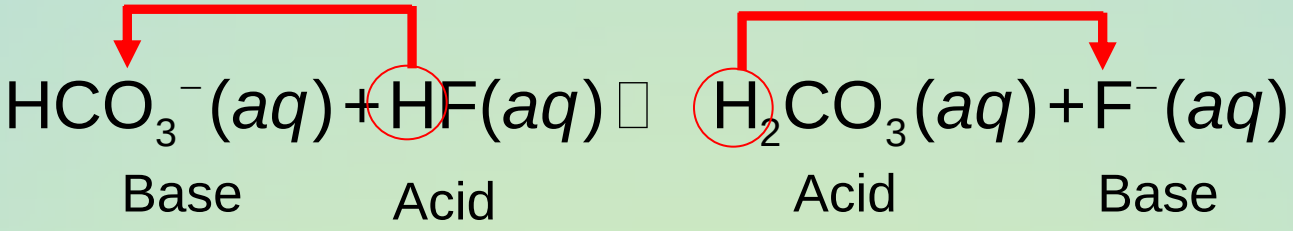
In the following equations, label each species as an acid or base. Show the conjugate acid–base pairs.

a. $HCO_3^-(aq) + HF(aq) \rightarrow H_2CO_3(aq) + F^-(aq)$

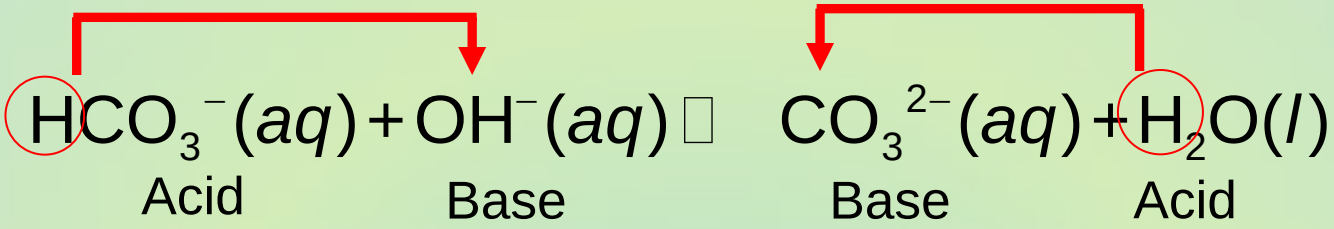
b. $HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$

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Solution

a. 

In this reaction, H_2CO_3 and HCO_3^- are the conjugate acid–base pair, as are HF and F^-.

b. 

Here HCO_3^- and CO_3^{2-} are the conjugate acid–base pair, as are H_2O and OH^- .

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Species that can act as either an acid or and a base, depending on the other reactant, are called **amphoteric species.**

Identify any amphiprotic species in the previous problem.

HCO_3^- was a base in the first reaction and an acid in the second reaction. It is amphiprotic.

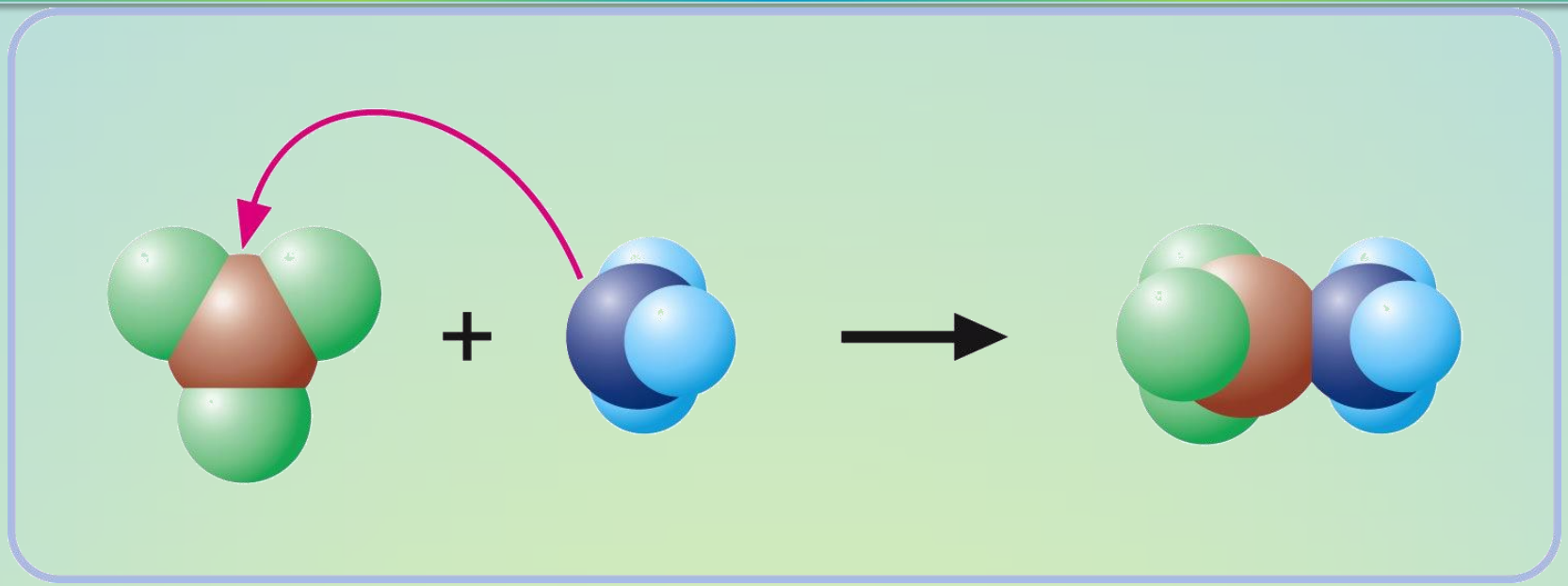
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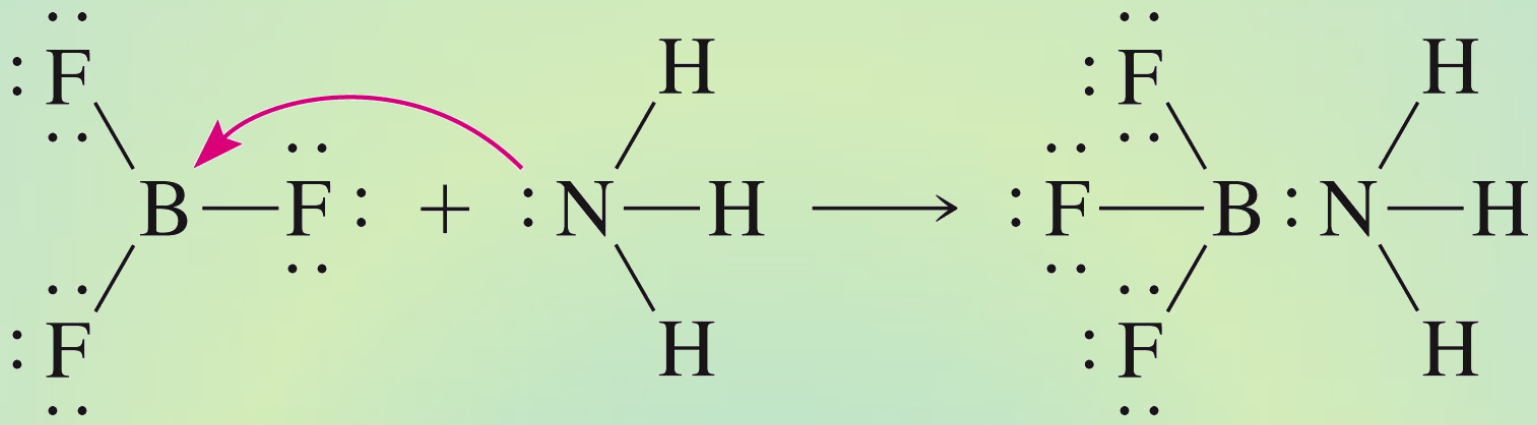
Lewis Concept of Acids and Bases

A **Lewis acid** is a species that can form a covalent bond by accepting an electron pair from another species.

A **Lewis base** is a species that can form a covalent bond by donating an electron pair to another species.

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In the following reaction, identify the Lewis acid and Lewis base.

$$Ag^{+} + 2NH_3 \rightarrow Ag(NH_3)_2^{+}$$

Solution

The silver ion, Ag^{+}, forms a complex ion with two NH_3 molecules.

$$Ag^{+} + 2 : NH_3 \rightarrow Ag(: NH_3)_2^{+}$$

Lewis acid

Lewis base

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Relative Strengths of Acids and Bases

The stronger an acid, the weaker its conjugate base.

The weaker an acid, the stronger its conjugate base.

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Table 15.2 Relative Strengths of Acids and Bases

	Acid	Base	
Strongest acids	$HClO_4$	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HClO	ClO^-	
	HBrO	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
	HS^-	S^{2-}	
Weakest acids	H_2O	OH^-	Strongest bases

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For the following reaction, decide which species (reactants or products) are favored at the completion of the reaction.

$$SO_4^{2-}(aq) + HCN(aq) \rightleftharpoons HSO_4^{-}(aq) + CN^{-}(aq)$$

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Solution

While comparing relative strengths of the two acids HCN and HSO_4^-, it can be noticed that HCN is weaker. Comparing bases SO_4^{2-} and CN^-, it can be seen that SO_4^{2-} is weaker. Hence the reaction would go from right to left.

$$SO_4^{2-}(aq) + HCN(aq) \leftarrow HSO_4^-(aq) + CN^-(aq)$$

weaker base	weaker acid	stronger acid	stronger base

The reactants are favored.

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The Equilibrium Constant, K_c

Equilibrium constant expression: Obtained by multiplying the concentrations of products, divided by the concentrations of reactants, and raising each concentration term to a power equal to its coefficient in the balanced chemical equation.

Equilibrium constant, K_c: Value obtained for the K_c expression when equilibrium concentrations are substituted.

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For the reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant expression is as follows:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Law of mass action: Values of the equilibrium constant expression K_c are constant for a specific reaction at a given temperature, whatever equilibrium concentrations are substituted.

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Write the equilibrium-constant expression K_c for catalytic methanation.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Solution

The expression for the equilibrium constant is:

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

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Equilibrium: A Kinetics Argument

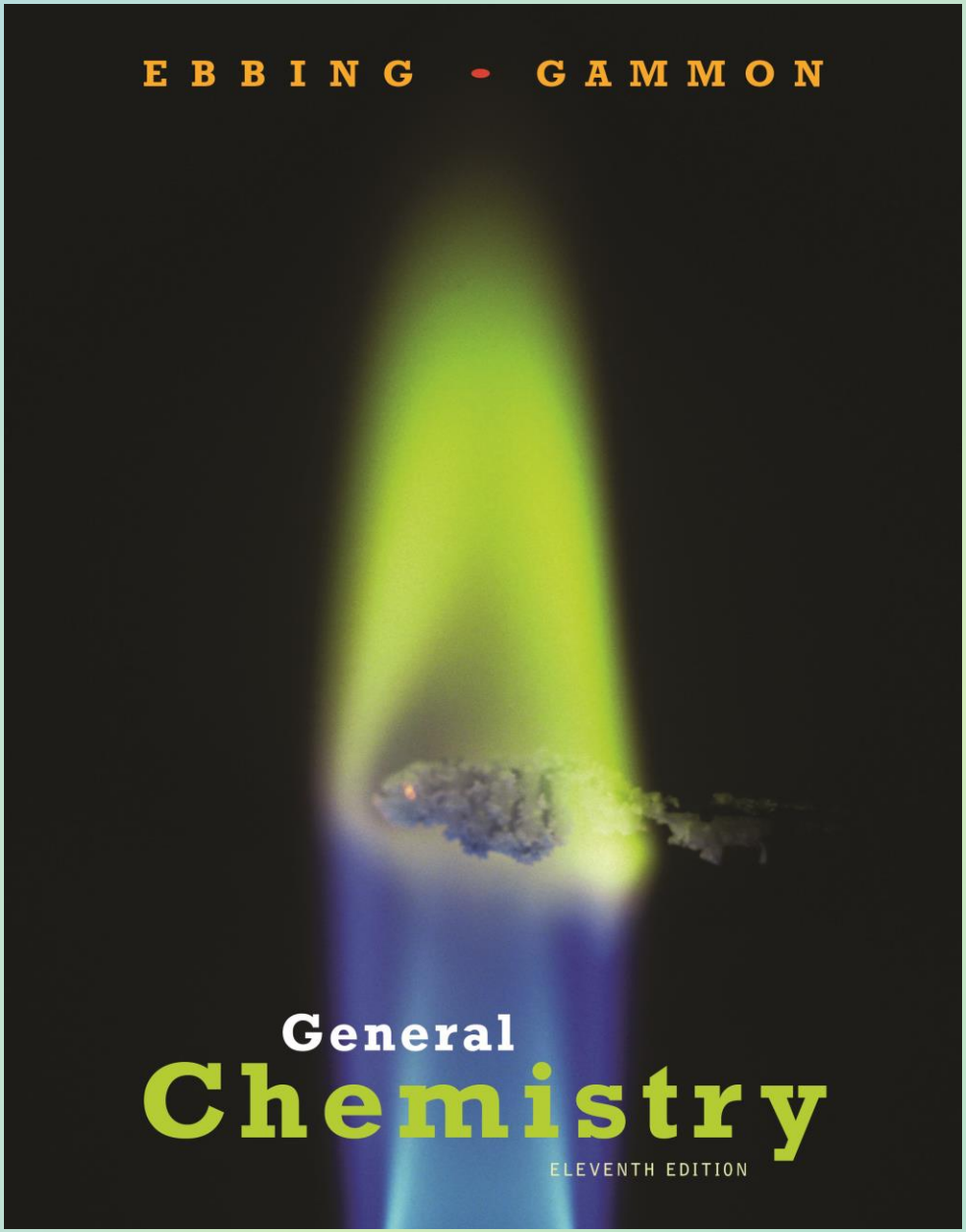
Equilibrium-constant expression is constant for a given temperature.

K_c is the ratio of rate constants for forward and reverse reactions.

$$K_c = \frac{k_f}{k_r}$$

When overall reaction occurs as a multistep mechanism, the equilibrium constant equals a product of ratios of rate constants.

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Chapter 16
Acid–Base Equilibria

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The simplest acid–base equilibria are those in which a weak acid or a weak base reacts with water.

We can write an acid equilibrium reaction for the generic monoprotic acid, HA.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

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Acetic acid is a weak acid. It reacts with water as follows:

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Here, A from the previous slide = $C_2H_3O_2^-(aq)$

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The equilibrium constant for the reaction of a weak acid with water is called the **acid-ionization constant** (or acid−dissociation constant), $\boldsymbol{K_a}$**.**

For the equation:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

The **degree of ionization** is the fraction of molecules that react with water to give ions.

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Nicotinic acid (niacin) is a monoprotic acid with the formula $HC_6H_4NO_2$. A solution that is 0.012 *M* in nicotinic acid has a pH of 3.39 at 25° C.

1. What is the acid-ionization constant, K_a, for this acid at 25° C?
2. What is the degree of ionization of nicotinic acid in this solution?

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Solution

Step 1

Concentration (M)	***HNic (aq) + H_2O (l)*** ⇌	***H_3O^+(aq) +***	***Nic^-(aq)***
Starting	0.012	~0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.012 - x$	x	x

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Step 2

The equilibrium-constant expression is

$$K_a = \frac{\left[H_3O^+\right]\left[Nic^-\right]}{\left[HNic\right]}$$

Substituting the expressions for the equilibrium concentrations:

$$K_a = \frac{x^2}{(0.012 - x)}$$

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Step 3

The value of x equals the numerical value of the molar hydronium-ion concentration and can be obtained from the pH of the solution.

$$x = \left[H_3O^+\right] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.39)$$

$$x = 4.1 \times 10^{-4} = 0.00041$$

Substitute this value into the equation obtained in step 2.

$$K_a = \frac{x^2}{(0.012 - x)} \approx \frac{x^2}{0.012} \approx \frac{(0.00041)^2}{0.012} = \mathbf{1.4 \times 10^{-5}}$$

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To obtain the degree of ionization, note that x mol out of 0.012 mol of nicotinic acid ionizes. Hence,

$$\text{Degree of ionization} = \frac{x}{0.012} = \frac{0.00041}{0.012}$$

Degree of ionization = 0.034

The percent of ionization is obtained by multiplying this amount by 100.

Percent ionization = 3.4%

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Table 16.1 Acid-Ionization Constants at 25°C*

Substance	Formula	K_a
Acetic acid	$HC_2H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HCO_3^-	4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulfide	H_2S	8.9×10^{-8}
	HS^-	$1.2 \times 10^{-13\dagger}$

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Table 16.1 Acid-Ionization Constants at 25°C*

Substance	Formula	K_a
Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}
	$HC_2O_4^-$	5.1×10^{-5}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
	$H_2PO_4^-$	6.2×10^{-8}
	HPO_4^{2-}	4.8×10^{-13}
Phosphorous acid	H_2PHO_3	1.6×10^{-2}
	$HPHO_3^-$	7×10^{-7}
Propionic acid	$HC_3H_5O_2$	1.3×10^{-5}
Pyruvic acid	$HC_3H_3O_3$	1.4×10^{-4}
Sulfurous acid	H_2SO_3	1.3×10^{-2}
	HSO_3^-	6.3×10^{-8}

*The ionization constants for polyprotic acids are for successive ionizations. For example, for H_3PO_4, the equilibrium is $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$. For $H_2PO_4^-$, the equilibrium is $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$.

†This value is in doubt. Some evidence suggests that it is about 10^{-19}. See R. J. Myers, *J. Chem. Educ.*, **63**, 687 (1986).

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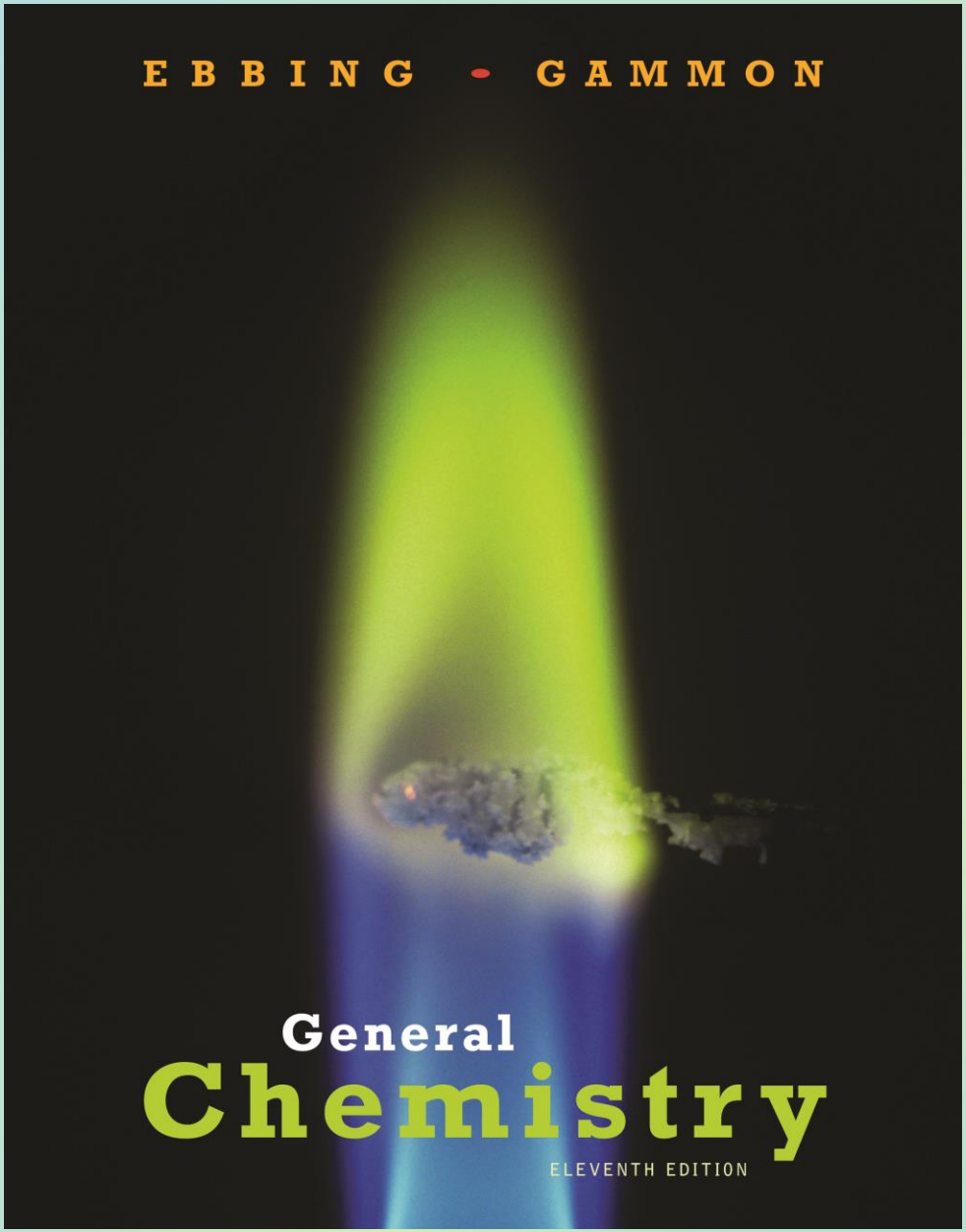
Calculations with K_a

Given the value of K_a and the initial concentration of HA, you can calculate the equilibrium concentration of all species.

Given the value of K_a and the initial concentration of HA, you can calculate the degree of ionization and the percent ionization.

Given the pH of the final solution and the initial concentration of HA, you can find the value of K_a and the percent ionization.

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Chapter 17 Solubility and Complex–Ion Equilibria

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To deal quantitatively with an equilibrium, you must know the equilibrium constant.

We will look at the equilibria of slightly soluble (or nearly insoluble) ionic compounds and show how you can determine their equilibrium constants.

Once you find these values for various ionic compounds, you can use them to answer questions about solubility or precipitation.

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When an excess of slightly soluble ionic compound is mixed with water, an equilibrium is established.

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium constant for this type of reaction is called the **solubility product constant, K_{sp}.**

For the above reaction:

$$K_{sp} = [M^+][X^-]$$

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Write the solubility−product expression for the following salts:

a. $AgCl$

b. Hg_2Cl_2

c. $Pb_3(AsO_4)_2$

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Solution

a.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-]$$

b.

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

c.

$$Pb_3(AsO_4)_2(s) \rightleftharpoons 3Pb^{2+}(aq) + 2AsO_4^{3-}(aq)$$

$$K_{sp} = [Pb^{2+}]^3[AsO_4^{3-}]^2$$

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The solubility−product constant, K_{sp}, of a slightly soluble ionic compound is expressed in terms of the molar concentrations of ions in the saturated solution.

These ion concentrations are, in turn, related to the *molar solubility* of the ionic compound, which is the number of moles of compound that dissolve to give one liter of saturated solution.

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A liter of a solution saturated at 25°C with calcium oxalate, CaC_2O_4 is evaporated to dryness, giving a 0.0061-g residue of CaC_2O_4. Calculate the solubility product constant for this salt at 25°C.

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Solution

The solubility of calcium oxalate is 0.0061 g/L of solution, and the formula mass of CaC_2O_4 is 128 amu. Convert grams per liter to moles per liter:

$$\text{Molar solubility of } CaC_2O_4 = 0.0061 \text{ g } CaC_2O_4/\text{L} \times \frac{1 \text{ mol } CaC_2O_4}{128 \text{ g } CaC_2O_4}$$

$$= 4.8 \times 10^{-5} \text{ mol } CaC_2O_4/\text{L}$$

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Step 1

Concentration (M)	$CaC_2O_4(s) \rightleftharpoons Ca_2^+(aq)$ +	$C_2O_4^{2-}(aq)$
Starting	0	0
Change	$+ 4.8 \times 10^{-5}$	$+ 4.8 \times 10^{-5}$
Equilibrium	4.8×10^{-5}	4.8×10^{-5}

Step 2

$$K_{sp} = \left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = \left(4.8 \times 10^{-5}\right)\left(4.8 \times 10^{-5}\right)$$

$$K_{sp} = 2.3 \times 10^{-9}$$

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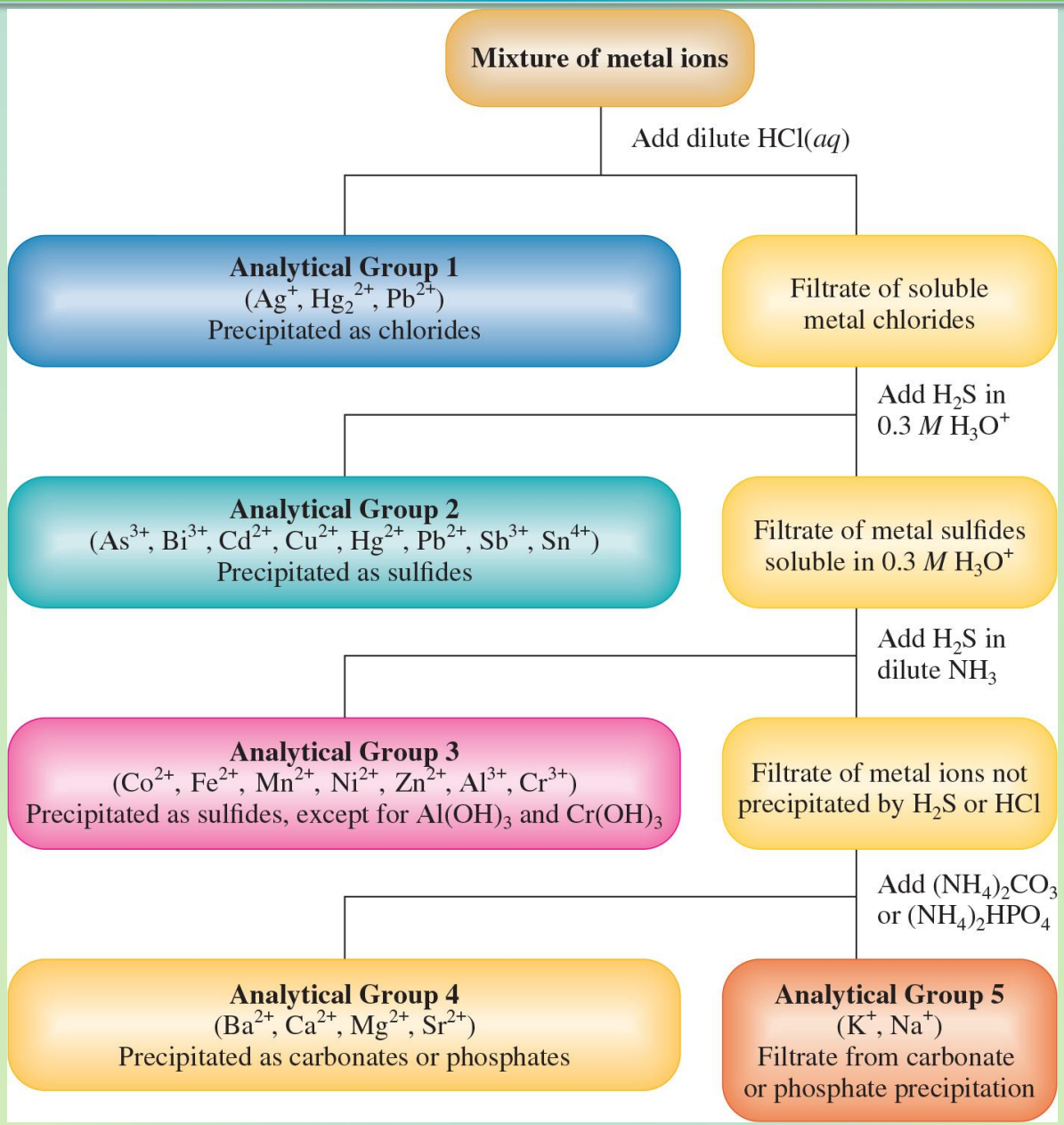
Qualitative analysis involve determining the identity of substances present in a mixture.

The combination of solubility and complex-ion equilibria can be applied to separate metal ions.

Cations can be separated into groups according to their precipitation properties.

In each major step, one group of cations precipitates out. After separating the precipitate, the remaining solution is treated with the next reagent, precipitating the next group of cations.

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