Chapter 8: Gases and Gas Laws.

The first substances to be produced and studied in high purity were gases. Gases are more difficult to handle and manipulate than solids and liquids, since any minor mistakes generally results in the gas escaping to the atmosphere. However, the ability to produce gases in very high purity made the additional difficulty acceptable. The most common way of producing a gas was by some sort of chemical reaction, and the gas was collected by liquid displacement (either water or mercury). Figure 8.1 shows the general process of collecting gas by liquid displacement.

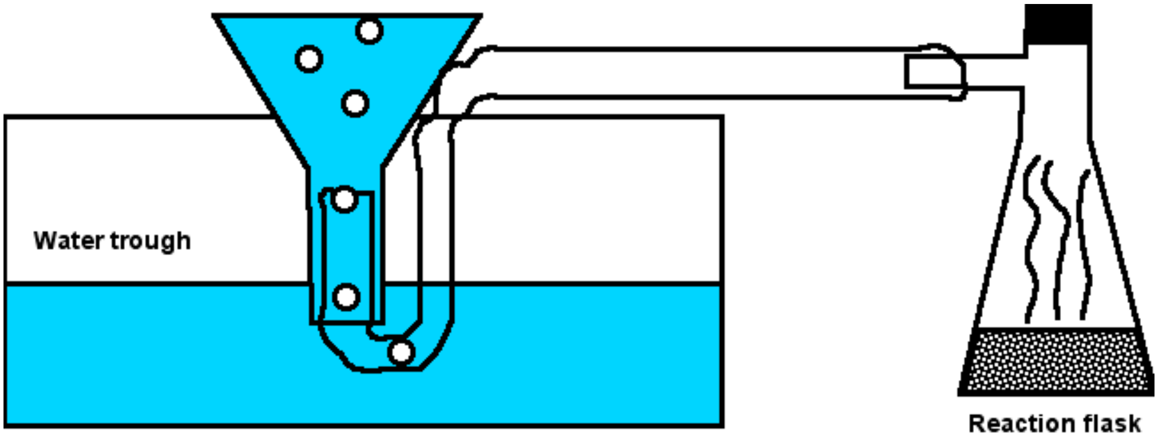

Figure 8.1. Method of displacement for collecting gases.

A water-filled container is inverted and placed into a water trough. A rubber hose is placed in the mouth of the container, with the other end attached to a reaction flask. The chemical reaction produces gas, which flows through the tube and displaces water from the container. By selecting the proper reactant masses, sufficient gas to fill 3 – 6 containers can be produced. Typically, the first container collected isn't saved, since it contains residual air from the reaction flask.

Using this general method, scientists produced and characterized hydrogen, oxygen, nitrogen, carbon dioxide, sulfur dioxide, chlorine, and several other gases. Once they obtained reasonably pure gases, systematic experimentation led to other discoveries.

Generally, gases have properties substantially different than solids or liquids. Gases do not have fixed volumes; instead their volume depends directly upon pressure and temperature. Gases don't have a fixed shape, but are said to "take the shape of their container". Gases do have a fixed mass, although measuring the mass may be difficult sometimes.

Boyle's law.

In 1662, English natural philosopher Robert Boyle (1627 – 1691) published what is now called Boyle's law – the product of a gas' pressure and volume is constant:

$$P \times V = k$$

Gases therefore show an inverse relationship between pressure and volume; as pressure increases, volume decreases and vise versa. For Boyle's law to be obeyed, the temperature has to remain constant.

Gas pressure are measured using a variety of units. Commonly encountered units are given in Table 8.1.

14.7 pounds per square inch (psi)	= 1 atmosphere (atm)
	= 760 mmHg
	= 760 Torr
	= 29.92 inches Mercury
	= 33.9 Feet of water
	= 101,325 Pascal (Pa)

Table 8.1. Pressure values and equivalents.

The weight of the atmosphere at sea level equals 14.7 pounds per square inch, and this is defined as 1 standard atmosphere of pressure. The average man has about 2945 in^2 total body surface area, while the average woman has about 2480 in^2. The total pressure exerted by the atmosphere is 21.6 tons for men and 18.2 tons for women.

One common method of measuring air pressure is by determining the height of a column of liquid supported by air pressure. This method was first used by Italian physicist and mathematician, Evangelista Torricelli (1608 – 1647). Torricelli was a colleague of Galileo, and both scientists were trying to solve an important practical problem. Pump makers were unable to build suction-type water pumps (Figure 8.2) that could raise water higher than about 10 meters. Galileo believed that the pumps were poorly built, but Torricelli had a different idea.

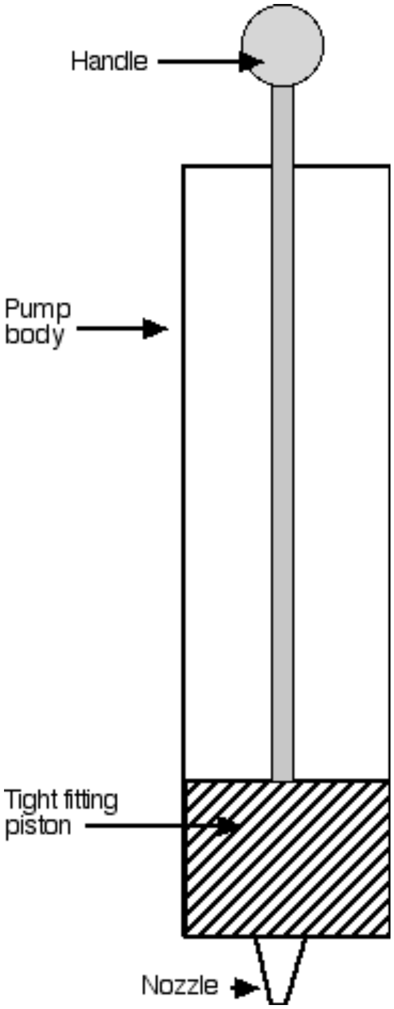

Figure 8.2. Simple suction pump. Pulling the handle out raises the piston and draws water into the pump body. Pushing the handle in lowers the piston and forces water out of the pump.

Torricelli experimented with tubes filled with water. He inverted these tubes over a container of water, discovering that a very long column of water could be maintained above the surface of water in the container. Torricelli realized that the liquid column would be inconveniently tall if he continued using water, and switched to mercury. When he used mercury in his tubes, the mercury in the tube fell a small distance and stopped (Figure 8.3).

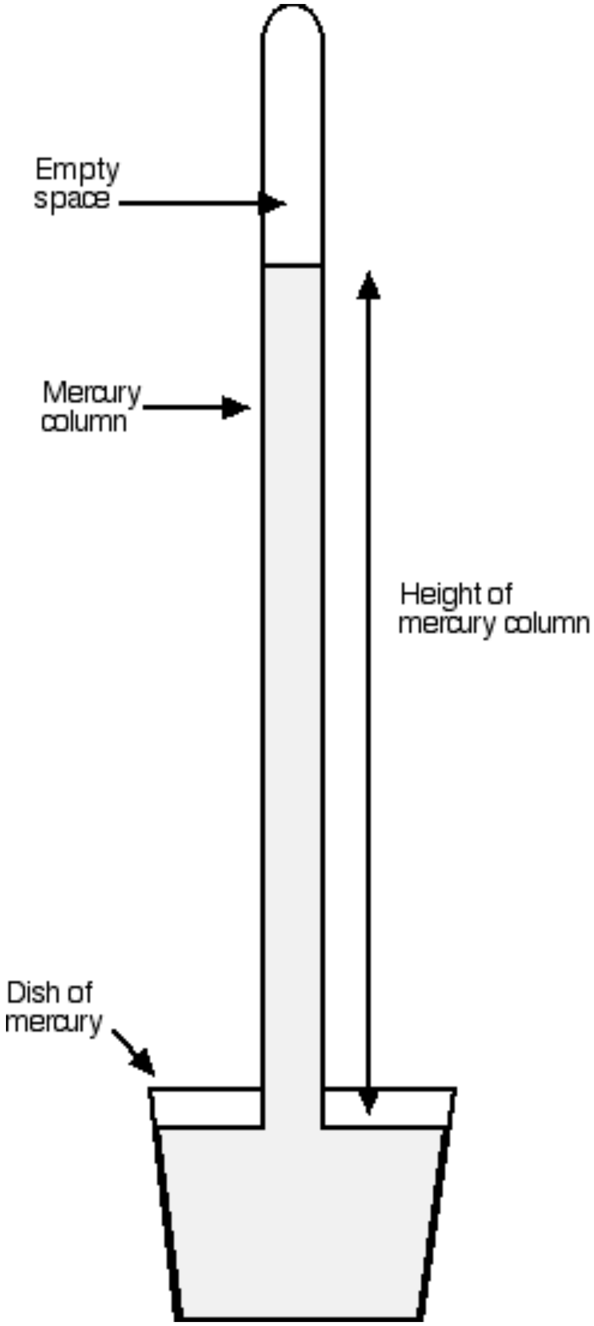

Figure 8.3. Torricelli's barometer.

Torricelli realized that the empty space in the tube was truly empty – a vacuum, now called a ***Torricellian vacuum*** in his honor. Torricelli calculated the weight of the mercury column, and the area of the column in contact with the surface of the mercury dish. The pressure exerted by the column of mercury was 14.7 psi. If the mercury column was exerting a pressure of 14.7 psi downward, then an exactly equal force must be exerted upward on the mercury column. If the forces weren't equal, then either the empty space in the tube would fill with mercury, or the mercury would flow out of the tube. This balancing force must come from the air: air presses down on the mercury in the dish, the force is transferred to the mercury at the bottom of the column, and is equal to the weight of mercury in the tube.

The unit "Torr" is named in Torricelli's honor, and is equivalent to 1 mmHg.

The metric unit of pressure uses metric units of force (Newtons, N) and area (square meters, m^2). 1 N/m^2 equals 1 Pascal (Pa), named for French physicist Blaise Pascal (1623 – 1662), who conducted pioneering experiments in hydraulics and hydrostatics.

Amontons' law.

In the late 1600's, French physicist Guillaume Amontons (1663 – 1705) investigated the relationship between temperature and pressure. Although his work was not very quantitative, it did point the way towards the idea of absolute zero. Amontons found that the pressure of a gas divided by temperature was equal to a constant. When the gas pressure was zero (the lowest pressure you can achieve), the equivalent temperature would be zero. Amontons' law commonly has the form:

$$\frac{P}{T} = k$$

In all gas calculations, we use Kelvin temperature ($^oC + 273 = K$) to avoid problems with negative values for Celsius or Fahrenheit temperatures.

Charles' law.

In 1783, French balloonist, inventor, and scientist Jacques Alexandre César Charles (1746 – 1832) used a hydrogen-filled balloon to ascend to an altitude of 3000 feet. In 1787, he noted in a general way that changes in pressure and temperature affected the volume of a gas.

As a balloonist, Charles was very interested in the properties of gases. However, Charles didn't clearly recognize anything approaching a natural law, nor did he produce any equation summarizing his observations. He did not provide any written description of his experiments, nor did he present any experimental data indicating he systematically studied the effect of temperature on pressure or volume.

He did communicate his general observations to French physicist and chemist Joseph Louis Gay-Lussac (1778 – 1850). Gay-Lussac systematically studied the effects of temperature on volume, maintaining a constant pressure during his experiments. He also investigated the temperature – volume relationship with several different gases. In his 1802 paper describing his experimental results, he acknowledged Charles' preliminary work describing the expansion of gases over a temperature range of 0 to 80 °C. Gay-Lussac's work became known as "Charles' Law":

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

If the temperature is measured in Kelvin, then a change of 1 K results in a volume change equal to 1/273 of the original volume. Imagine we have 1.00000 L of gas at 298 K (25 °C). We raise the temperature to 299 K. The volume increases to 1.003 66 L (1/273 = 0.003 66). To double the volume of gas, the temperature must rise to 596 K (323 °C). This relationship between volume change and temperature complimented Amontons' law, but Gay-Lussacs experiments were much more quantitative than were Amontons'.

Frequently, Amontons' and Charles' laws are combined together to produce the combined gas law:

$$\frac{P \times V}{T} = k$$

We often use the combined gas law to calculate equivalent values at standard temperature and pressure (STP). Standard pressure is 1.00 atmosphere, and standard temperature is 0 °C (273 K). To make this conversion we recognize that any three values for pressure, volume and temperature must give us the same value for the constant *k*. We can then write the equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \left(\text{or } \frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}\right)$$

In the alternate version, *i* and *f* indicate initial and final sets of P,V, and T.

Kinetic molecular theory.

The gas laws of Boyle, Charles, Amontons, and Gay-Lussac eventually led to the development of the kinetic molecular theory. Although initially applied just to gases, the theory was eventually extended to solids and liquids. There are several postulates to the theory:

1. Gases are composed of tiny particles (atom or molecules) in constant motion.

2. The distance between individual particles is relatively large compared to the size of the gas particles.

3. There are virtually no interactions between the individual gas particles, other than collisions. During these collisions, no chemical reactions occur – just the exchange of kinetic energy.

4. Temperature is directly related to kinetic energy and therefore velocity. The average kinetic energy is equal to 3kT/2, where k is the Boltzmann constant (1.38×10^{-23} J/K).

Avogadro's law.

In 1811 an obscure Italian physicist, Lorenzo Romano Amedeo Carlo Avogadro (1776 – 1856) wrote *"Essay on Determining the Relative Masses of the Elementary Molecules of Bodies"* in which he proposed that for constant temperature and pressure, equal volumes of two different gases contained identical numbers of particles. If we set the number of particles equal to *n*, then Avogadro's law becomes:

$$\frac{V}{n} = k$$

By this time, chemists had made numerous measurements of the compositions of gases such as nitric oxide (NO), and accepted the idea that elements combine in fixed proportions by weight and by volume, with these combinations giving the same chemical formula. However, there were difficulties with this idea. Some chemists used the terms "atom", "molecule", "atomic weight", "molecular weight", and "equivalent weight" interchangeably. This led to significant confusion in their calculations and in their understanding of exactly what was happening in chemical reactions. Consider the reaction between nitrogen and oxygen to make nitric oxide:

$$\begin{array}{ccccc} \mathrm{N} & + & \mathrm{O} & \rightarrow & \mathrm{NO} \\ 14.00\ \mathrm{g} & + & 16.00\ \mathrm{g} & \rightarrow & 30.00\ \mathrm{g} \\ 1.00\ \mathrm{L} & + & 1.00\ \mathrm{L} & \rightarrow & 2.00\ \mathrm{L} \end{array}$$

When 14.00 grams of nitrogen combines with 16.00 grams of oxygen, 30.00 grams of nitric oxide forms. Therefore, the simplest formula for nitric oxide is NO, containing one atom each of nitrogen and oxygen. If equal volumes of gases contain equal number of atoms, then 1.00 liter of nitrogen should combine with 1.00 liter of oxygen to produce 1.00 liter of nitric oxide. However, this isn't what happens – instead 2.00 liters of nitric oxide are produced!

This same problem happens when hydrogen combines with chlorine to make hydrogen chloride (H + Cl → HCl), or when hydrogen combines with oxygen to produce water (H + O → HO)(!).

The underlying problem was the belief that gases were simple individual atoms (although some problems were traceable to misunderstandings of the chemical formula of compounds, such as HO for water). Avogadro didn't believe that all gases were necessarily single atoms. If nitrogen and oxygen were N_2 and O_2, then:

$$\begin{array}{ccccc} N_2 & + & O_2 & \rightarrow & 2NO \\ 14.00\text{ g} & + & 16.00\text{ g} & \rightarrow & 30.00\text{ g} \\ 1.00\text{ L} & + & 1.00\text{ L} & \rightarrow & 2.00\text{ L} \\ n\text{ particles} & + & n\text{ particles} & \rightarrow & 2n\text{ particles} \end{array}$$

The ratio of nitrogen/oxygen is still 14.00/16.00 (7/8), so the mass composition values are consistent, and now the combining volumes make sense and are also consistent with the mass values.

Avogadro's controversial idea wasn't generally accepted until after 1860.

Ideal Gas Law.

Combining all of the other gas laws together produces the Ideal Gas Law:

$$PV = nRT$$

P, V, and *T* are pressure, volume, and temperature, *n* is the number of particles, and *R* is the gas constant. While *R* can have a variety of values depending on units, the most commonly used value is 0.0821 L-atm/mol-K. Since all other gas laws were combined to produce the Ideal Gas Law, it shouldn't surprise you that all other gas laws can be obtained from it.

If I have a fixed number of moles of gas (if my gas is in a closed container for example), then *n* and *R* are constant, and the (mathematical) product of two constants is a constant. Then the Ideal Gas Law becomes:

$$PV = kT$$

$$\frac{PV}{T} = k$$

which is the combined gas law.

If we have fixed *n* and *T*, then *nrT* is constant and we get Boyle's law. If *n* and *P* are fixed, then our equation becomes Charles' law, while if *n* and *V* are fixed, we get Amontons' law. If we fix *V* and *P*, then we get Avogadro's law. The only gas law you need is the Ideal Gas Law, and a little bit of algebra.

Dalton's law of partial pressures.

One of the most interesting characters in chemical history is the Quaker chemist, physicist, and meteorologist John Dalton (1766 – 1844). Dalton is known not only for his research into atomic theory, but also his study of colorblindness, once called *Daltonism*: Dalton was colorblind. In developing his atomic theory, Dalton relied heavily on years of meteorology measurements to help guide his understanding of the atmosphere. To aid his analysis, Dalton drew simple sketches (Figure 8.4) helping him visualize how atmospheric gases mixed.

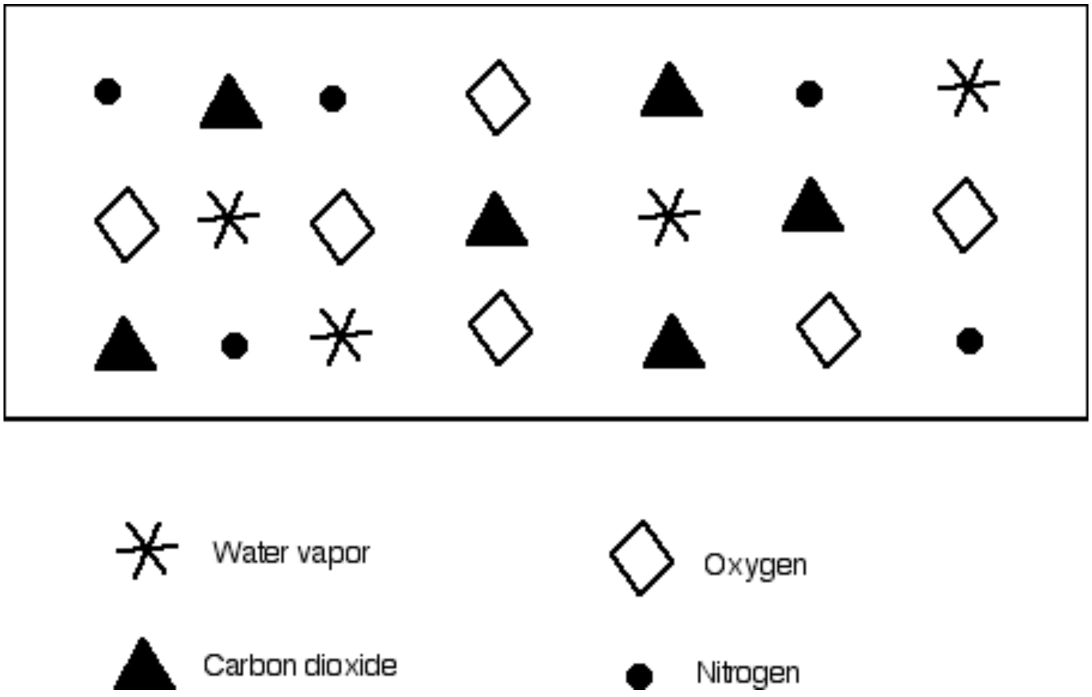

Figure 8.4. Dalton's representation of gases in the atmosphere.

In 1801, Dalton stated his Law of Partial Pressure: the total pressure of a gas mixture is the sum of the individual pressures exerted by each gas in the mixture. This law can be easily understood by reference to Figure 8.4. The total pressure is due to the total number of individual atoms in the gas (I am using the term "atom" as Dalton understood it – an atom was the smallest particle of a particular substance. Some of Dalton's atoms were actually molecules!). The partial pressure of water vapor is proportional to the relative amount of water vapor in the gas mixture; the partial pressure of oxygen is proportional to the relative amount of oxygen in the mixture, etc. In our sketch we have 21 total particles of gas, and 4 particles of water vapor. The partial pressure of water vapor is proportional to 4/21 of the total gas pressure. Similarly, the partial pressure of oxygen is 6/21, the partial pressure of carbon dioxide is 6/21, and the partial pressure of nitrogen is 5/21 of the total pressure. Mathematically, Dalton's Law of Partial Pressure is:

$$P_{Total} = p_{oxygen} + p_{nitrogen} + p_{water} \cdots$$

where p_{oxygen}, $p_{nitrogen}$, p_{water}, and so on are the partial pressures of each gas.

Our atmosphere is composed of many gases mixed together, but the three most important are nitrogen (78% of total), oxygen (21% of total), and argon (1% of total). At 760 Torr pressure, nitrogen exerts 593 Torr, oxygen exerts 160 Torr, and argon exerts 7 Torr.

Vapor pressure.

Imagine we have a closed container: an ordinary bottle of water. Above the water is a small airspace (Figure 8.5).

In the liquid water, water molecules are constantly moving and colliding with each other. Since any given water molecule is surrounded by many others, an individual water molecule doesn't travel very far through the water.

At the surface, the situation is different, because there aren't any water molecules above the surface. Just by chance, some water molecules will travel "up" and escape from the liquid water. When this happens, the water molecule is now in the gas phase, and is described as water vapor. As a gas, water molecules are still constantly moving, and colliding with the walls of the container and other molecules. Sooner or later, a water molecule collides with the surface of the liquid water and is re-absorbed into the liquid. When the rate of water molecules escaping into the air space is equal to the rate of water molecules returning to the liquid, we have *equilibrium*. At equilibrium, some fraction of the total air pressure in the bottle is due to water vapor; water vapor has a partial pressure. This partial pressure at equilibrium is called the ***vapor pressure***.

We are most often interested in the vapor pressure due to water vapor, although other liquids and solids easily convert to gas and therefore also have vapor pressures. One way we express water vapor pressure is by ***relative humidity***. The relative humidity is the ratio of the actual vapor pressure of water in the atmosphere to the saturation vapor pressure of water (the maximum amount of water vapor pressure possible under the existing conditions of pressure and temperature):

$$\% \text{ relative humidity} = \frac{P_{vapor,actual}}{P_{vapor,saturation}}$$

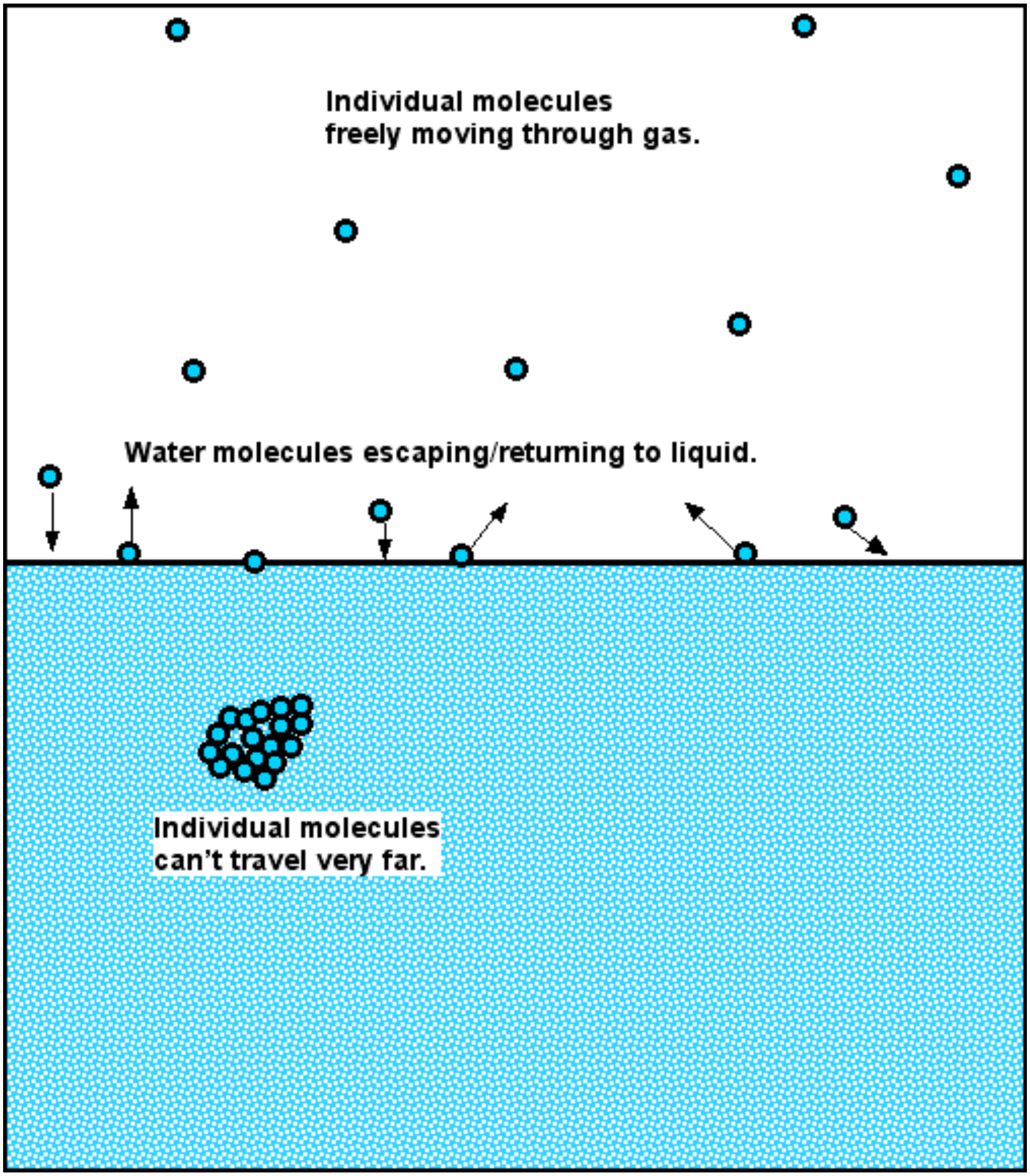

Figure 8.5. Vapor pressure.

The saturation vapor pressure is a function of total pressure and temperature. If we hold pressure constant, then saturation vapor pressure depends only on temperature. For water, Figure 8.6 shows the relationship between temperature and saturation vapor pressure.

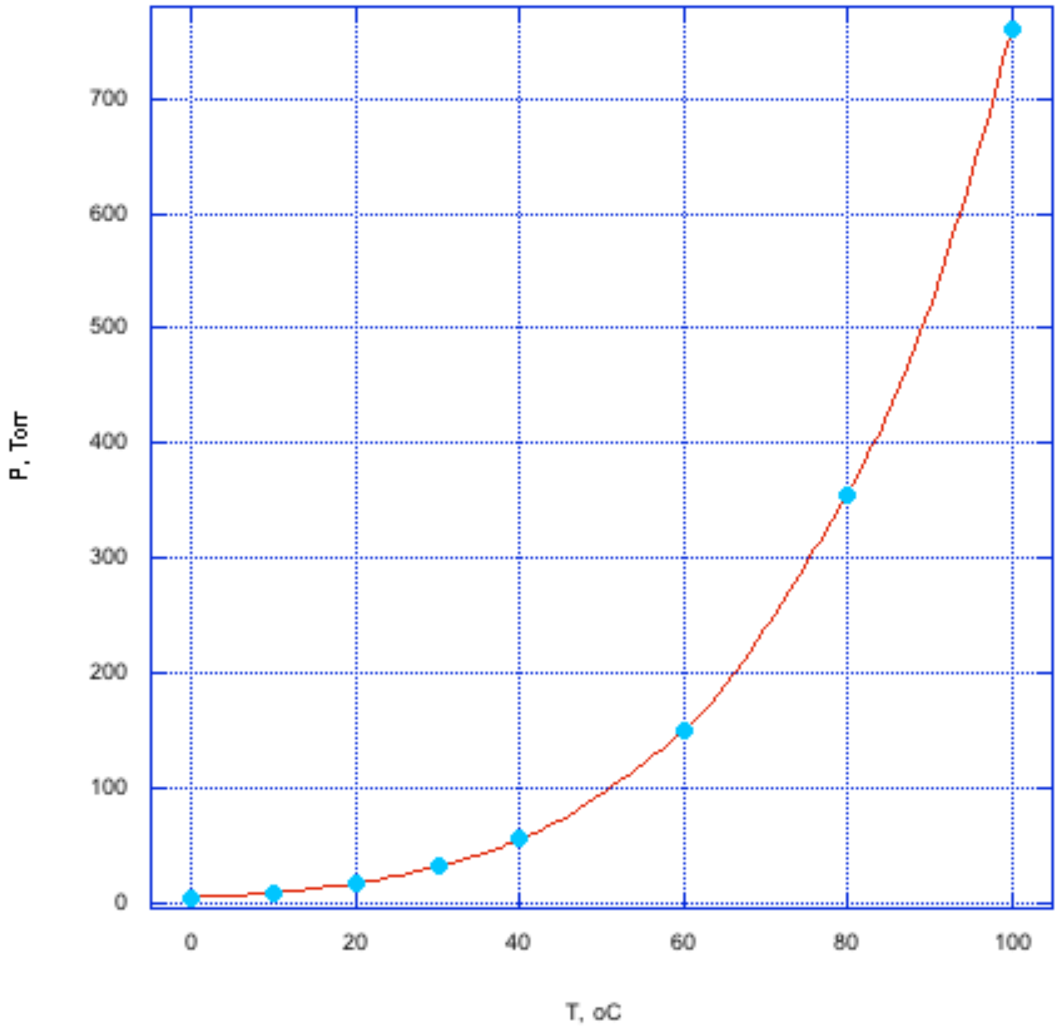

Figure 8.6. Saturation vapor pressure versus temperature.

When the temperature reaches 100 °C, the saturation vapor pressure equals the local atmospheric pressure and the water ***boils***. The ***boiling point*** is the temperature necessary for the saturation vapor pressure to equal the local atmospheric pressure. If I reduce the pressure inside the container, the water boils at a lower temperature. For example, reducing the pressure to 100 Torr reduces the boiling point to 50 °C.

Some of you may have seen "high altitude" recipes on cake mixes. These recipes specify higher temperatures and longer baking times. At high altitudes, local pressure is lower, water boils at a lower temperature, and you have to cook for a longer time at a higher temperature. We can reverse this situation using pressure cookers; tightly closed pots that allow pressure to build up above local atmospheric pressure. At higher pressure, the boiling point increases and more heat is available. Therefore, cooking time is shorter.

Weathermen will often say "it's more humid in the summer, because warm air holds more moisture than cold air".

NONSENSE!! The air doesn't "hold" water. Unless there is a specific chemical reaction between water and a gas, water molecules and gas molecules ignore each other's presence. At a given temperature, the vapor pressure has a fixed value, regardless of the gas present. At 20 ^{o}C, water's vapor pressure is 17.5 Torr. It doesn't matter if the other gas present is air, or nitrogen, or helium, or methane – the vapor pressure is 17.5 Torr. In fact, if I use a vacuum pump to remove the air, when the pressure drops to 17.5 Torr at 20 ^{o}C, the water boils. In this case, the only gas present will be water vapor and the total pressure is the saturation vapor pressure. There is no air to "hold" the water vapor – there is only water vapor.

It is more humid in the summer, because everything – including standing bodies of water, is warmer. Warmer water has a higher vapor pressure. In winter, everything is colder, and cold water has a lower vapor pressure. Air doesn't have a thing to do with it, except to act as a transport medium – the water vapor has to be someplace and it's in the air.

Weathermen are trained as scientists and should know better.

Chapter 8 Homework:

Vocabulary. The following terms are defined and explained in the text. Make sure that you are familiar with the meanings of the terms as used in chemistry. Understand that you may have been given incomplete or mistaken meanings for these terms in earlier courses. The meanings given in the text are correct and proper.

Boyle's Law
Kinetic Molecular Theory
Vapor pressure
Dalton's Law of Partial Pressure
Amontons' Law
Avogadro's Law
Relative humidity
Charles' Law
Ideal Gas Law
Boiling point

1. Boyle's law: $P_1V_1 = P_2V_2$

   Fill in the missing values in the table below.

V_1	P_1	V_2	P_2
250.0 mL	1.00 atm	350.0 mL	
	158 Torr	27.3 mL	24 Torr
1.50 L		0.799 L	7.5 PSI
3600 cm^3	550 mmHg		440 mmHg
	15.0 atm	25.5 mL	0.75 atm
75.0 mL		1.0 mL	760 Torr
1.05 L	880 Torr		200 Torr
19.25 mL	14.7 PSI	35.0 mL	

2. Amontons' Law. Fill in the missing values in the table below.

Initial Pressure	Initial Temp	Final Pressure	Final Temp.
760 mmHg	35 ^{o}C	1500 mmHg	
	298 K	14.7 PSI	273 K
350 Torr	1300 K		50 K
144 atm		25 atm	52 ^{o}C
745 Torr	473 K	780 mmHg	
	37 ^{o}C	760 mmHg	25 ^{o}C
3.55 atm	298 K		100 ^{o}C
14.7 PSI		760 Torr	0 ^{o}C

3. Charles' Law. Fill in the missing values in the table below.

Initial Volume	Final Volume	Initial Temp.	Final Temp.
269 mL	760 mL	298 K	
1.59 L	2500 mL		39 ^{o}C
66 cm^3		75 ^{o}C	18 ^{o}C
	35.57 mL	176 K	352 K
0.789 L	270 mL	1555 K	
770 mL	238 mL		350 K
155 mL		289 K	982 K
	88 mL	174 K	29 ^{o}C

4. Ideal gas law. Fill in the missing values in the table below. Use 0.0821 L-atm/mol-K for R (gas constant).

Pressure	Volume	Moles (n)	Temp
1.00 atm	75.0 L	1.00	
544 Torr	85.0 mL		26 ^oC
13.9 PSI		5.33	218 K
	36.0 cm^3	0.59	273 K
0.788 atm	0.788 L	0.788	
615 mmHg	159 L		988 K
14.7 PSI		2.35	273 K
	89.9 mL	56.7	-40 ^oC

5. A gas mixture contains 62% hydrogen, 28% nitrogen, 5% water vapor, and 5 % argon. If the total pressure is 1670 Torr, what is the partial pressure of each gas component?

Answers.

1. Boyle's law. Fill in the missing values in the table below.

Initial Volume	Initial Pressure	Final Volume	Final Pressure
250.0 mL	1.00 atm	350.0 mL	0.714 atm
4.15 mL	158 Torr	27.3 mL	24 Torr
1.50 L	4.0 PSI	799 mL	7.5 PSI
3600 cm^3	550 mmHg	4500	440 mmHg
1.275 mL	15.0 atm	25.5 mL	0.75 atm
75.0 mL	10.13 Torr	1.0 mL	760 Torr
1.05 L	880 Torr	4.62 L	200 Torr
19.25 mL	14.7 PSI	35.0 mL	8.085 PSI

2. Amontons' Law. Fill in the missing values in the table below.

Initial Pressure	Initial Temp	Final Pressure	Final Temp.
760 mmHg	35 ^{o}C	1500 mmHg	607.9 K
16.0 PSI	298 K	14.7 PSI	273 K
350 Torr	1300 K	13.5 Torr	50 K
144 atm	1872 K	25 atm	52 ^{o}C
745 Torr	473 K	780 mmHg	495.2 K
790.6 mmHg	37 ^{o}C	760 mmHg	25 ^{o}C
3.55 atm	298 K	4.44 atm	100 ^{o}C
14.7 PSI	273 K	760 Torr	0 ^{o}C

3. Charles' Law. Fill in the missing values in the table below.

Initial Volume	Final Volume	Initial Temp.	Final Temp.
269 mL	760 mL	298 K	842 K
1.59 L	2500 mL	198 K	39 °C
66 cm^3	55.2 cm^3	75 °C	18 °C
17.78 mL	35.57 mL	176 K	352 K
0.789 L	270 mL	1555 K	532 K
770 mL	238 mL	1132 K	350 K
155 mL	527 mL	289 K	982 K
50.7 mL	88 mL	174 K	29 °C

4. Ideal gas law. Fill in the missing values in the table below. Use 0.0821 L-atm/mol-K for R (gas constant).

Pressure	Volume	Moles (n)	Temp
1.00 atm	75.0 L	1.00	914 K
544 Torr	85.0 mL	0.00248	26 °C
13.9 PSI	100.8 L	5.33	218 K
367.3 atm	36.0 cm^3	0.59	273 K
0.788 atm	0.788 L	0.788	9.6 K
615 mmHg	159 L	1.59	988 K
14.7 PSI	52.6 L	2.35	273 K
12064 atm	89.9 mL	56.7	-40 °C

5. A gas mixture contains 62% hydrogen, 28% nitrogen, 5% water vapor, and 5 % argon. If the total pressure is 1670 Torr, what is the partial pressure of each gas component?

(62/100) × 1670 Torr = 1035.4 Torr hydrogen
(28/100) × 1670 Torr = 467.6 Torr nitrogen
(5/100) × 1670 Torr = 83.5 Torr water vapor
(5/100) × 1670 Torr = 83.5 Torr argon