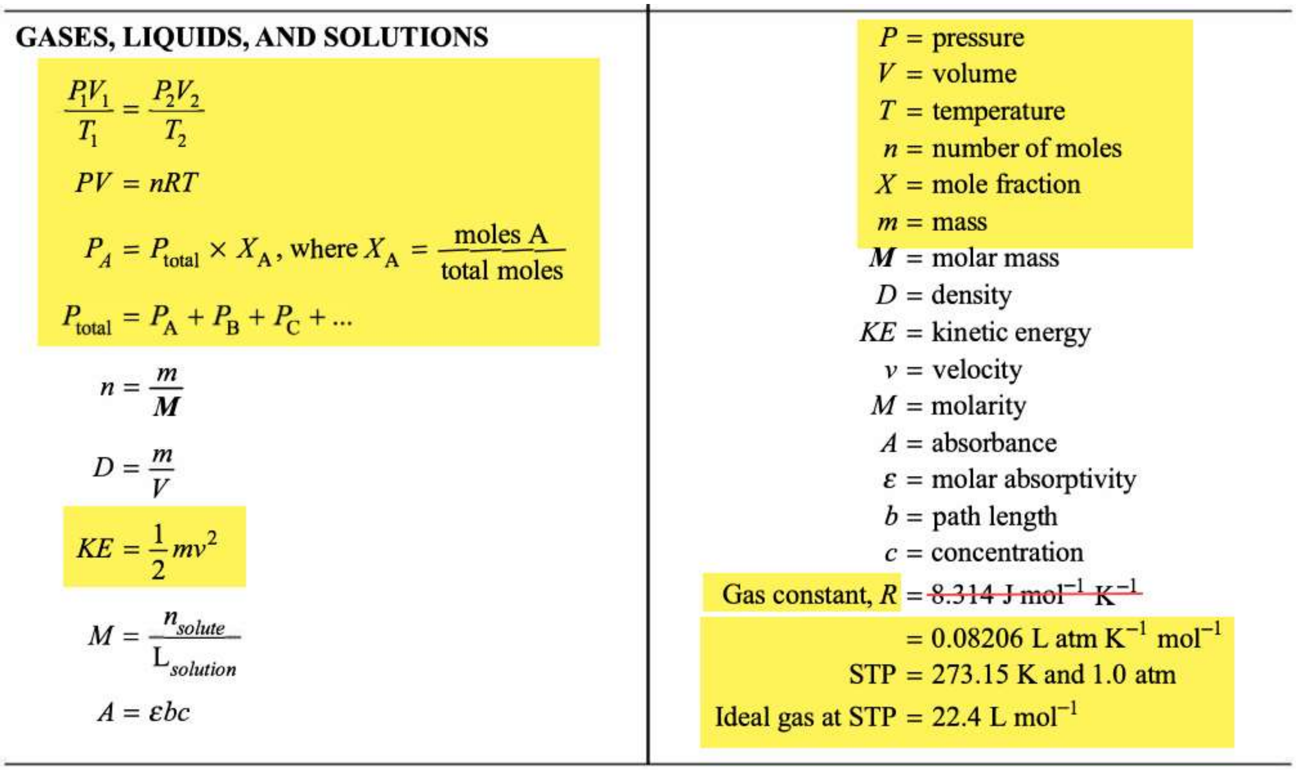
Chapter 5 Gases

The depth of coverage in the textbook exceeds what is required for the AP Chemistry exam.
Use this summary as your primary resource for this unit and only use the textbook for additional explanations.
The WebAssignment questions will also help explain the concepts and show you what you will need to know for this topic.

Chemistry by Chang and Goldsby

Chapter 5 – Gases
5.1 Substance That Exist as Gases
5.2 Pressure of a Gas
5.3 The Gas Laws
5.4 The Ideal Gas Equation
5.5 Gas Stoichiometry
5.6 Daltons Law of Partial Pressures
5.7 The Kinetic Molecular Theory of Gases
5.8 Deviation from the Ideal Behavior (without the van der Waals equation)

You should be aware of the gas law equations on the equations sheet.



GASES, LIQUIDS, AND SOLUTIONS

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

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A\text{, where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \ldots$$

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

$$D = \frac{m}{V}$$

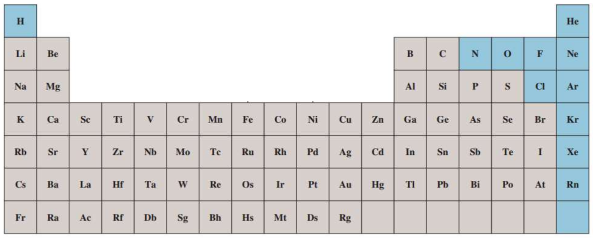
$$KE = \frac{1}{2}mv^2$$

$$M = \frac{n_{solute}}{\text{L}_{solution}}$$

$$A = \varepsilon bc$$

P = pressure
V = volume
T = temperature
n = number of moles
X = mole fraction
m = mass
$\boldsymbol{M}$ = molar mass
D = density
KE = kinetic energy
v = velocity
M = molarity
A = absorbance
ε = molar absorptivity
b = path length
c = concentration
Gas constant, R = ~~$8.314\text{ J mol}^{-1}\text{ K}^{-1}$~~
= $0.08206\text{ L atm K}^{-1}\text{ mol}^{-1}$
STP = 273.15 K and 1.0 atm
Ideal gas at STP = 22.4 L mol^{-1}

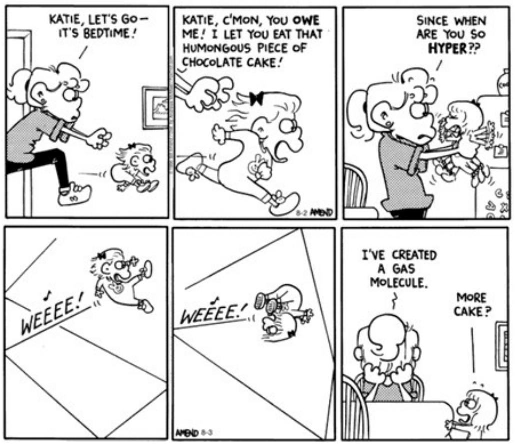
5.1 Substances that Exist as Gases

Gases at normal atmospheric pressure, 1 atm and 25°C Molecular Gases: H_2, N_2, O_2, O_3, F_2, Cl_2 Monatomic Gases: He, Ne, Ar, Kr, Xe, Rn	

To be a gas at room temperature the attractions between molecules must be weak.

Most gases are colorless.	Notable exceptions Cl_2 yellow-green Br_2 brown-orange[1] I_2 violet[2] NO_2 brown 

Gases: assume the volume & shape of containers
are compressible
mix evenly in a container
at room temperature and pressure, they have densities about 1/1000 of liquids or solids
gas density is expressed in g/L (room pressure air ≈ 1 g/L)



Gases are all bounce with little substance.
At room temperature and pressure, a sample of gas is over 99% empty space.
The word gas was coined by chemist Jan Baptist van Helmont in1648 from Ancient Greek (kháos), "chasm, void, empty space."

In contrast to solids and liquids, **gas volume is not the volume of the molecules themselves**, but rather **the volume of the confining container.**

Gas properties are explained in terms of the kinetic effects of moving molecules.

The ideal gas law equations are premised on the movement of gas particles.

It doesn't matter what the gas is, all gases follow the same bouncing rules!

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

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A\text{, where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \ldots$$

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[1] While a liquid at room temp bromine vaporizes enough to produce enough to produce a visible gas.
[2] A solid at room temperature, but when warmed its purple violet are visible.

5.2 Pressure of a Gas

Gases exert pressure (force/area) on any surface they contact because of molecular collisions[3].

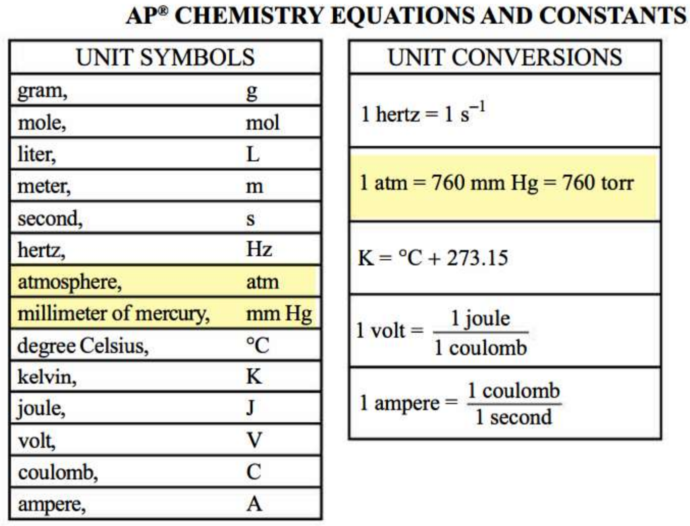
> Even though the density of gases is low, their molecular motion provides many collisions with their container walls. The microscopic molecular collisions of gas molecules provide lift for the largest of airplanes and the destructive effects of tornadoes and hurricanes.

SI Units of Pressure

The pressure is the force per given area.
The metric unit for force is the newton and the metric unit for area would be a square meter.
The metric pressure unit (N/m^2) is the pascal, Pa.

The nonmetric English pressure uses force of unit pounds and the area of a square inch, lb/in^2.
The conversion is 1 pascal = 0.000145 pounds per square inch. Because the pascal is such a small value kPa, kilopascals are typically used for metric pressure measurements.

However, neither Pa nor kPa are listed as a unit on the AP Chemistry equation sheet. Instead, the AP test uses mmHg (torr) and atmospheres (atm) as its preferred units of pressure. The AP Chemistry exam has only used kilopascals once. The question did not require any special knowledge of the unit other than knowing that kPa measured pressure.



AP® CHEMISTRY EQUATIONS AND CONSTANTS

UNIT SYMBOLS	
gram,	g
mole,	mol
liter,	L
meter,	m
second,	s
hertz,	Hz
atmosphere,	atm
millimeter of mercury,	mm Hg
degree Celsius,	°C
kelvin,	K
joule,	J
volt,	V
coulomb,	C
ampere,	A

UNIT CONVERSIONS
$1 \text{ hertz} = 1 \text{ s}^{-1}$
1 atm = 760 mm Hg = 760 torr
K = °C + 273.15
$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$
$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}}$

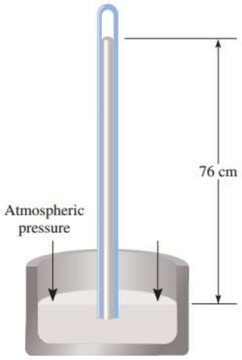
Now to explain the mmHg and atm.

Since we are at the bottom of an ocean of air, the pressure around us is a factor that must be taken into account.

> Standard pressure = 1 atm (the approximate pressure of air at sea level)
> Standard pressure = 760 mm Hg or 760 torr

The collisions of atmospheric air molecules on the surface of a pool of mercury at sea level will push mercury into an evacuated tube to a total height of 76 cm. Liquid mercury is used because mercury's density is thirteen times that of water. If water were used instead of mercury the barometers would have to be over 30 feet high. (Also, the water at the top of the column would boil.)

Watch how mercury barometers are set up in the unit video.
The video mad in 1970 uses large amounts of mercury. With concerns of toxicity of mercury vapor the videos would not be done today.



Present day barometers and manometers use microelectromechanical systems, MEMS, to measure pressure.

Standard pressure = 1 atm = 760 mm Hg = 101 kPa

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[3] The proof that molecules existed and the derivation of the Avogadro number of atoms was based on the statistical effects of the gas molecules bombardment of smoke particles by Albert Einstein and Jean Baptiste Perrin in 1909.

5.3 The Gas Laws are based on gases trapped in a container so gas volume and pressure can be measured.

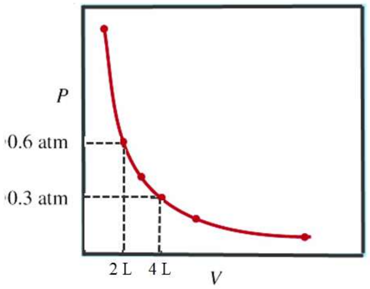
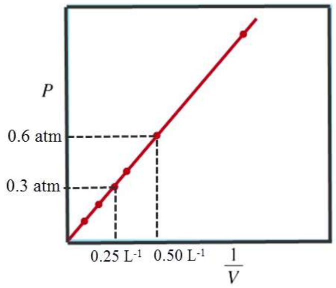
Some of the gas laws are named after the 17th and 18th century scientists who developed the laws. The names are convenient for identifying the laws but are not tested or part of the AP Chemistry curriculum.

The Pressure-Volume Relationship: Boyle's Law

Pressure and volume are inversely related: P × V = k

In a flexible container, as pressure increases ↑, volume decreases ↓.
Multiplying P and V results in a constant.

This relationship can be expressed by two graphs.

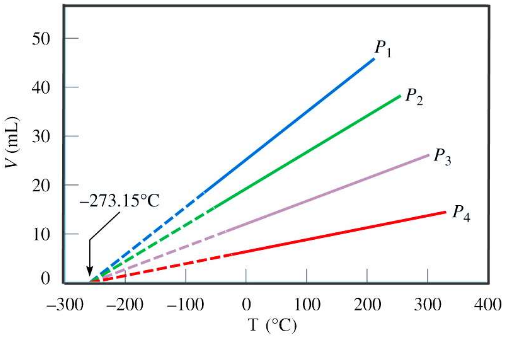
	
The P, V graph shows the inverse relationship	The P, 1/V is a straight line with a constant slope.
Understand both the curved P, V graph and the straight-line P, 1/V graph conceptually and mathematically.	

The equation used to solve changes in pressure and volume of a sample of gas at a constant temperature: $\mathbf{P_1 \times V_1 = P_2 \times V_2}$

The Temperature-Volume Relationship

IMPORTANT: Temperature must be measured in kelvins!

Volume of a fixed amount of gas in a flexible container (at constant P) is directly proportional to the absolute temperature of the gas. As temperature increases volume increases.

A gas in a flexible container is cooled. Each line is at a different initial pressure. The dotted lines are extrapolations since all gases eventually condense into liquids at low temperatures.[4] Any gas cooled with volume or pressure plotted against temperature will produce a straight line that extrapolates to the **lowest possible temperature, -273.15°C, absolute zero.** A similar graph can be produced keeping the volume constant while measuring pressure plotted on the y-axis.	

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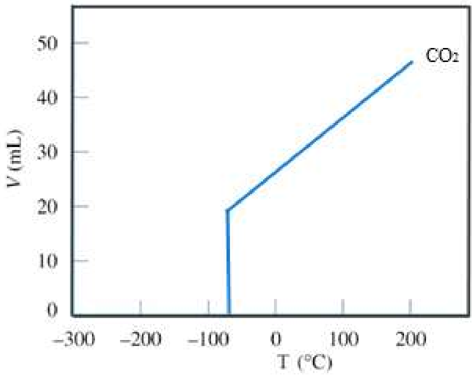
[4] Helium-3, a rare isotope of helium, has the lowest boiling point of any substance, 3 K or , -270.°C. So liquid helium-3 would be needed for cooling quantum computers.

The kelvin temperature scale starts at absolute zero and has divisions equal to ˚C.

The kelvin degree Celsius conversion equation is on the equation sheet, but it is used so often you should have it memorized, to the whole degree.	**K = 273 + ˚C** (memorize!)[5]

Temperature gas relationship equations[6] for all gases:

Temperature **must be in kelvins**! $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ $\frac{P_1}{T_1} = \frac{P_2}{T_2}$	These equations only work at temperatures where the gases are not close to condensing into liquids. As soon as temperatures drop to condensation temperatures, the volume and pressures will decrease dramatically as the gas condenses to a liquid or solid. In this example, carbon dioxide condenses into a solid at -78°C. The change in the gas law temperature curve in the graph at the right is due to condensation into a liquid and has been used in AP Chemistry questions.	

The gas pressure, volume, and temperature equations can be combined.

If volume and pressure units are the same in measurements 1 and 2, any unit of volume and pressure may be used. However, **the temperature must always be changed into kelvins**. **°C is never to be used in gas law problems!**	This equation is **on the equation sheet, but should be memorized anyway.** $\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$

Pressure, volume, and temperature problems are often used on the multiple-choice section of the test.
The problems commonly use simple numbers where conditions are changed in whole multiples.
Look for multiples in these problems.

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[5] Most textbooks use 273.15 which would be used if you were converting a degree Celsius temperature known to the hundredth of a degree Celsius. However, typically gas law problems have temperatures rounded to the whole degree Celsius. With any AP Chemistry problem 273 will do just fine.

[6]  Temperature will alter volume and pressure following the gas law ratios. However, changes in pressure and volume do not change temperature in the same way. As an analogy temperature is the dog and pressure or the volume are the tail. The dog wags the tail. The tail does not wag the dog.

The Volume-Amount Relationship: Avogadro's Law

Equal volumes at the same pressure and temperature contain the same number of molecules.

If you have P, V, and T of a gas you can find moles of the gas.

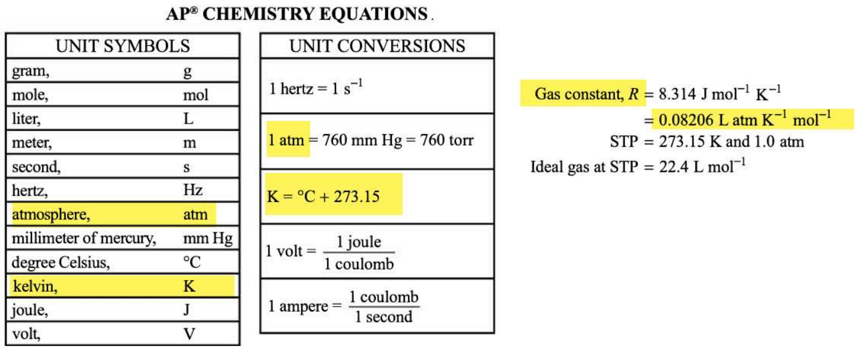
5.4 The Ideal Gas Equation[7]: **PV = nRT** even though it is on the equation sheet it should be memorized.

AP Equation Sheet

Use the ideal equation with the correct gas constant and units!

$R = 0.08206$ L atm K^{-1} mol^{-1}

***P* must be in atm**
***V* must be in L**
***T* must be in K**



AP® CHEMISTRY EQUATIONS

UNIT SYMBOLS	
gram,	g
mole,	mol
liter,	L
meter,	m
second,	s
hertz,	Hz
atmosphere,	atm
millimeter of mercury,	mm Hg
degree Celsius,	°C
kelvin,	K
joule,	J
volt,	V

UNIT CONVERSIONS
1 hertz = 1 s^{-1}
1 atm = 760 mm Hg = 760 torr
K = °C + 273.15
1 volt = $\frac{1 \text{ joule}}{1 \text{ coulomb}}$
1 ampere = $\frac{1 \text{ coulomb}}{1 \text{ second}}$

Gas constant, R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atm K^{-1} mol^{-1}
STP = 273.15 K and 1.0 atm
Ideal gas at STP = 22.4 L mol^{-1}

When using the gas constant $R = 0.08206$ L atm K^{-1} mol^{-1}

CAVEAT! Common errors:

The first value for R, 8.314 J/mol K, is used for energy calculations and should not be used for gas law problems.[8]

Many AP Chem exam gas law questions will have its data in units other than atm, L, and K. The test wants to test students to see if they must have the correct units when using the ideal gas law.

Standard Temperature and Pressure, STP = 1 atm and a chilly 273K, 0°C.

6.02×10^{23} molecules at 273 K will collide with the walls of a 22.4 liter container to produce 1 atm of pressure.

At STP 22.4 L of any gas contains 6.02×10^{23} molecules

At STP 22.4 L of any gas contains 1 mole of gas.

This is a fast and easy way of relating moles of gas and volume and vice versa.

You can use the easily remembered 22.4 L/mol to quickly estimate moles and volume of any gas at close to room conditions.

(If you have a good memory, you can remember that 24 L/mol is even closer because that value is for 25°C.)

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[7] At pressures and temperatures close to room temperature and pressure the law works very well. However, at low temps and high pressures there are deviations from law that depend on molecular size and intermolecular attractions of the gas molecules.

[8] 8.314 J/mol K, could be used for gas law problems with metric units of pascals as pressure and cubic meters for volume. This is because J/mol can also be expressed as m^3·Pa/K·mol.

There are several experimental (empirical) methods used to find the molecular mass (moles per mass) of an unknown gas that can be used as lab questions on the exam. The methods all involve weighing the gas (finding grams) and using its volume and pressure at a temperature to find the moles, n = PV/RT.
With mass and moles you can find molecular mass, grams per mol (g/mol).

(1) A tank of compressed gas is weighed. Some of the gas is collected, often by water displacement, where its P, V, and T are measured (*n*, moles of gas can be found from this data). The weight of the tank is measured a second time. The difference is the mass of the gas. With mass of the gas and *n* = PV/RT, you can find molar mass, g/mol.

Note: If the gas was collected by water displacement, bubbling through water, you must find the dry pressure of the gas by subtracting the water vapor pressure that is present when a gas is bubbled through water.

(2) Another method measures the mass of the container that has had the air pumped out of it[9]. The container is then filled with the gas and weighed again. The difference is the mass of the gas. The P, V, and T of the gas are determined and *n*, mol, is calculated using the gas law.

(3) A third experimental method is used for gases that are liquids at room temp. The liquid is put in a preweighed flask of known volume and then heated to vaporize the liquid. As the liquid vaporizes, the gas phase of the substance displaces the air in the flask. The P, and V, and T of the vapor are measured to find the *n*, moles of the vapor. The container is then cooled allowing the gas to condense back into a liquid. The flask is reweighed with the condensed gas. The difference between the empty flask and flask with the condensed gas is the mass of the liquid that was vaporized.

(4) Molar mass of a gas can be calculated if the density of the gas is known since density is the mass/volume ratio.

$$\text{molar mass of a gas} = \frac{\text{Density} \times RT}{\text{P}}$$

The molar mass from the gas density equation is worth memorizing so that you can solve molar mass/gas problems. Often mnemonics can help with equations. This one is commonly used with the gas molar mass equation: “All good moles put dirt over their pee (molar mass =dRT/P)”.

5.5 Gas Stoichiometry

Stoichiometry with gas volumes or pressures is easier than with masses since you can treat volumes or pressures of gases like moles. You can use the coefficients of the balanced reaction directly with gas volumes or pressures.

If you have a stoichiometry question with only gas volumes or pressures, there is no need to convert to moles.

You can use the gas volumes or pressures just like moles. The volumes-pressures in the change row an ICE chart will match the stoichiometric ratios of the balanced reactions.

Example:

$3\ H_2(g)$	+	$N_2(g)$	→	$2\ NH_3(g)$
3 moles		1 mole		2 moles
3 volumes		1 volume		2 volumes
3 atm		1 atm		2 atm

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[9] The container must have a vacuum for the first measurement. Otherwise, the difference in mass will just be a comparison of the mass of air in the container and the mass of gas that was put in the container.

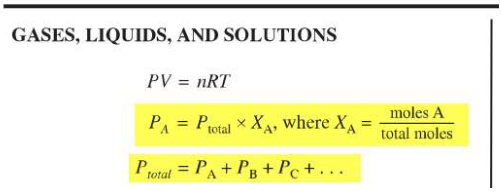
5.6 Dalton's Law of **Partial Pressures**

With a mixture of gases, there will be a total pressure, P_{total}, and each molar component of the gas mixture adds to this total pressure.

The Partial Pressure problems use the equation: $P_{total} = P_A + P_B + P_C + \ldots$

The mole fraction[10] of each gas, *X*, is proportional to the partial pressure of each gas.

The mole fraction is the moles of the component gas divided by the total moles of gas.



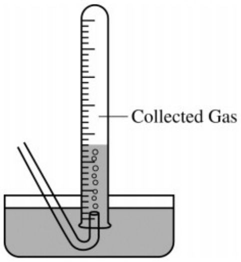
GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{total} = P_A + P_B + P_C + \ldots$$

Some lab experiments require you to collect insoluble gases by bubbling the gas through water. When collected this way, water vapor will be responsible for some of the pressure in the collecting vessel. To accurately determine the pressure of the gas you are collecting, the dry pressure of the gas, you must subtract the *water vapor pressure*[11] from the total pressure in the container. This equation, based on the Law of Partial Pressures, will allow you to determine the dry pressure of a gas collected by water displacement.



$$P_{dry\ gas} = P_{total} - P_{water\ vapor}$$

While collecting gases by water displacement is a common lab practice, some gases such as ammonia, hydrogen chloride, sulfur dioxide, and carbon dioxide are soluble in water and cannot be collected using water displacement.

5.7 The Kinetic Molecular Theory of Gases, KMT

The equations in section 5.7 are not part of the AP Chemistry curriculum. The equations take into account molecular factors that cause deviations from the ideal gas.

You will not have to perform calculations using the van der Walls equation.
While you won't have to use the van der Walls equation, you will be asked to explain what causes the deviations from the ideal gas law.

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[10] The mole fraction is always represented as a decimal value.

[11] Water vapor pressure will depend on the temperature of the water. Water vapor pressure-temperature tables are in most chemistry textbooks.

Ideal gas law equations are based on the Kinetic Molecular Theory of gases:

The four assumptions of the KMT:

(1) Ideal Gas molecules molecular volume is negligible which may not be true when pressures are high.

For real gases at 1 atm, 99.9% of the volume of a gas is empty space. Only 0.1% is molecular volume. At higher pressures caused by increased numbers of molecules in the container the volume of molecules can become higher than 0.1%. High pressures are not ideal for gases.

(2) Ideal Gas molecules are in constant motion having frequent, perfectly elastic collisions, which produce the pressure and volume of the gas.

The molecules of 1 liter of nitrogen at room temperature and pressure have an average speed of 1,200 miles per hour with 10 billion collisions a second. Extremely low temperatures have slower molecular motions so that the attractions between the molecules will become significant causing deviations in KMT predictions. Low temps are not ideal for gases.

(3) Ideal Gas molecules do not attract or repel one another.

Because gases are mostly empty space at room pressure, intermolecular attractions and repulsions do not significantly alter the random movement of molecules. When gases near their condensation points because of high pressure or low temperatures, the KMT predictions will no longer be valid because the motion of the molecules is affected by the attractions between the molecules.

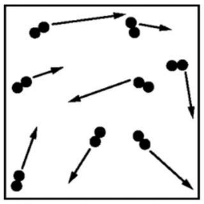
(4) The average kinetic energy of molecules is proportional to the temperature in kelvins.

Both the mass of the object, m, and the square of its speed, v^2, determine a moving object's kinetic energy. This will not affect the ideal gas law. However, you must know the relationship of the kinetic energy, molecular speed, and molecular mass of gases.

Distribution of Molecular Speeds

At any given instant the speed of individual gas molecules varies over a wide range. The distribution curve of these speeds is shown in the Maxwell-Boltzmann distribution curve.

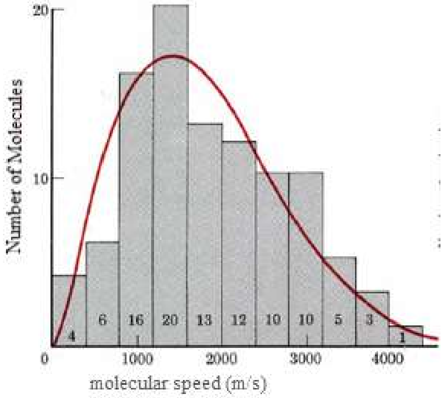
The diagram at the right is a particulate diagram that was used on an AP Chemistry exam. The vector arrows represent the speeds of molecules. The longer the arrow, the faster the speed.



Even though the macroscopic temperature is a steady value, on the microscopic scale, the molecules have a wide range of speeds which can be seen on the Maxwell-Boltzmann curve.

The Maxwell-Boltzmann speed distribution curve is a way of representing the speeds of gas molecules. The curve in the Maxwell-Boltzmann graph plots the numbers of atoms (height of curve) vs. speed or KE on the x-axis.

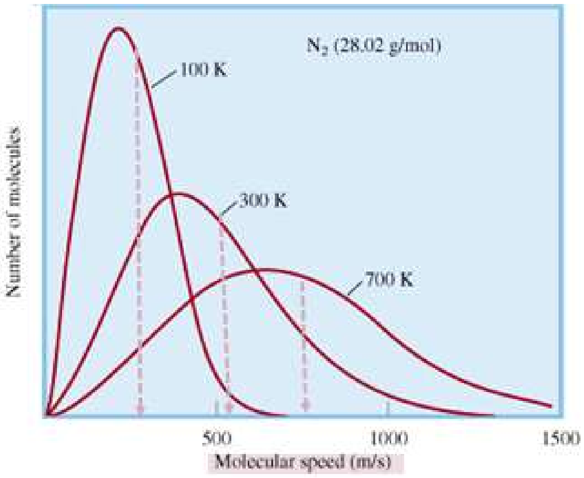
The **peak of the curve is the average** speed (KE) of the molecules at a given temperature.
The x-axis position of the peak indicates temperature of the gas (avg KE).
The y-axis height of the peak represents the number of molecules.
AP Chem exams have Maxwell-Boltzmann curve questions. You may even have to sketch one.



Changes in the Maxwell Boltzmann curve caused by Temperature

The flatter the curve, the higher the temperature of the gas.

High temperatures and low molecular weight will produce flatter graphs.

Temperature and the Maxwell-Boltzmann: **Nitrogen's molecular speeds at different temperatures**:  **As the temperature increases the "average" speed moves to the right, and the peak of the curve becomes lower because of a greater "spread" of speeds.**	Note the axes of this Maxwell-Boltzmann distribution curve. y axis ↑is the # of molecules x axis → is the energy or speed of the molecules The total number of molecules, the area under each curve, remains constant as temp changes. At 100 K (leftmost curve), the sample of nitrogen has a root mean square[12] molecular speed, μ_{rms}, of about 300 m/s (dotted line points to molecular speed). But not that at higher temperatures the spread of molecular speeds that increases. This flattens the curve and the average speed that the dotted line points to increases. at 100 K, μ_{rms} = 300 m/s at 300 K μ_{rms} = 520 m/s at 700 K μ_{rms} = 790 m/s

Common AP FRQ question:

Given a temperature's curve you should be able to sketch in a second temperature's Max-B curve.

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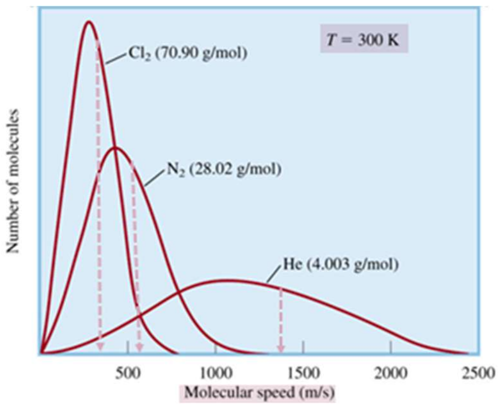
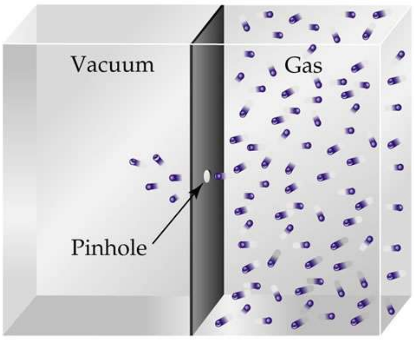
[12] The root means square is a special average. It is determined by taking each gas particle's velocity, squaring the velocities, averaging the squares of the velocities, and then taking the square root of the average.

Changes in the Maxwell Boltzmann curve caused by molecular mass

Different gases and the Maxwell-Boltzmann: The three curves represent the same amount gas for three **different gases at the same temperature**.  	All three gases have the same average kinetic energy, **300 K.** But the average speeds, μ_{rms}, of these different gases are very different. μ_{rms} He 4.0 g/mol = 1400 m/s μ_{rms} N_2 28 g/mol = 520 m/s μ_{rms} Cl_2 71 g/mol = 320 m/s The heaviest gas, Cl_2, is the slowest gas with the most compact and highest peak curve. Helium is the fastest gas with the most spread out curves whose peak is lowest but furthest to the right.

In a nutshell	**Higher temperatures = faster molecules,** Maxwell-Boltzmann **peak shifts → and is lower**. **Lighter molecules = faster molecules, Maxwell**-Boltzmann **peak shifts → and is lower**.

You will not need to calculate the root-mean-square speed.

 	**Effusion:** Escape of a gas through a pinhole to a vacuum or area of low pressure. At a given temperature, the heavier molecules move more slowly hitting the walls of the container less frequently. Therefore, a gas with a greater molecular mass will "escape" less often through the pinhole than a lower molecular mass gas. Bottom line: **Molecules with a greater molecular mass effuse more slowly than lighter molecules.**

5.8 Deviation from Ideal Behavior

Deviations for the ideal gas law are based on deviations from the ideal gas assumptions.

(1) The assumption that molecular volume in a gas is negligible
(2) The assumption that gas molecules do not attract one another.

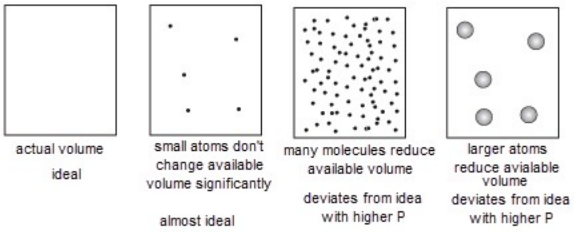
The van der Waals equation **is not part of the AP curriculum.**
While you will not use the van der Waals equation, you must be able to identify and explain two causes of deviations from the ideal gas.

Deviation from assumption 1:

Molecular volume is significant and **causes higher pressures** than predicted by the ideal gas law.
At high pressures (large number of molecules in a small space), **the volume of the molecules becomes a significant part of the total volume of the container**. This produces greater pressures than predicted by the ideal gas law. This is because the molecular volume reduces the empty space for the molecules to bounce around in.

Why do gases have **higher pressures than predicted** by the ideal gas law?

Answer: **Molecular volume is not negligible**
Explanation: The molecular volume takes up some of the empty space in the container decreasing the free volume resulting in more molecular collisions against the walls of the container.



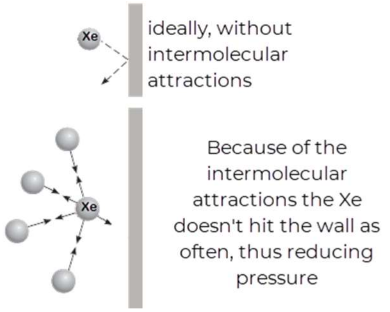
Deviation from assumption 2:

Intermolecular attractions produce lower pressures than predicted by the ideal gas law.

Intermolecular attractions cause gases to deviate from their straight-line motion decreasing the number of collisions with the sides of the container. This causes lower pressures than predicted

Why do gases have **lower pressures than predicted** by the ideal gas law?

Explanation: Gas molecules do not have independent motion because they attract one another resulting in fewer collisions with the container walls, thus lowering the pressure.



Under what conditions are gases most like ideal gases and why?

Answer: Gases are most **ideal at low pressures and high temperatures.**

Explanation: At low pressures, molecular volume is insignificant, so the volume of the container equals the volume allowed for molecular collisions.
At elevated temperatures, kinetic energies are so high, that intermolecular attractions have little effect on molecular motion.

Which gases are most like ideal gases and why?

Answer: Gases with **small molecular volume and low intermolecular attractions** will be ideal.

Energy (work) and gas volume and pressure are NOT part of the AP Chemistry curriculum.