States of Matter

Classifications of Matter

Matter is *anything that occupies space and has mass*, and ***chemistry*** is *the study of matter and the changes it undergoes.* There are two principal ways of classifying matter: **by its physical state** as a *solid*, *liquid*, or *gas* and **by its chemical constitution** as an *element*, *compound*, or *mixture*.

Solids, Liquids, and Gases

Commonly, a given kind of matter exists in different physical forms under different conditions. Water, for example, exists as ice (solid water), as liquid water, and as steam (gaseous water). The main identifying characteristic of solids is their *rigidity*: they tend to maintain their shapes when subjected to outside forces. Liquids and gases, however, are *fluids;* that is, they flow easily and change their shapes in response to slight outside forces.

What distinguishes a gas from a liquid is the characteristic of *compressibility* (and its opposite, *expansibility*). A gas is easily compressible, whereas a liquid is not. These two characteristics, rigidity (or fluidity) and compressibility (or expansibility), can be used to frame definitions of the three common states of matter:

- **Solid** *the form of matter characterized by rigidity;* a solid is relatively incompressible and has fixed shape and volume.
- **Liquid** *the form of matter that is a relatively incompressible fluid;* a liquid has a fixed volume but no fixed shape.
- **Gas** *the form of matter that is an easily compressible fluid;* a given quantity of gas will fit into a container of almost any size and shape.

Elements, Compounds, and Mixtures

To understand how matter is classified by its chemical constitution, we must first distinguish between *physical and chemical changes* and between *physical and chemical properties*. A **physical change** is *a change in the form of matter but not in its chemical identity.* Changes of physical state are examples of physical changes. The process of dissolving one material in another is a further example of a physical change. For instance, sodium chloride (table salt) dissolves in water. The result is a clear liquid, like pure water, though many of its other characteristics are different from those of pure water. The water and sodium chloride in this liquid retain their chemical identities and can be separated by some method that depends on physical changes. *Distillation* is one way to separate the sodium chloride and water components of this liquid.

A **chemical change,** or **chemical reaction,** is *a change in which one or more kinds of matter are transformed into a new kind of matter or several new kinds of matter.* The rusting of iron, during which iron combines with oxygen in the air to form a new material called rust, is a chemical change. The original materials (iron and oxygen) combine chemically and cannot be separated by any physical means. To recover the iron and oxygen from rust requires a chemical change or a series of chemical changes.

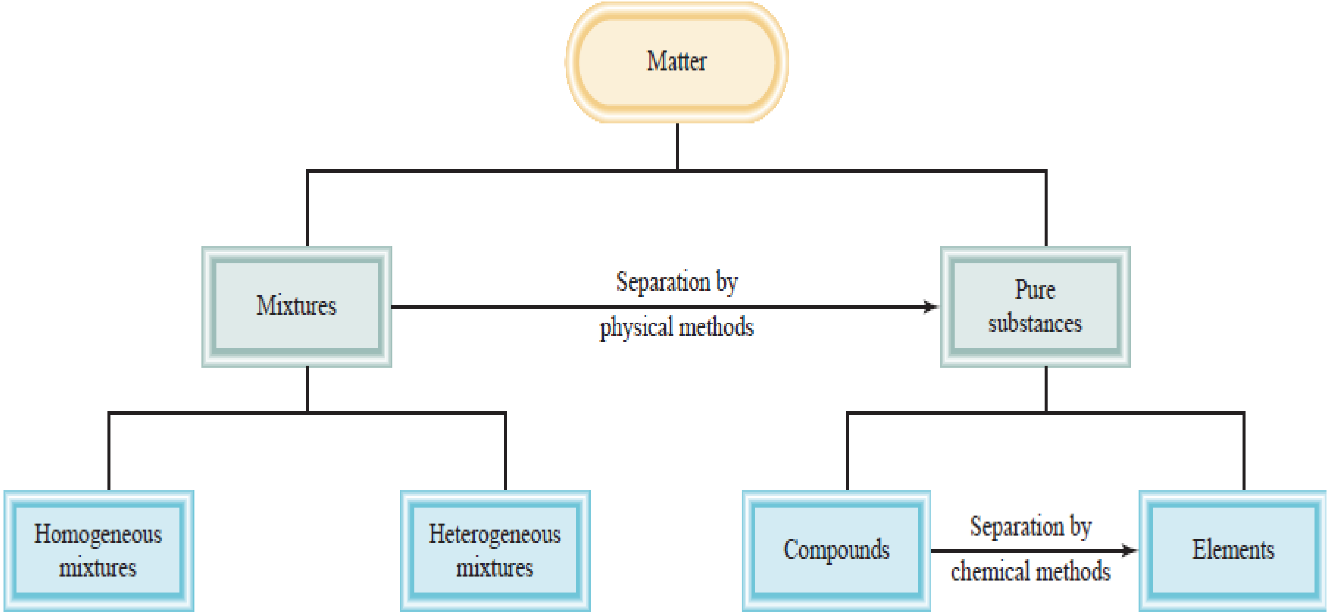
A material can be characterized or identified by its various properties, which may be either *physical* or *chemical*. A **physical property** is *a characteristic that can be observed for a material without changing its chemical identity*. Examples are physical state (solid, liquid, or gas), melting point, and color. A **chemical property** is *a characteristic of a material involving its chemical change.* A chemical property of iron is its ability to react with oxygen to produce rust.

The various materials around us are either substances or mixtures of substances. A **substance** is *a kind of matter that cannot be separated into other kinds of matter by any physical process.* For example, it is possible to separate the sodium chloride from the water by the physical process of distillation, but sodium chloride is itself a substance and cannot be separated by physical processes into new materials. Similarly, pure water is a substance. A substance always has the same characteristic properties.

A substance can be either an *element* or a *compound*. An **element** is *a substance that cannot be separated into simpler substances by chemical means.* Today 116 elements are known. Most substances are compounds. A **compound** is *a substance composed of two or more elements chemically combined.* Hydrogen gas, for example, burns in oxygen gas to form water, a compound whose properties are distinctly different from those of the starting materials. Water is made up of two parts of hydrogen and one part of oxygen. This composition does not change.

Most of the materials around us are mixtures. A **mixture** is *a material that can be separated by physical means into two or more substances.* Mixtures are classified into two types. A **heterogeneous mixture** is *a mixture that consists of physically distinct parts, each with different properties.* A **homogeneous mixture** (also known as a **solution**) is *a mixture that is uniform in its properties throughout given samples.* Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar can be recovered from a water solution by heating the solution and evaporating it to dryness. Condensing the water vapor will give us back the water component. To separate the iron-sand mixture, we can use a magnet to remove the iron filings from the sand, because sand is not attracted to the magnet. After separation, the components of the mixture will have the same composition and properties as they did to start with.

The relationships among elements, compounds, and other categories of matter are summarized in the Figure below. Materials are either substances or mixtures. Substances can be mixed by physical processes, and other physical processes can be used to separate the mixtures into substances. Substances are either elements or compounds. Elements may react chemically to yield compounds, and compounds may be decomposed by chemical reactions into elements.



Classification of matter

All measurable properties of matter fall into two categories: extensive properties and intensive properties. The measured value of an ***extensive property*** *depends on how much matter is being considered.* Mass, length, and volume are extensive properties. More matter means more mass. Values of the same extensive property can be added together. For example, two copper pennies have a combined mass that is the sum of the masses of each penny, and the total volume occupied by the water in two beakers is the sum of the volumes of the water in each of the beakers.

The measured value of an ***intensive property*** *does not depend on the amount of matter being considered.* Temperature is an intensive property. Suppose that we have two beakers of water at the same temperature. If we combine them to make a single quantity of water in a larger beaker, the temperature of the larger amount of water will be the same as it was in two separate beakers. Unlike mass and volume, temperature and other intensive properties such as melting point, boiling point, and density are not additive.

Atomic mass

The **atomic mass** *or* **atomic mass unit (amu)** of an element is *the average atomic mass for the naturally occurring element, expressed in atomic mass units* (atomic mass is sometimes referred to as atomic weight).

Molar mass and Molecular mass

The **molar mass** of a substance is *the mass of one mole of the substance.* The **molecular mass** (MM) of a substance is *the sum of the atomic masses of all the atoms in a molecule of the substance.* For all substances, the molar mass in grams per mole is numerically equal to the molecular mass in atomic mass units. Ethanol, for example, whose molecular formula is C_2H_6O has a molecular mass of 46.1 amu and a molar mass of 46.1 g/mol.

Mole $\left[mole = \frac{weight\ (g)}{Mwt\ (\frac{g}{mole})} \right]$

A **mole** (symbol **mol**) is defined as *the quantity of a given substance that contains as many molecules or formula units as the number of atoms in exactly 12 g of carbon-12.* One mole of ethanol, for example, contains the same number of ethanol molecules as there are carbon atoms in 12 g of carbon-12. *The number of atoms in a 12-g sample of carbon-12* is called **Avogadro's number** (symbol N_A) (this number give the value 6.02×10^{23}).

A mole of a substance contains Avogadro's number (6.02×10^{23}) of molecules. When using the term *mole,* it is important to specify the formula of the unit to avoid any misunderstanding. For example, a mole of oxygen atoms (with the formula O) contains 6.02×10^{23} O atoms. A mole of oxygen molecules (formula O_2) contains 6.02×10^{23} O_2 molecules—that is, $2 \times (6.02 \times 10^{23})$ O atoms.

Molar Concentration

When we dissolve a substance in a liquid, we call the substance the **solute** and the liquid the **solvent**. The general term **concentration** refers to the quantity of solute in a standard quantity of solution. **Molar concentration,** or **molarity (*M*),** is defined as *the moles of solute dissolved in one liter (cubic decimeter) of solution.*

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

Example: A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck, dissolving the solid. What is the molarity of the resulting solution?

Qualitatively, we say that a solution is **dilute** when the solute concentration is low and **concentrated** when the solute concentration is high. Usually these terms are used in a comparative sense and do not refer to a specific concentration. We say that one solution is more dilute, or less concentrated, than another. The relationship between the molarity of the solution before dilution (the *initial molarity*) and that after dilution (the *final molarity*) is:

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

where M_i for the initial molar concentration, V_i for the initial volume of solution, M_f (the final molar concentration) and V_f (the final volume).

Example: You are given a solution of 14.8 M NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 M NH_3 when diluted.

GASES

Particles in a gas are far apart, fast-moving, and are not organized in any particular way. Unlike the particles in solids and liquids, the atoms and molecules in gases are not particularly attracted to each other.

In gases, the intermolecular forces that hold molecules together in liquids and some solids are still present, but gas molecules overcome these intermolecular forces with speed. Individual gas molecules are always on the move; they have a lot of energy that keeps them moving constantly.

As a result, within a gas, the atoms or molecules pass each other regularly and interact only for a brief moment of time. This short bit of time is not enough for intermolecular forces to take hold and act. As a result, the atoms and molecules in a gas continue on their own way.

This lack of force holding atoms or molecules together is what determines the most unique properties of gases. A gas will expand in all directions to fill any space, and will spread to take on the shape of its container. But it is not the same as a liquid. There are no other forces, with the exception of gravity, to hold a gas in place.

In this state of matter, it’s not so much the forces acting between atoms or molecules that are important. Instead, three other factors determine the movements of atoms or molecules in a gas: *temperature*, *pressure*, and *volume*. Chemists relate these three factors in a series of gas laws.

Volume

Volume is *length (m) cubed,* so its SI-derived unit is the cubic meter (m^3). Generally, however, chemists work with much smaller volumes, such as the cubic centimeter (cm^3) and the cubic decimeter (dm^3):

$$1\ \mathrm{cm}^3 = 1\times10^{-6}\ \mathrm{m}^3$$

$$1\ \mathrm{dm}^3 = 1\times10^{-3}\ \mathrm{m}^3$$

Another common, non-SI unit of volume is the liter (L). A ***liter*** is *the volume occupied by one cubic decimeter*. Chemists generally use L and mL for liquid volume. One liter is equal to 1000 milliliters (mL) or 1000 cubic centimeters:

$$1\ \mathrm{L} = 1000\ \mathrm{mL}$$

$$1\ \mathrm{L} = 1000\ \mathrm{cm}^3$$

$$1\ \mathrm{L} = 1\ \mathrm{dm}^3$$

and one milliliter is equal to one cubic centimeter:

$$1\ \mathrm{mL} = 1\ \mathrm{cm}^3$$

Temperature

Temperature is not just about how hot or cold something feels. **Temperature** is actually a measurement of the average kinetic energy in a material. **Kinetic energy** refers to the energy of motion. Particles within matter are always in motion. The faster the particles within a sample of matter move, the higher its kinetic energy, or temperature.

The slower the particles move, the lower its kinetic energy, or temperature. Gases at warm temperatures have fast-moving particles.

Pressure

Pressure is one of the most readily measurable properties of a gas. It may be expressed in many different units. To understand how we measure the pressure of a gas, it is helpful to know how the units of measurement are derived.

SI Units of Pressure

We begin with velocity and acceleration. *Velocity* is defined as the change in distance with elapsed time; that is,

$$\text{velocity} = \frac{\text{distance moved}}{\text{elapsed time}}$$

The SI unit for velocity is **m/s**, although we also use **cm/s**.

Acceleration is the change in velocity with time, or

$$\text{acceleration} = \frac{\text{change in velocity}}{\text{elapsed time}}$$

Acceleration is measured in **m/s^2** (or **cm/s^2**).

The second law of motion, formulated by Sir Isaac Newton in the late seventeenth century, defines another term, from which the units of pressure are derived, namely, *force*. According to this law,

$$\text{force} = \text{mass} \times \text{acceleration}$$

In this context, the *SI unit of force* is the ***newton (N),*** where

$$1\ \text{N} = 1\ \text{kg m/s}^2$$

Finally, we define ***pressure*** as *force applied per unit area* - pounds per square inch (**lb/in.^{2}**), commonly known as **psi**:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

The SI unit of pressure is the ***pascal (Pa),*** defined as *one newton per square meter:*

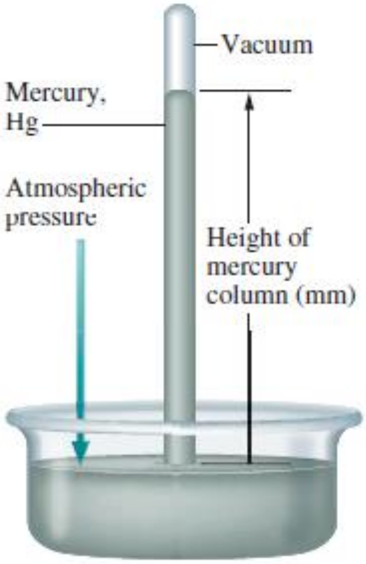
$$1\ \text{Pa} = 1\ \text{N/m}^2$$

Atmospheric Pressure

The atoms and molecules of the gases in the atmosphere, like those of all other matter, are subject to Earth's gravitational pull. As a consequence, the atmosphere is much denser near the surface of Earth than at high altitudes. In fact, the density of air decreases very rapidly with increasing distance from Earth. Not surprisingly, the denser the air is, the greater the pressure it exerts. The force experienced by any area exposed to Earth's atmosphere is equal to the weight of the column of air above it. ***Atmospheric pressure*** is the pressure exerted by Earth's atmosphere. The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

Does atmospheric pressure only act downward, as you might infer from its definition? Imagine what would happen, then, if you were to hold a piece of paper tight with both hands above your head. You might expect the paper to bend due to the pressure of air acting on it, but this does not happen. The reason is that air, like water, is a fluid. The pressure exerted on an object in a fluid comes from all directions—downward and upward, as well as from the left and from the right. At the molecular level, air pressure results from collisions between the air molecules and any surface with which they come in contact. The magnitude of pressure depends on how often and how strongly the molecules impact the surface. It turns out that there are just as many molecules hitting the paper from the top as there are from underneath, so the paper stays flat.

How is atmospheric pressure measured? The ***barometer*** is probably the most familiar *instrument for measuring atmospheric pressure.* A simple barometer consists of a long glass tube, closed at one end and filled with mercury. If the tube is carefully inverted in a dish of mercury so that no air enters the tube, some mercury will flow out of the tube into the dish, creating a vacuum at the top.



The weight of the mercury remaining in the tube is supported by atmospheric pressure acting on the surface of the mercury in the dish. ***Standard atmospheric pressure (1 atm)*** is equal to *the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0 ^oC at sea level.* In other words, the standard atmosphere equals a pressure of 760 mmHg, where mmHg represents the pressure exerted by a column of mercury 1 mm high. The mmHg unit is also called the *torr*, after the Italian scientist Evangelista Torricelli, who invented the barometer. Thus,

$$1 \text{ torr} = 1 \text{ mmHg}$$

and

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mmHg (exactly)} \\ &= 760 \text{ torr} \end{aligned}$$

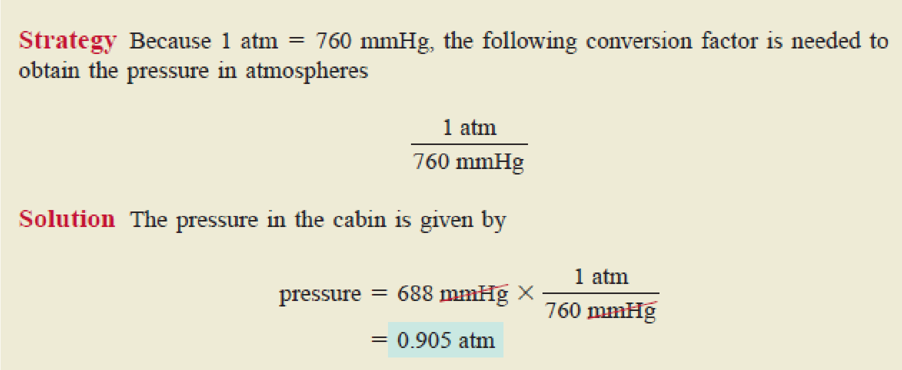
The relation between atmospheres and pascals is:

$$\begin{aligned} 1 \text{ atm} &= 101{,}325 \text{ Pa} \\ &= 1.01325 \times 10^5 \text{ Pa} \end{aligned}$$

and because 1000 Pa = 1 kPa (kilopascal)

$$1 \text{ atm} = 1.01325 \times 10^2 \text{ kPa}$$

Example: *The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?*



Strategy Because 1 atm = 760 mmHg, the following conversion factor is needed to obtain the pressure in atmospheres

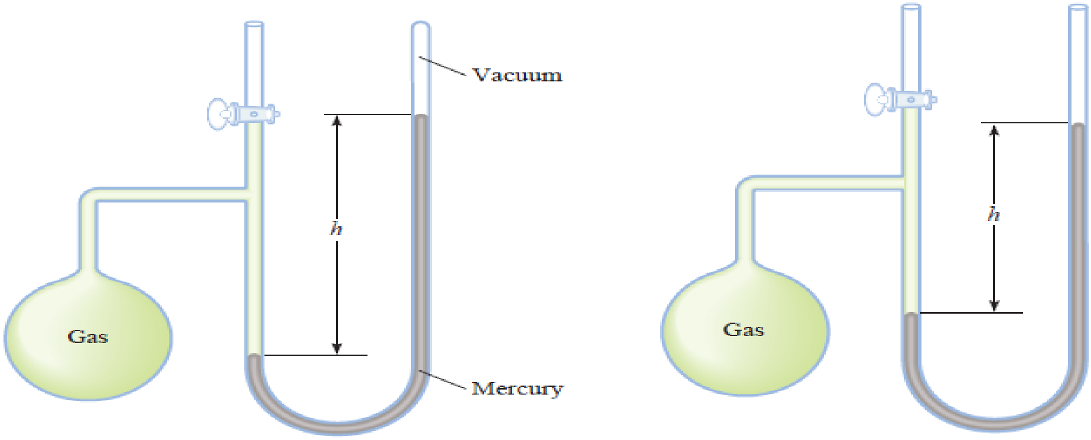
$$\frac{1\ \text{atm}}{760\ \text{mmHg}}$$

Solution The pressure in the cabin is given by

$$\begin{aligned}\text{pressure} &= 688\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}}\\ &= \boxed{0.905\ \text{atm}}\end{aligned}$$

Manometer

A ***manometer*** is a device used to measure the pressure of gases other than the atmosphere. The principle of operation of a manometer is similar to that of a barometer. There are two types of manometers as shown in Figure below. The closed-tube manometer is normally used to measure pressures below atmospheric pressure [Figure (a)], whereas the open-tube manometer is better suited for measuring pressures equal to or greater than atmospheric pressure [Figure (b)].



$P_{\text{gas}} = P_h$

(a)

$P_{\text{gas}} = P_h + P_{\text{atm}}$

(b)

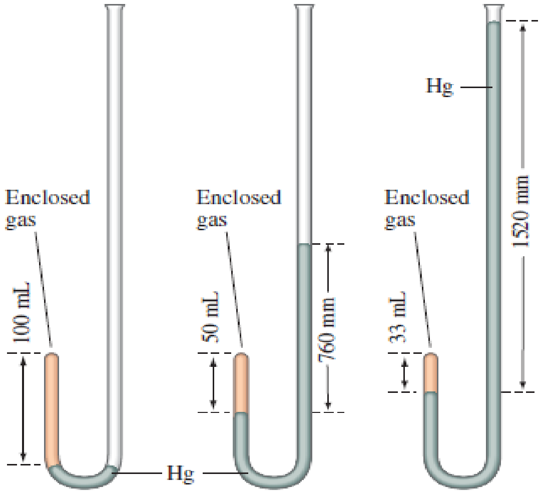
Nearly all barometers and most manometers use mercury as the working fluid, despite the fact that it is a toxic substance with a harmful vapor. The reason is that mercury has a very high density (13.6 g/mL) compared with most other liquids. Because the height of the liquid in a column is inversely proportional to the liquid's density, this property enables the construction of manageably small barometers and manometers.

Empirical Gas Laws

All gases under moderate conditions behave quite simply with respect to pressure, temperature, volume, and molar amount. By holding any two of these physical properties constant, it is possible to show a simple relationship between the other two. Throughout history there have been multiple versions of gas laws developed and named after many different people. *Boyle's Law* (1662), *Charles's Law* (1802), and *Avogadro's Law* (1811) are a few examples.

Boyle's Law: Relating Volume and Pressure

One characteristic property of a gas is its compressibility—its ability to be squeezed into a smaller volume by the application of pressure. By comparison, liquids and solids are relatively incompressible. The compressibility of gases was first studied quantitatively by Robert Boyle in 1661. When he poured mercury into the open end of a J-shaped tube, the volume of the enclosed gas decreased (*see Figure below*). Each addition of mercury increased the pressure on the gas, decreasing its volume. From such experiments, he formulated the law now known by his name. According to **Boyle's law,** *the volume of a sample of gas at a given temperature varies inversely with the applied pressure*.



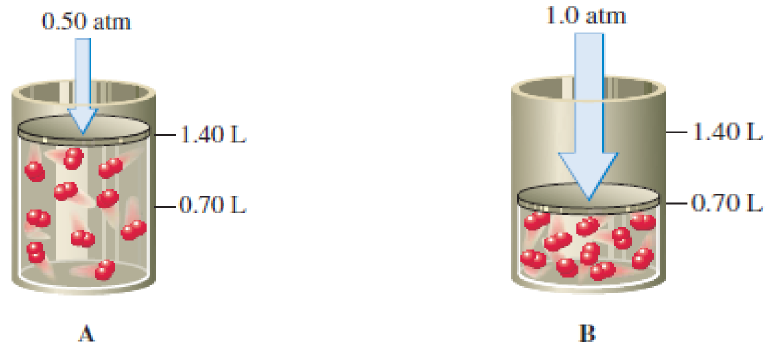
$V \propto \frac{1}{P}$, meaning "Volume is directly proportional to 1 divided by Pressure", or

$P \propto \frac{1}{V}$, meaning "Pressure is directly proportional to 1 divided by Volume"

Another way to describing it is saying that their products are constant.

$PV = k$

When pressure goes up, volume goes down. When volume goes up, pressure goes down.

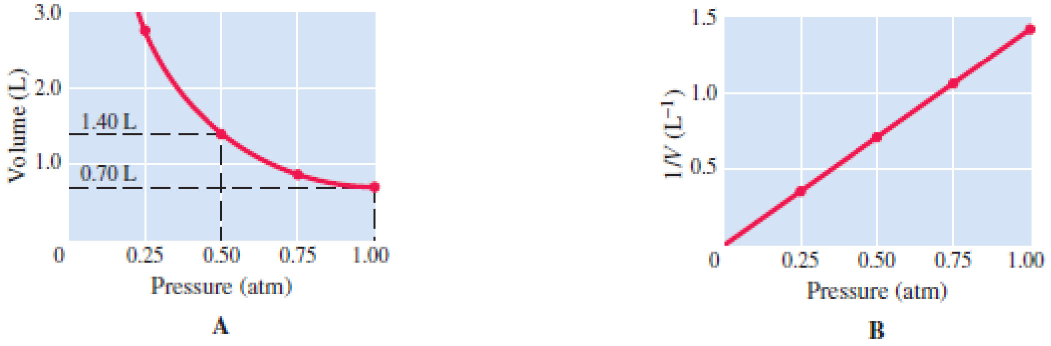


Model of gas pressure–volume relationship at a constant temperature:

(**A**) When a 1.000-g sample of O_2 gas at 0 ^{o}C is placed in a container at a pressure of 0.50 atm, it occupies a volume of 1.40 L.

(**B**) When the pressure on the O_2 sample is doubled to 1.0 atm, the volume is reduced to 0.70 L, which is half the original volume.

By plotting the volume of the oxygen at different pressures, you obtain a graph showing the inverse relationship of ***P*** and ***V***.



Gas pressure–volume relationship:

(**A**) Plot of volume vs. pressure for a sample of oxygen. The volume (of 1.000 g O_2 at 0 ^{o}C) decreases with increasing pressure. When the pressure is doubled (from 0.50 atm to 1.00 atm), the volume is halved (from 1.40 L to 0.70 L).

(**B**) Plot of $1/V$ vs. pressure (at constant temperature) for the same sample. The straight line indicates that volume varies inversely with pressure.

From the equation above, this can be derived:

$$P_1V_1 = P_2V_2 = P_3V_3 \text{ etc.}$$

This equation states that the product of the initial volume and pressure is equal to the product of the volume and pressure after a change in one of them under constant temperature. For example, if the initial volume was 500 mL at a pressure of 760 torr, when the volume is compressed to 450 mL, what is the pressure?

Solution:

$P_1V_1 = P_2V_2$

(760 torr)(500 mL) = P_2 (450 mL)

760 torr x 500 mL/450 mL = P_2 844 torr

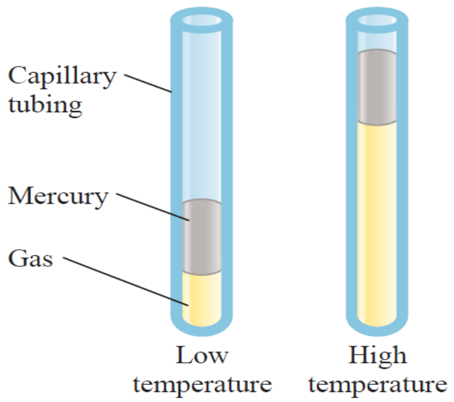
P_2 = 844 torr.

- *A volume of air occupying 12.0 dm3 at 98.9 kPa is compressed to a pressure of 119.0 kPa. The temperature remains constant. What is the new volume?*
- *A volume of carbon dioxide gas, CO_2, equal to 20.0 L was collected at 23 ^oC and 1.00 atm pressure. What would be the volume of carbon dioxide collected at 23 ^oC and 0.830 atm?*

In fact, all gases follow Boyle's law at low to moderate pressures but deviate from this law at high pressures. The extent of deviation depends on the gas.

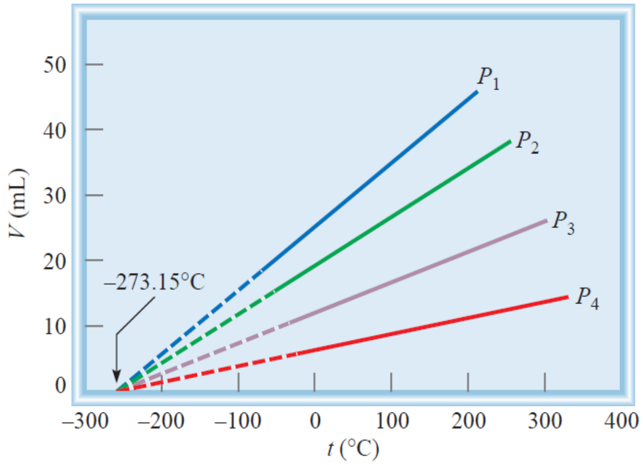
Charles's Law: Relating Volume and Temperature

Boyle's law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas? Let's first look at the effect of temperature on the volume of a gas. The earliest investigators of this relationship were French scientists, Jacques Charles. His study showed that, at constant pressure, the volume of a gas sample expands when heated and contracts when cooled:



Variation of the volume of a gas sample with temperature, at constant pressure. The pressure exerted on the gas is the sum of the atmospheric pressure and the pressure due to the weight of the mercury.

The quantitative relations involved in changes in gas temperature and volume turn out to be remarkably consistent. For example, we observe an interesting phenomenon when we study the temperature-volume relationship at various pressures. At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be –273.15 ^{o}C. At any other pressure, we obtain a different straight line for the volume-temperature plot, but we get the *same* zero-volume temperature intercept at –273.15 ^{o}C (see Figure below). This seems to say that if the substances remain gaseous, the volumes occupied will be zero at –273.15 ^{o}C. This could not happen, however; all gases liquefy before they reach this temperature, and Charles's law does not apply to liquids. These extrapolations do show that we can express the volume variation of a gas with temperature more simply by choosing a different thermometer scale.



Variation of the volume of a gas sample with temperature, at constant pressure. Each line represents the variation at a certain pressure. The pressures increase from P_1 to P_4. All gases ultimately condense (become liquids) if they are cooled to sufficiently low temperatures; the solid portions of the lines represent the temperature region above the condensation point. When these lines are extrapolated, or extended (the dashed portions), they all intersect at the point representing zero volume a temperature of –273.15 ^{o}C.

In 1848 the Scottish physicist Lord Kelvin realized the significance of this phenomenon. He identified –273.15 ^{o}C as *absolute zero*, theoretically the lowest attainable temperature. Then he set up an *absolute temperature scale*, now called the ***Kelvin temperature scale***, *with absolute zero as the starting point*. On the Kelvin scale, one kelvin (**K**) is equal *in magnitude* to one degree Celsius. The only difference between the absolute temperature scale and the Celsius scale is that the zero position is shifted. Important points on the two scales match up as follows:

	Kelvin Scale	**Celsius Scale**
Absolute zero	0 K	−273.15°C.
Freezing point of water	273.15 K	0°C
Boiling point of water	373.15 K	100°C

In most calculations we will use 273 instead of 273.15 as the term relating K and ^{o}C.

The dependence of the volume of a gas on temperature is given by:

$$V \propto T$$

$$V = k_2T$$

or

$$\frac{V}{T} = k_2$$

where k_2 is the proportionality constant. Equation above is known as ***Charles's law***, which states that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*. For pressure-volume relationships at constant temperature, we can compare two sets of volume-temperature conditions for a given sample of gas at constant pressure.

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where V_1 and V_2 are the volumes of the gas at temperatures T_1 and T_2 (both in kelvins), respectively. As the volume goes up, the temperature also goes up, and *vice-versa*. Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$V_1 / T_1 = V_2 / T_2 = V_3 / T_3$ etc.

Gay-Lussac's Law: The Pressure Temperature Law

This law states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

$P \propto T$

Same as before, a constant can be put in:

$P / T = k$

As the pressure goes up, the temperature also goes up, and vice-versa. Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$P_1 / T_1 = P_2 / T_2 = P_3 / T_3$ etc.

Avogadro's Law: The Volume Amount Law

The work of the Italian scientist Amedeo Avogadro complemented the studies of Boyle, Charles, and Gay-Lussac. In 1811 he published a hypothesis stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic). It follows that the volume of any given gas must be proportional to the number of moles of molecules present; that is:

$$V \propto n$$

$$\boxed{V = k_4 n}$$

where n represents the number of moles and k_4 is the proportionality constant. This equation is the mathematical expression of ***Avogadro's law,*** which states that *at constant pressure and temperature, the volume of a gas is directly proportional to thenumber of moles of the gas present.*

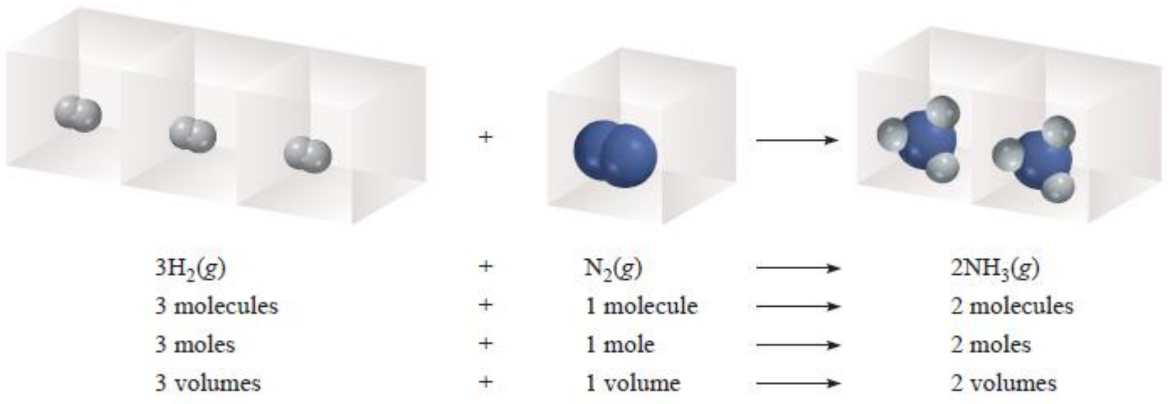
According to Avogadro's law we see that when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio. For example, consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:

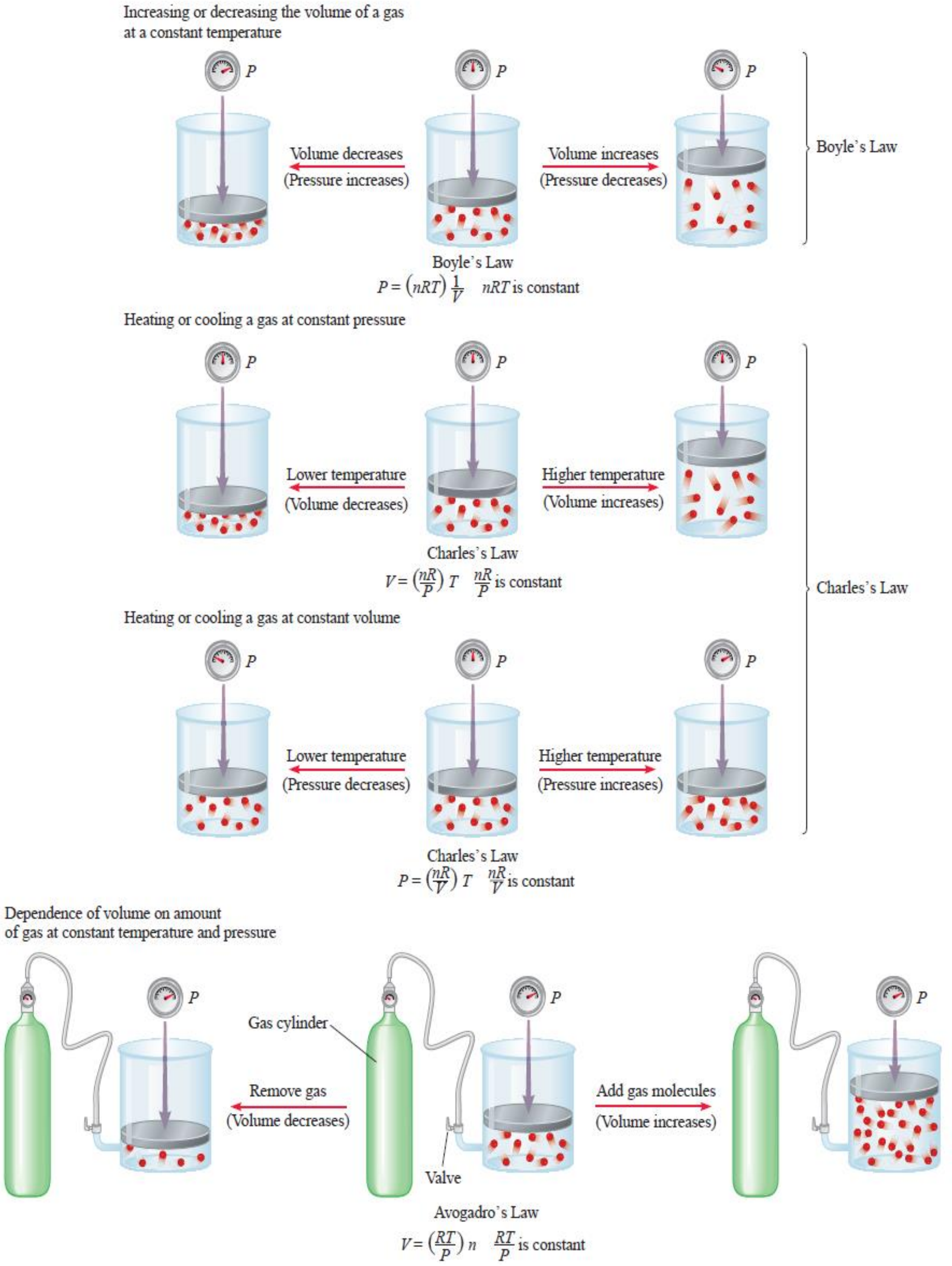
$$\begin{array}{ccccc} 3H_2(g) & + & N_2(g) & \longrightarrow & 2NH_3(g) \\ \text{3 mol} & & \text{1 mol} & & \text{2 mol} \end{array}$$

Because, at the same temperature and pressure, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write:

$$\begin{array}{ccccc} 3H_2(g) & + & N_2(g) & \longrightarrow & 2NH_3(g) \\ \text{3 volumes} & & \text{1 volume} & & \text{2 volumes} \end{array}$$

The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2 (see Figure below).





Schematic illustrations of Boyle's law, Charles's law, and Avogadro's law.

The Ideal Gas Law

The gas laws that have been discussed so far, can be summarized:

$$\text{Boyle's law: } V \propto \frac{1}{P} \quad (\text{at constant } n \text{ and } T)$$
$$\text{Charles's law: } V \propto T \quad (\text{at constant } n \text{ and } P)$$
$$\text{Avogadro's law: } V \propto n \quad (\text{at constant } P \text{ and } T)$$

All three expressions can combine to form a single master equation for the behavior of gases:

$$V \propto \frac{nT}{P}$$
$$V = R\frac{nT}{P}$$

or

$$PV = nRT$$

where ***R,*** *the proportionality constant,* is called the ***gas constant.*** This equation, which is called the ***ideal gas equation,*** *describes the relationship among the four variables P, V, T, and n.* An ***ideal gas*** is *a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation.* The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container. Although there is no such thing in nature as an ideal gas, discrepancies in the behavior of real gases over reasonable temperature and pressure ranges do not significantly affect calculations. Thus, the ideal gas equation can safely use to solve many gas problems.

Before the ideal gas equation can apply to a real system, the gas constant *R* must evaluated. At **0 ^{o}C (273.15 K**) and **1 atm** pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, **1 mole** of an ideal gas occupies **22.414 L**. *The conditions 0 ^{o}C and 1 atm* are called ***standard temperature and pressure,*** often abbreviated ***STP.*** From the ideal gas equation, we can write:

$$\mathbf{R} = \frac{PV}{nT} = \frac{(1\ \text{atm})\,(22.414\ \text{L})}{(1\ \text{mol})\,(273.16\ \text{K})} \Longrightarrow \mathbf{R} = 0.08205\ \ \mathbf{L\,.\,atm\,/\,K\,.\,mol}$$

$T = 273.16$ K, $P = 1$ atm $= 1.0133 \times 10^6$ dynes/cm^2, 1 mole, $V = 22.414$ cm^3

$$\mathbf{R} = \frac{PV}{nT} = \frac{(1.0133 \times 10^6)\,(22.414)}{(1)\,(273.16)} = 8.314 \times 10^7\ \ \mathbf{erg\,/\,K\,.\,mol}$$

$$1\ \text{Joule} = 10^7\ \text{ergs} \Longrightarrow \mathbf{R} = 8.314\ \mathbf{J\,/\,K\,.\,mol}$$

1 cal. = 4.184 Joules :

$$\mathbf{R} = \frac{8.314\ \text{J.}\,/\,\text{mol. deg.}}{4.184\ \text{J.}\,/\,\text{cal.}} \Longrightarrow \mathbf{R} = 1.987\ \mathbf{cal\,/\,deg\,.\,mol}$$

***Example**: Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 45 ^{o}C.*

Solution: Because no changes in gas properties occur, the ideal gas equation can use to calculate the pressure. Rearranging:

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(45 + 273)\ \text{K}}{5.43\ \text{L}} \\ &= 8.75\ \text{atm} \end{aligned}$$

The ideal gas equation is useful for problems that do not involve changes in *P*, *V*, *T*, and *n* for a gas sample. When conditions change, a modified form of the ideal gas equation that takes into account the initial and final conditions must employ. The modified equation derives as follows:

$$R = \frac{P_1V_1}{n_1T_1} \text{ (before change)} \quad \text{and} \quad R = \frac{P_2V_2}{n_2T_2} \text{ (after change)}$$

Therefore,

$$\frac{P_1V_1}{n_1T_1} = R = \frac{P_2V_2}{n_2T_2}$$

If $n_1 = n_2$, as is usually the case because the amount of gas normally does not change, the equation then becomes:

$$\frac{P_1V_1}{n_1T_1} = R = \frac{P_2V_2}{n_2T_2}$$

Example: *A small bubble rises from the bottom of a lake, where the temperature and pressure are 8 ^{o}C and 6.4 atm, to the water's surface, where the temperature is 25 ^{o}C and the pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.*

<u>*Solution:*</u> The given information is summarized:

Initial Conditions	**Final Conditions**
$P_1 = 6.4$ atm	$P_2 = 1.0$ atm
$V_1 = 2.1$ mL	$V_2 = ?$
$T_1 = (8 + 273)$ K $= 281$ K	$T_2 = (25 + 273)$ K $= 298$ K

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

The amount of air in the bubble remains constant, that is, $n_1 = n_2$ so that:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Rearranging equation above gives:

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\ &= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}} \\ &= 14 \text{ mL} \end{aligned}$$

Practice Exercise:

- What is the volume (in liters) occupied by 49.8 g of HCl at STP?
- A gas initially at 4.0 L, 1.2 atm, and 66 ^{o}C undergoes a change so that its final volume and temperature are 1.7 L and 42 ^{o}C. What is its final pressure? Assume the number of moles remains unchanged.

Density and Molar Mass of a Gaseous Substance

The ideal gas equation can be applied to determine the density or molar mass of a gaseous substance. Rearranging this equation gives:

$$\frac{n}{V} = \frac{P}{RT}$$

The number of moles of the gas, *n*, is given by:

$$n = \frac{m}{\mathcal{M}}$$

in which *m* is the mass of the gas in grams and $\mathcal{M}$ is its molar mass. Therefore,

$$\frac{m}{\mathcal{M}V} = \frac{P}{RT}$$

Because density, *d*, is mass per unit volume, therefore:

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

The equation above enables to calculate the density of a gas (given in units of grams per liter). More often, the density of a gas can be measured, so this equation can be rearranged to calculate the molar mass of a gaseous substance:

$$\mathcal{M} = \frac{dRT}{P}$$

In a typical experiment, a bulb of known volume is filled with the gaseous substance under study. The temperature and pressure of the gas sample are recorded, and the total mass of the bulb plus gas sample is determined (see Figure below). The bulb is then evacuated (emptied) and weighed again. The difference in mass is the mass of the gas. The density of the gas is equal to its mass divided by the volume of the bulb. Then the molar mass of the substance can be calculated using the last equation.

An apparatus for measuring the density of a gas. A bulb of known volume is filled with the gas under study at a certain temperature and pressure. First the bulb is weighed, and then it is emptied (evacuated) and weighed again. The difference in masses gives the mass of the gas. Knowing the volume of the bulb, we can calculate the density of the gas.

Example: *A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36 ^oC and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.*

Solution:

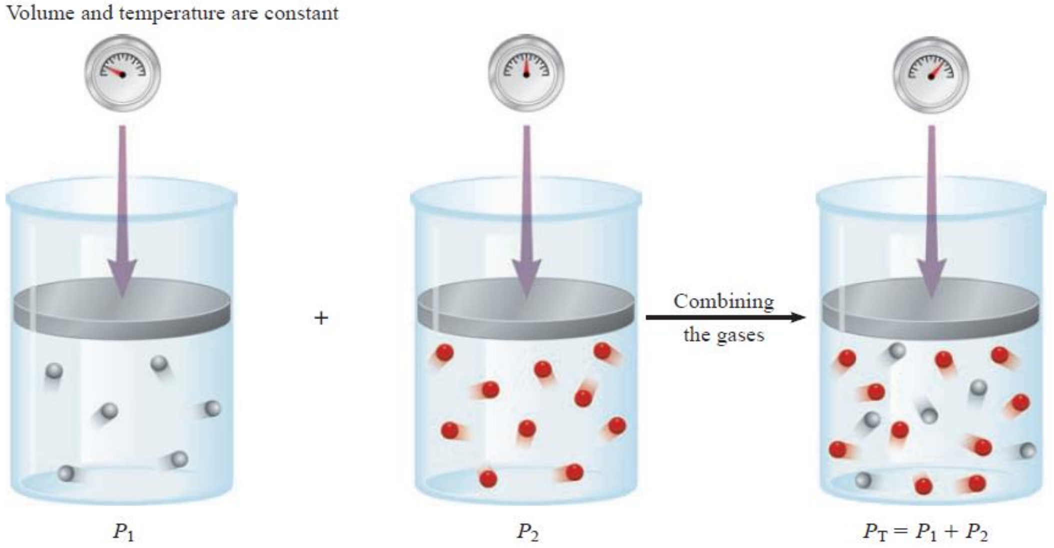
$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71\ \text{g/L})(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(36 + 273)\ \text{K}}{2.88\ \text{atm}} \\ &= 67.9\ \text{g/mol}\end{aligned}$$

The molecular formula of the compound can be determined by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). A compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus, the compound must contain one Cl atom and two O atoms and have the formula ClO_2, which has a molar mass of 67.45 g.

Practice Exercise: *The density of a gaseous organic compound is 3.38 g/L at 40 ^oC and 1.97 atm. What is its molar mass?*

Dalton’s Law of Partial Pressures

The experimental studies very often involve mixtures of gases. For example, for a study of air pollution, the pressure-volume-temperature relationship of a sample of air, which contains several gases, may be interested. In this case, and all cases involving mixtures of gases, the total gas pressure is related to ***partial pressures,*** that is, *the pressures of individual gas components in the mixture.* In 1801 Dalton formulated a law, now known as ***Dalton’s law of partial pressures,*** which states that *the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone.* Figure below illustrates Dalton’s law.



Consider a case in which two gases, **A** and **B**, are in a container of volume V. The pressure exerted by gas A, according to the ideal gas equation, is:

$$P_A = \frac{n_A RT}{V}$$

where n_A is the number of moles of **A** present. Similarly, the pressure exerted by gas **B** is:

$$P_B = \frac{n_B RT}{V}$$

In a mixture of gases **A** and **B**, the total pressure P_T is the result of the collisions of both types of molecules, **A** and **B**, with the walls of the container. Thus, according to Dalton's law:

$$\begin{aligned} P_\mathrm{T} &= P_\mathrm{A} + P_\mathrm{B} \\ &= \frac{n_\mathrm{A}RT}{V} + \frac{n_\mathrm{B}RT}{V} \\ &= \frac{RT}{V}(n_\mathrm{A} + n_\mathrm{B}) \\ &= \frac{nRT}{V} \end{aligned}$$

where n, the total number of moles of gases present, is given by $n = n_A + n_B$, and P_A and P_B are the partial pressures of gases **A** and **B**, respectively. For a mixture of gases, then, P_T depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by:

$$P_\mathrm{T} = P_1 + P_2 + P_3 + \cdots$$

where P_1, P_2, P_3, . . . are the partial pressures of components 1, 2, 3, ... To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases **A** and **B**. Dividing P_A by P_T, can obtain:

$$\begin{aligned} \frac{P_\mathrm{A}}{P_\mathrm{T}} &= \frac{n_\mathrm{A}RT/V}{(n_\mathrm{A} + n_\mathrm{B})RT/V} \\ &= \frac{n_\mathrm{A}}{n_\mathrm{A} + n_\mathrm{B}} \\ &= X_\mathrm{A} \end{aligned}$$

where X_A is called the mole fraction of **A**. The mole fraction is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present. In general, the mole fraction of component i in a mixture is given by:

$$X_i = \frac{n_i}{n_T}$$

where n_i and n_T are the number of moles of component i and the total number of moles present, respectively. The mole fraction is always smaller than 1. The partial pressure of **A** can now express as:

$$P_A = X_A P_T$$

Similarly,

$$P_B = X_B P_T$$

Note that the sum of the mole fractions for a mixture of gases must be unity. If only two components are present, then:

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

If a system contains more than two gases, then the partial pressure of the *i*th component is related to the total pressure by:

$$P_i = X_i P_T$$

How are partial pressures determined? A manometer can measure only the total pressure of a gaseous mixture. To obtain the partial pressures, the mole fractions of the components are needed to know, which would involve elaborate chemical analyses. The most direct method of measuring partial pressures is using a mass spectrometer. The relative intensities of the peaks in a mass spectrum are directly proportional to the amounts, and hence to the mole fractions, of the gases present.

Example: *A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.*

Solution: The partial pressure of Ne (P_{Ne}) is equal to the product of its mole fraction (X_{Ne}) and the total pressure (P_T):

$$\underset{\text{want to calculate}}{P_{Ne}} = \overset{\text{need to find}}{X_{Ne}}\underset{\text{given}}{P_T}$$

The mole fraction of Ne can calculate as follows:

$$X_{Ne} = \frac{n_{Ne}}{n_{Ne} + n_{Ar} + n_{Xe}} = \frac{4.46\text{ mol}}{4.46\text{ mol} + 0.74\text{ mol} + 2.15\text{ mol}} = 0.607$$

Therefore,

$$\begin{aligned} P_{Ne} &= X_{Ne}P_T \\ &= 0.607 \times 2.00\text{ atm} \\ &= 1.21\text{ atm} \end{aligned}$$

Similarly,

$$\begin{aligned} P_{Ar} &= X_{Ar}P_T \\ &= 0.10 \times 2.00\text{ atm} \\ &= 0.20\text{ atm} \end{aligned}$$

and

$$\begin{aligned} P_{Xe} &= X_{Xe}P_T \\ &= 0.293 \times 2.00\text{ atm} \\ &= 0.586\text{ atm} \end{aligned}$$

Check: Make sure that the sum of the partial pressures is equal to the given total pressure; that is, (1.21 + 0.20 + 0.586) atm = 2.00 atm.

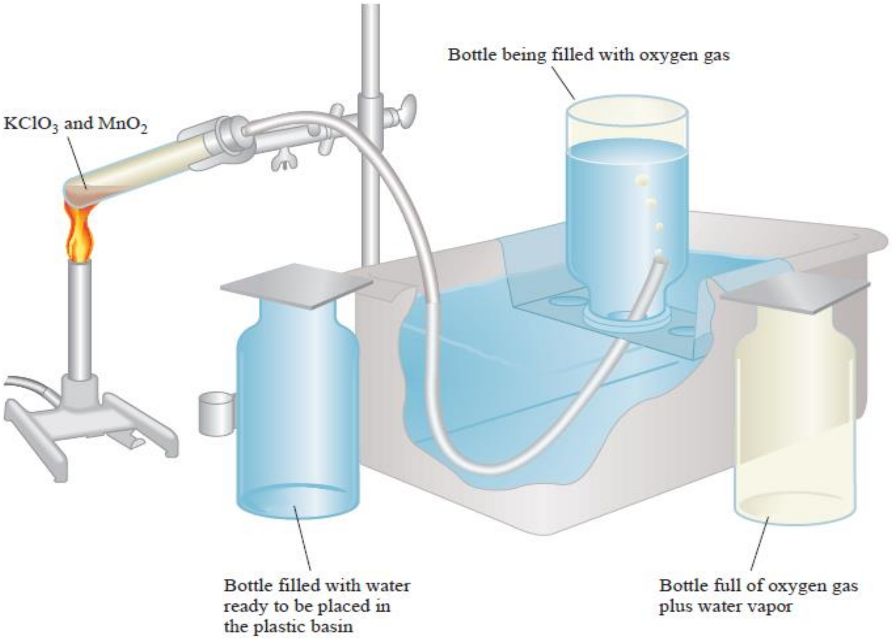
Practice Exercise: *A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?*

Dalton's law of partial pressures is useful for calculating volumes of gases collected over water. For example, when potassium chlorate (**$KClO_3$**) is heated, it decomposes to **KCl** and **O_2**:

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

The oxygen gas can be collected over water, as shown in Figure as follows:

An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate ($KClO_3$) in the presence of a small amount of manganese dioxide (MnO_2), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in the bottle is pushed into the trough by the oxygen gas.



Initially, the inverted bottle is completely filled with water. As oxygen gas is generated, the gas bubbles rise to the top and displace water from the bottle. This method of collecting a gas is based on the assumptions that the gas does not react with water and that it is not appreciably soluble in it. These assumptions are valid for oxygen gas, but not for gases such as NH_3, which dissolves readily in water. The oxygen gas collected in this way is not pure, however, because water vapor is also present in the bottle. The total gas pressure is equal to the sum of the pressures exerted by the oxygen gas and the water vapor:

$$P_T = P_{O_2} + P_{H_2O}$$

Consequently, the pressure caused by the presence of water vapor when the amount of O_2 generated calculates must be allowed.

Example: *Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure above. The volume of oxygen collected at 24 ^{o}C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24 ^{o}C is 22.4 mmHg.*

Solution: From Dalton’s law of partial pressures:

$$P_{\mathrm{T}} = P_{\mathrm{O_2}} + P_{\mathrm{H_2O}}$$

Therefore,

$$\begin{aligned} P_{\mathrm{O_2}} &= P_{\mathrm{T}} - P_{\mathrm{H_2O}} \\ &= 762\ \mathrm{mmHg} - 22.4\ \mathrm{mmHg} \\ &= 740\ \mathrm{mmHg} \end{aligned}$$

From the ideal gas equation:

$$PV = nRT = \frac{m}{\mathcal{M}}RT$$

where m and are the mass of O_2 collected and the molar mass of O_2, respectively. *Rearranging:*

$$\begin{aligned} m = \frac{PV\mathcal{M}}{RT} &= \frac{(740/760)\ \mathrm{atm}\ (0.128\ \mathrm{L})(32.00\ \mathrm{g/mol})}{(0.0821\ \mathrm{L \cdot atm/K \cdot mol})(273 + 24)\ \mathrm{K}} \\ &= 0.164\ \mathrm{g} \end{aligned}$$

Gas Diffusion and Effusion

Gas Diffusion

A direct demonstration of random motion is provided by ***diffusion,*** *the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.* Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the bench to the other. Thus, diffusion of gases always happens gradually, and not instantly as molecular speeds seem to suggest. Furthermore, because the root-mean-square speed of a light gas is greater than that of a heavier gas (refer to example above), a lighter gas will diffuse through a certain space more quickly than will a heavier gas.

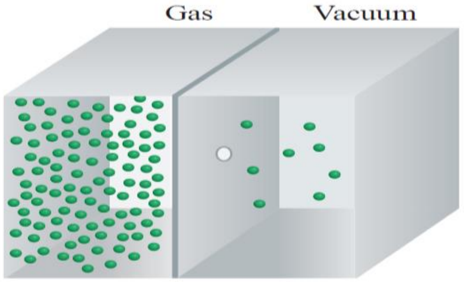
In 1832 the Scottish chemist Thomas Graham found that *under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses.* This statement, now known as ***Graham's law of diffusion,*** is expressed mathematically as:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

where r_1 and r_2 are the diffusion rates of gases 1 and 2, and $\mathcal{M}_1$ and $\mathcal{M}_2$ are their molar masses, respectively.

Gas Effusion

Whereas diffusion is a process by which one gas gradually mixes with another, ***effusion*** is *the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening.* The effusion of a gas into a vacuum can depict in Figure:



Gas effusion. Gas molecules move from a high-pressure region (left) to a low-pressure one through a pinhole.

Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion (see the equation above). A helium-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for the lighter helium atoms than for the air molecules. Industrially, gas effusion is used to separate uranium isotopes in the forms of gaseous $^{235}UF_6$ and $^{238}UF_6$. By subjecting the gases to many stages of effusion, scientists were able to obtain highly enriched ^{235}U isotope, which was used in the construction of atomic bombs during World War II.

Example: *A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.*

<u>Solution:</u> From the molar mass of Br_2:

$$r_1/r_2 = t_2/t_1 = \sqrt{\mathcal{M}_2/\mathcal{M}_1},$$

where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.

$$\frac{1.50\ \text{min}}{4.73\ \text{min}} = \sqrt{\frac{\mathcal{M}}{159.8\ \text{g/mol}}}$$

where $\mathcal{M}$ is the molar mass of the unknown gas. Solving for $\mathcal{M}$, can obtain:

$$\mathcal{M} = \left(\frac{1.50\ \text{min}}{4.73\ \text{min}}\right)^2 \times 159.8\ \text{g/mol}$$
$$= 16.1\ \text{g/mol}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane (CH_4).

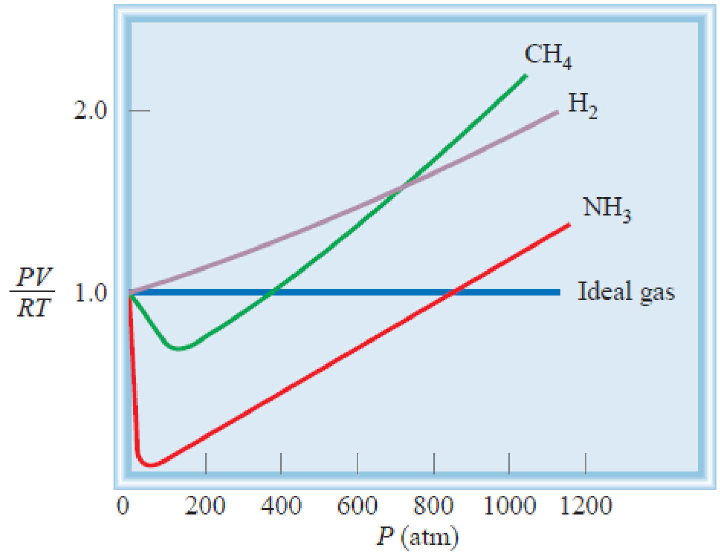
Practice Exercise: *It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of* N_2 *gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?*

Deviation from Ideal Behavior

The gas laws and the kinetic molecular theory assume that molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another. The other assumption is that the volume of the molecules is negligibly small compared with that of the container. A gas that satisfies these two conditions is said to exhibit *ideal behavior.*

Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions. For example, without intermolecular forces, gases could not condense to form liquids. The important question is: Under what conditions will gases most likely exhibit nonideal behavior?

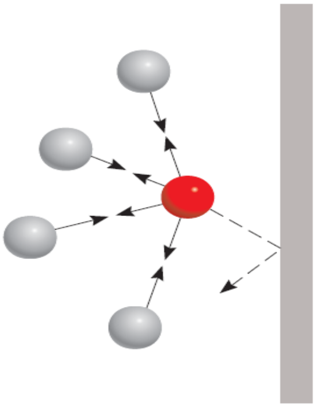
Figure below shows PV/RT plotted against P for three real gases and an ideal gas at a given temperature. This graph provides a test of ideal gas behavior. According to the ideal gas equation (for 1 mole of gas), PV/RT equals 1, regardless of the actual gas pressure. (When $n = 1$, $PV = nRT$ becomes $PV = RT$, or $PV/RT = 1$.) For real gases, this is true only at moderately low pressures (≤ 5 atm); significant deviations occur as pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.



Plot of PV_RT versus P of 1 mole of a gas at 0 °C. For 1 mole of an ideal gas, PV/RT is equal to 1, no matter what the pressure of the gas is. For real gases, we observe various deviations from ideality at high pressures. At very low pressures, all gases exhibit ideal behavior; that is, their PV/RT values all converge to 1 as P approaches zero.

Another way to observe the nonideal behavior of gases is to lower the temperature. Cooling a gas decreases the molecules' average kinetic energy, which in a sense deprives molecules of the drive they need to break from their mutual attraction.

To study real gases accurately, then, we need to modify the ideal gas equation, taking into account intermolecular forces and finite molecular volumes. Such an analysis was first made by the Dutch physicist J. D. van der Waals in 1873. Besides being mathematically simple, van der Waals's treatment provides us with an interpretation of real gas behavior at the molecular level. Consider the approach of a particular molecule toward the wall of a container:



Effect of intermolecular forces on the pressure exerted by a gas. The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as great as it would be if no intermolecular forces were present. In general, the measured gas pressure is lower than the pressure the gas would exert if it behaved ideally.

The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Van der Waals suggested that the pressure exerted by an ideal gas, P_{ideal}, is related to the experimentally measured; that is, observed pressure, P_{obs}, by the equation:

$$P_{\text{ideal}} = \underset{\substack{\uparrow \\ \text{observed} \\ \text{pressure}}}{P_{\text{real}}} + \underset{\substack{\uparrow \\ \text{correction} \\ \text{term}}}{\frac{an^2}{V^2}}$$

where a is a constant and n and V are the number of moles and volume of the gas, respectively. The correction term for pressure (an^2/V^2) can be understood as follows. The intermolecular interaction that gives rise to nonideal behavior depends on how frequently any two molecules approach each other closely. The number of such "encounters" increases with the square of the number of molecules per unit volume, $(n/V)^2$, because the presence of each of the two molecules in a particular region is proportional to n/V. The quantity P_{ideal} is the pressure we would measure if there were no intermolecular attractions, and so a is just a proportionality constant.

Another correction concerns the volume occupied by the gas molecules. In the ideal gas equation, V represents the volume of the container. However, each molecule does occupy a finite, although small, intrinsic volume, so the effective volume of the gas becomes ($V - nb$), where n is the number of moles of the gas and b is a constant. The term nb represents the volume occupied by n moles of the gas.

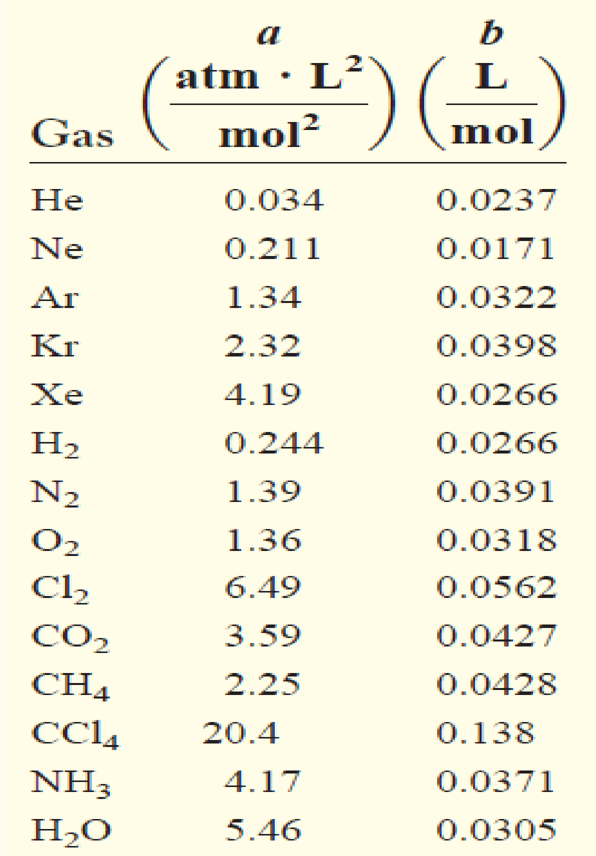
Having taken into account the corrections for pressure and volume, the ideal gas equation can rewrite as follows:

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\substack{\text{corrected} \\ \text{pressure}}} \underbrace{(V - nb)}_{\substack{\text{corrected} \\ \text{volume}}} = nRT$$

This equation, *relating P, V, T, and n for a nonideal gas*, is known as the ***van der Waals equation.*** The van der Waals constants *a* and *b* are selected to give the best possible agreement between above equation and observed behavior of a particular gas.

Table below lists the values of *a* and *b* for a number of gases. The value of *a* indicates how strongly molecules of a given type of gas attract one another. The table shows that helium atoms have the weakest attraction for one another, because helium has the smallest *a* value. There is also a rough correlation between molecular size and *b*. Generally, the larger the molecule (or atom), the greater *b* is, but the relationship between *b* and molecular (or atomic) size is not a simple one.

Table of van der Waals Constants of Some Common Gases



Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Example: *Given that 3.50 moles of* NH_3 *occupy 5.20 L at 47* ^oC*, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.*

<u>Solution:</u> **(a)** Using the ideal gas equation:

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(320 \text{ K})}{5.20 \text{ L}} \\ &= 17.7 \text{ atm} \end{aligned}$$

(b) By using van der Waals equation and from the Table above, we get *a* and *b* values for NH_3:

$a = 4.17$ atm . L^2/mol^2

$b= 0.0371$ L/mol

so that the correction terms for pressure and volume are:

$$\begin{aligned} \frac{an^2}{V^2} &= \frac{(4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm} \\ nb &= (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L} \end{aligned}$$

Finally, substituting these values in the van der Waals equation:

$$\begin{gathered} (P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(320 \text{ K}) \\ P = 16.2 \text{ atm} \end{gathered}$$

<u>Practice Exercise:</u> *Calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38* ^oC*. Compare the pressure with that calculated using the ideal gas equation. (**a** and **b** values for chlorine are:**a**=* 6.49 atm . L^2/mol^2; ***b***= 0.0562 L/mol*).*

Types of Chemical Reactions

Chemical reactions can be classified as:

1. Oxidation–reduction reactions.
2. Combination reactions.
3. Decomposition reactions.
4. Displacement reactions.
5. Metathesis reactions.
6. Gas-formation reactions.

1. Oxidation–Reduction Reactions

The term “**oxidation**” originally referred to the combination of a substance with oxygen. This results in an increase in the oxidation state of an element in that substance. **Oxidation** is an increase in oxidation state and corresponds to the loss, or apparent loss, of electrons. **Reduction** is a decrease in oxidation state and corresponds to a gain, or apparent gain, of electrons. Oxidation and reduction always occur simultaneously, and to the same extent, in ordinary chemical reactions. So they are referred to as **oxidation–reduction reactions** (usually we call them **redox reaction**).

EX.: The formation of rust, Fe_2O_3, iron(III) oxide:

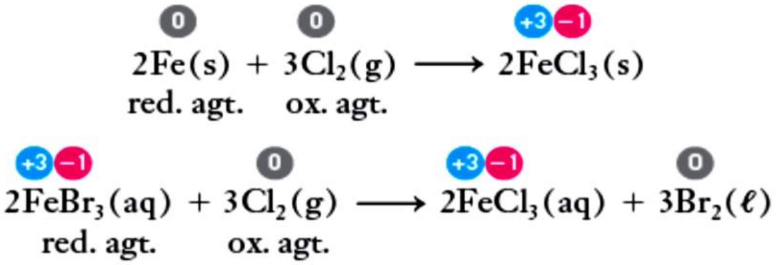
$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

oxidation state of Fe

$0 \longrightarrow +3$

Oxidizing agents are species that:	**Reducing agents** are species that:
(1) oxidize other substances.	(1) reduce other substances.
(2) contain atoms that are reduced.	(2) contain atoms that are oxidized.
(3) gain (or appear to gain) electrons.	(3) lose (or appear to lose) electrons.

The following equations represent examples of redox reactions. Oxidation states are shown above the formulas, and oxidizing and reducing agents are indicated:



$$\underset{\text{red. agt.}}{\overset{0}{2Fe(s)}} + \underset{\text{ox. agt.}}{\overset{0}{3Cl_2(g)}} \longrightarrow \overset{+3\;-1}{2FeCl_3(s)}$$

$$\underset{\text{red. agt.}}{\overset{+3\;-1}{2FeBr_3(aq)}} + \underset{\text{ox. agt.}}{\overset{0}{3Cl_2(g)}} \longrightarrow \overset{+3\;-1}{2FeCl_3(aq)} + \overset{0}{3Br_2(\ell)}$$

2. Combination Reactions

Reactions in which two or more substances combine to form a single compound are called **combination reactions**. They may involve:

(1) The combination of two elements to form a compound.

(2) The combination of an element and a compound to form a single new compound.

(3) The combination of two compounds to form a single new compound.

1 Element + Element ⟶ Compound

For this type of combination reaction, each element goes from an uncombined state, where its oxidation state is zero, to a combined state in a compound, where its oxidation state is not zero. Thus reactions of this type are oxidation–reduction reactions. Most metals (low electronegativity) react with most nonmetals (higher electronegativity) to form binary ionic compounds.

Metal + Nonmetal → Binary Ionic Compound

$$2M(s) + X_2 \longrightarrow 2(M^+X^-)(s)$$

M = Li, Na, K, Rb, Cs

X = F, Cl, Br, I

$$M(s) + X_2 \longrightarrow MX_2(s) \qquad \begin{array}{l} M = Be, Mg, Ca, Sr, Ba \\ X = F, Cl, Br, I \end{array}$$

When two nonmetals combine with each other, they form binary *covalent* compounds. In such reactions, the oxidation state of the element with the more positive oxidation state is often variable, depending on reaction conditions. For example, phosphorus combines with a *limited amount* of chlorine to form phosphorus trichloride, in which phosphorus exhibits the +3 oxidation state.

$$P_4(s) + 6Cl_2(g) \rightarrow 4\overset{+3}{P}Cl_3(\ell) \qquad \text{(with limited } Cl_2\text{)} \qquad \text{(mp } -112°C\text{)}$$

With an excess of chlorine, the product is phosphorus pentachloride, which contains phosphorus in the +5 oxidation state:

$$P_4(s) + 10Cl_2(g) \longrightarrow 4\overset{+5}{P}Cl_5(s) \qquad \text{(with excess } Cl_2\text{)} \qquad \text{(decomposes at 167°C)}$$

In general, *a higher oxidation state of a nonmetal is formed when it reacts with an excess of another more electronegative nonmetal.*

2 Compound + Element ⟶ Compound

Combination reactions of this type are also oxidation–reduction reactions.

$$\overset{+3}{P}Cl_3(\ell) + Cl_2(g) \longrightarrow \overset{+5}{P}Cl_5(s)$$

$$\overset{+4}{S}F_4(g) + F_2(g) \longrightarrow \overset{+6}{S}F_6(g)$$

3 Compound + Compound ⟶ Compound

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$$

$$CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(aq)$$

3. Decomposition Reactions

Decomposition reactions are those in which a compound decomposes to produce:

(1) Two elements.

$$\text{Compound} \longrightarrow \text{Element} + \text{Element}$$

$$2H_2O(\ell) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$

(2) One or more elements and one or more compounds.

$$\text{Compound} \longrightarrow \text{Compound} + \text{Element}$$

$$2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g)$$

(3) Two or more compounds.

$$\text{Compound} \longrightarrow \text{Compound} + \text{Compound}$$

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

4. Displacement Reactions

Reactions in which one element displaces another from a compound are called **displacement reactions**. These reactions are always redox reactions. The lower the electronegativity of a metal, the more readily that metal undergoes oxidation. More active (less electronegative) metals displace less active (more electronegative) metals or hydrogen from their compounds in aqueous solution to form the oxidized form of the more active metal and the reduced (free metal) form of the other metal or hydrogen gas.

The *electronegativity* of an element is a measure of the relative tendency of an atom to attract electrons to itself when it is chemically combined with another atom. Elements with *high electronegativities (nonmetals)* often gain electrons to form anions. The higher the electronegativity, the more stable the anions that are formed. While elements with *low electronegativities (metals)* often lose electrons to form cations. The lower the electronegativity, the more stable the cations that are formed. For the representative elements in the periodic table, electronegativities usually increase from left to right across periods and decrease from top to bottom within groups.

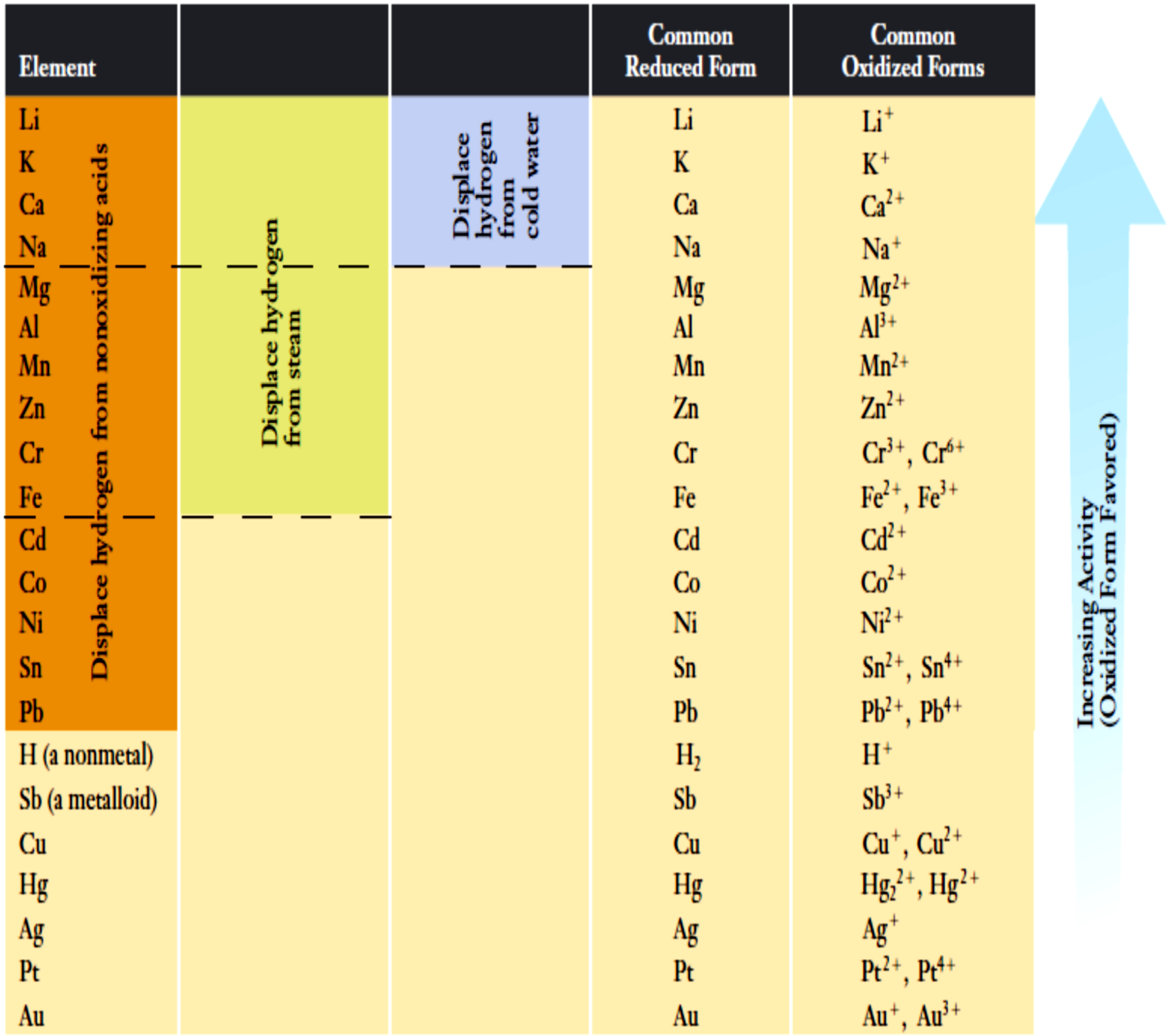
$$1\ \begin{bmatrix}\text{More Active Metal} + \\ \text{Salt of Less Active Metal}\end{bmatrix} \longrightarrow \begin{bmatrix}\text{Less Active Metal} + \\ \text{Salt of More Active Metal}\end{bmatrix}$$

$$2AgNO_3(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

$$2\ [\text{Active Metal} + \text{Nonoxidizing Acid}] \longrightarrow [\text{Hydrogen} + \text{Salt of Acid}]$$

$$Zn(s) + \underset{\text{strong acid}}{H_2SO_4(aq)} \longrightarrow \underset{\text{soluble salt}}{ZnSO_4(aq)} + H_2(g)$$

Activity Series of Some Elements



Element				Common Reduced Form	Common Oxidized Forms
Li	Displace hydrogen from nonoxidizing acids	Displace hydrogen from steam	Displace hydrogen from cold water	Li	Li^+
K				K	K^+
Ca				Ca	Ca^{2+}
Na				Na	Na^+
Mg				Mg	Mg^{2+}
Al				Al	Al^{3+}
Mn				Mn	Mn^{2+}
Zn				Zn	Zn^{2+}
Cr				Cr	Cr^{3+}, Cr^{6+}
Fe				Fe	Fe^{2+}, Fe^{3+}
Cd				Cd	Cd^{2+}
Co				Co	Co^{2+}
Ni				Ni	Ni^{2+}
Sn				Sn	Sn^{2+}, Sn^{4+}
Pb				Pb	Pb^{2+}, Pb^{4+}
H (a nonmetal)				H_2	H^+
Sb (a metalloid)				Sb	Sb^{3+}
Cu				Cu	Cu^+, Cu^{2+}
Hg				Hg	Hg_2^{2+}, Hg^{2+}
Ag				Ag	Ag^+
Pt				Pt	Pt^{2+}, Pt^{4+}
Au				Au	Au^+, Au^{3+}

When any metal listed above hydrogen in this series is added to a solution of a *nonoxidizing* acid such as hydrochloric acid, HCl, or sulfuric acid, H_2SO_4, the metal dissolves to produce hydrogen, and a salt is formed.

$$3\ \left[\begin{array}{c}\text{Active Nonmetal} + \\ \text{Salt of Less Active Nonmetal}\end{array}\right] \longrightarrow \left[\begin{array}{c}\text{Less Active Nonmetal} + \\ \text{Salt of More Active Nonmetal}\end{array}\right]$$

Many *nonmetals* displace less active nonmetals from combination with a metal or other cation.

$$\underset{\text{chlorine}}{\mathrm{Cl_2(g)}} + \underset{\text{sodium bromide}}{2[\mathrm{Na^+(aq)} + \mathrm{Br^-(aq)}]} \longrightarrow \underset{\text{sodium chloride}}{2[\mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}]} + \underset{\text{bromine}}{\mathrm{Br_2}(\ell)}$$

Each halogen will displace less active (less electronegative) halogens from their binary salts; that is, the order of decreasing activities is:

$$\mathbf{F_2 > Cl_2 > Br_2 > I_2}$$

Conversely, a halogen will not displace more active (more electronegative) members from their salts:

$$\mathrm{I_2(s)} + 2\mathrm{F^-} \longrightarrow \text{no reaction}$$

5. Metathesis Reactions

In many reactions between two compounds in aqueous solution, the positive and negative ions appear to “change partners” to form two new compounds, with *no change in oxidation numbers*. Such reactions are called **metathesis reactions** (sometimes referred to as double displacement reactions).

$$\mathrm{AX} + \mathrm{BY} \longrightarrow \mathrm{AY} + \mathrm{BX}$$

$$\mathrm{AgNO_3(aq)} + \mathrm{NaCl(aq)} \longrightarrow \mathrm{AgCl(s)} + \mathrm{NaNO_3(aq)}$$

<u>Metathesis reactions can be classified into:</u>

1 Acid–Base (Neutralization) Reactions: Formation of a Nonelectrolyte

Acid–base reactions are among the most important kinds of chemical reactions. The reaction of an acid with a metal hydroxide base produces a salt and water. Such reactions are called **neutralization reactions** because the typical properties of acids and bases are neutralized. In nearly all neutralization reactions, the driving force is the combination of $H^+(aq)$ from an acid and $OH^-(aq)$ from a base (or a base plus water) to form water molecules.

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

$$[H^+(aq) + Cl^-(aq)] + [Na^+(aq) + OH^-(aq)] \longrightarrow H_2O(\ell) + [Na^+(aq) + Cl^-(aq)]$$

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

2 Precipitation Reactions

In **precipitation reactions** an insoluble solid, a *precipitate*, forms and then settles out of solution. The driving force for these reactions is the strong attraction between cations and anions. This results in the removal of ions from solution by the formation of a precipitate.

$$Pb(NO_3)_2(aq) + K_2CrO_4(aq) \longrightarrow PbCrO_4(s) + 2KNO_3(aq)$$

$$[Pb^{2+}(aq) + 2NO_3^-(aq)] + [2K^+(aq) + CrO_4^{2-}(aq)] \longrightarrow PbCrO_4(s) + 2[K^+(aq) + NO_3^-(aq)]$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

6. Gas-Formation Reactions

When there are no gaseous reactants, the formation of an insoluble or slightly soluble gas provides a driving force for a type of reaction that we call a gas-formation reaction. The only common gases that are very soluble in water are HCl(g) and NH_3(g). The low solubility of other gases can force a reaction to proceed if they are formed as a reaction product.

When an acid—for example, hydrochloric acid—is added to solid calcium carbonate, a reaction occurs in which carbonic acid, a weak acid, is produced.

$$2HCl(aq) + CaCO_3(s) \longrightarrow H_2CO_3(aq) + CaCl_2(aq)$$

$$2[H^+(aq) + Cl^-(aq)] + CaCO_3(s) \longrightarrow H_2CO_3(aq) + [Ca^{2+}(aq) + 2Cl^-(aq)]$$

$$2H^+(aq) + CaCO_3(s) \longrightarrow H_2CO_3(aq) + Ca^{2+}(aq)$$

The heat generated in the reaction causes thermal decomposition of carbonic acid to gaseous carbon dioxide and water:

$$H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O(\ell)$$

Most of the CO_2 bubbles off, and the reaction goes to completion (with respect to the limiting reactant). The net effect is the conversion of ionic species into nonionized molecules of a gas (CO_2) and water.

$$2HCl(aq) + CaCO_3(s) \longrightarrow CO_2(g) + H_2O(\ell) + CaCl_2(aq)$$