General Chemistry II

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By: John Hutchinson

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Chapter 1. The Ideal Gas Law

Foundation

We assume as our starting point the atomic molecular theory. That is, we assume that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound.

Goals

The individual molecules of different compounds have characteristic properties, such as mass, structure, geometry, bond lengths, bond angles, polarity, diamagnetism or paramagnetism. We have not yet considered the properties of mass quantities of matter, such as density, phase (solid, liquid or gas) at room temperature, boiling and melting points, reactivity, and so forth. These are properties which are not exhibited by individual molecules. It makes no sense to ask what the boiling point of one molecule is, nor does an individual molecule exist as a gas, solid, or liquid. However, we do expect that these material or bulk properties are related to the properties of the individual molecules. Our ultimate goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise.

Achieving this goal will require considerable analysis. In this Concept Development Study, we begin at a somewhat more fundamental level, with our goal to know more about the nature of gases, liquids and solids. We need to study the relationships between the physical properties of materials, such as density and temperature. We begin our study by examining these properties in gases.

Observation 1: Pressure-Volume Measurements on Gases

It is an elementary observation that air has a "spring" to it: if you squeeze a balloon, the balloon rebounds to its original shape. As you pump air into a bicycle tire, the air pushes back against the piston of the pump. Furthermore, this resistance of the air against the piston clearly increases as the piston is pushed farther in. The "spring" of the air is measured as a pressure, where the pressure P is defined

$$P = \frac{F}{A} \tag{1.1}$$

F is the force exerted by the air on the surface of the piston head and A is the surface area of the piston head.

For our purposes, a simple pressure gauge is sufficient. We trap a small quantity of air in a syringe (a piston inside a cylinder) connected to the pressure gauge, and measure both the volume of air trapped inside the syringe and the pressure reading on the gauge. In one such sample measurement, we might find that, at atmospheric pressure (760 torr), the volume of gas trapped inside the syringe is 29.0 ml. We then compress the syringe slightly, so that the volume is now 23.0 ml. We feel the increased spring of the air, and this is registered on the gauge as an increase in pressure to 960 torr. It is simple to make many measurements in this manner. A sample set of data appears in Table 1.1. We note that, in agreement with our experience with gases, the pressure increases as the volume decreases. These data are plotted **here**.

Table 1.1. Sample Data from
Pressure-Volume Measurement

Pressure (torr)	Volume (ml)
760	29.0
960	23.0
1160	19.0
1360	16.2
1500	14.7
1650	13.3
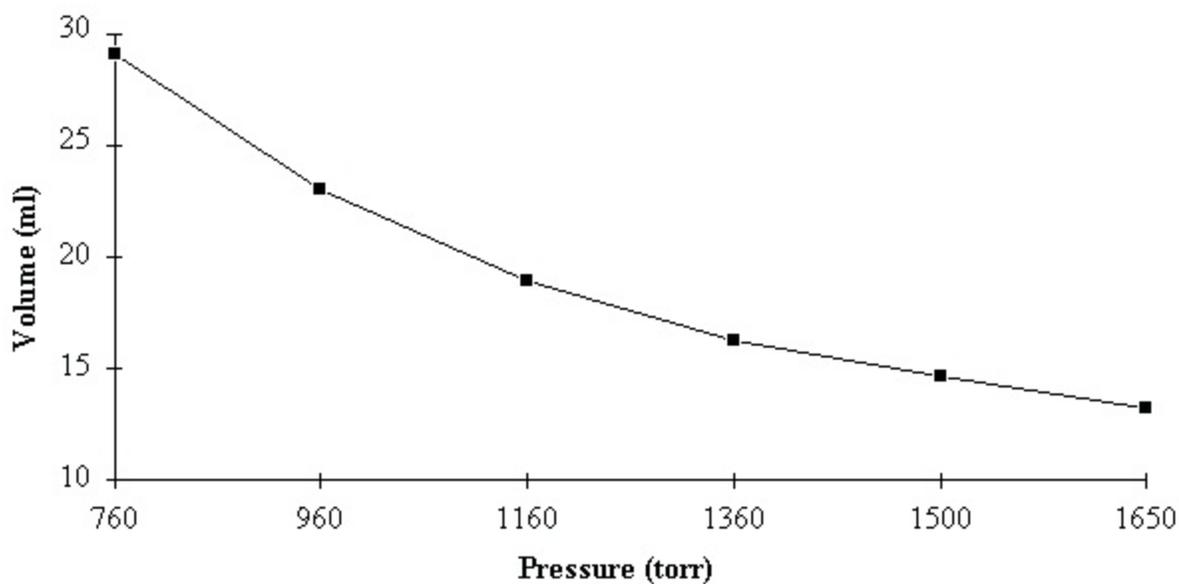
Figure 1.1. Measurements on Spring of the Air

An initial question is whether there is a quantitative relationship between the pressure

measurements and the volume measurements. To explore this possibility, we try to plot the data in such a way that both quantities increase together. This can be accomplished by plotting the pressure versus the inverse of the volume, rather than versus the volume. The data are given in Table 1.2 and plotted **here**.

Table 1.2. Analysis of Sample Data

Pressure (torr)	Volume (ml)	1/Volume (1/ml)	Pressure × Volume
760	29.0	0.0345	22040
960	23.0	0.0435	22080
1160	19.0	0.0526	22040
1360	16.2	0.0617	22032
1500	14.7	0.0680	22050
1650	13.3	0.0752	21945
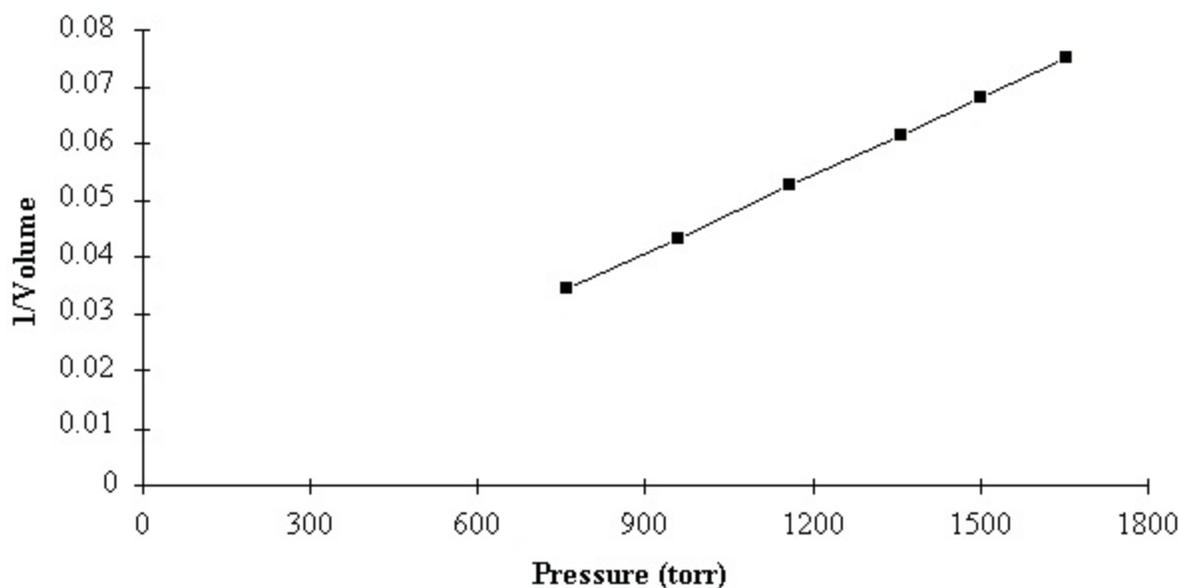
Figure 1.2. Analysis of Measurements on Spring of the Air

Notice also that, with elegant simplicity, the data points form a straight line. Furthermore, the straight line seems to connect to the origin {0, 0}. This means that the pressure must simply be a constant multiplied by $\frac{1}{V}$:

$$P = \left(k \times \frac{1}{V} \right)$$

(1.2)

If we multiply both sides of this equation by V, then we notice that

$$PV=k \tag{1.3}$$

In other words, if we go back and multiply the pressure and the volume together for each experiment, we should get the same number each time. These results are shown in the last column of Table 1.2, and we see that, within the error of our data, all of the data points give the same value of the product of pressure and volume. (The volume measurements are given to three decimal places and hence are accurate to a little better than 1%. The values of (Pressure × Volume) are all within 1% of each other, so the fluctuations are not meaningful.)

We should wonder what significance, if any, can be assigned to the number 22040(*torrml*) we have observed. It is easy to demonstrate that this "constant" is not so constant. We can easily trap any amount of air in the syringe at atmospheric pressure. This will give us any volume of air we wish at 760 torr pressure. Hence, the value 22040(*torrml*) is only observed for the particular amount of air we happened to choose in our sample measurement. Furthermore, if we heat the syringe with a fixed amount of air, we observe that the volume increases, thus changing the value of the 22040(*torrml*). Thus, we should be careful to note that the **product of pressure and volume is a constant for a given amount of air at a fixed temperature**. This observation is referred to as **Boyle's Law**, dating to 1662.

The data given in Table 1.1 assumed that we used air for the gas sample. (That, of course, was the only gas with which Boyle was familiar.) We now experiment with varying the composition of the gas sample. For example, we can put oxygen, hydrogen, nitrogen, helium, argon, carbon dioxide, water vapor, nitrogen dioxide, or methane into the cylinder. In each case we start with 29.0 ml of gas at 760 torr and 25°C. We then vary the volumes as in Table 1.1 and measure the pressures. Remarkably, we find that the pressure of each gas is exactly the same as every other gas at each volume given. For example, if we press the syringe to a volume of 16.2 ml, we observe a pressure of 1360 torr, no matter which gas is in the cylinder. This result also applies equally well to mixtures of different gases, the most familiar example being air, of course.

We conclude that the pressure of a gas sample depends on the volume of the gas and the temperature, but not on the composition of the gas sample. We now add to this result a conclusion from a **previous study**. Specifically, we recall the **Law of Combining Volumes**, which states that, when gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios. We further recall that this result can be explained in the context of the atomic molecular theory by hypothesizing that equal volumes of gas contain equal numbers of gas particles, independent of the type of gas, a conclusion we call **Avogadro's Hypothesis**. Combining this result with Boyle's law reveals that the **pressure** of a gas depends on the **number** of gas particles, the **volume** in which they are contained, and the **temperature** of the sample. The pressure does **not** depend on the type of gas particles in the sample or whether they are even all the same.

We can express this result in terms of Boyle's law by noting that, in the equation $PV=k$, the "constant" k is actually a function which varies with both number of gas particles in the sample

and the temperature of the sample. Thus, we can more accurately write

$$PV=k(N, t) \tag{1.4}$$

explicitly showing that the product of pressure and volume depends on N, the number of particles in the gas sample, and t,the temperature.

It is interesting to note that, in 1738, Bernoulli showed that the inverse relationship between pressure and volume could be proven by assuming that a gas consists of individual particles colliding with the walls of the container. However, this early evidence for the existence of atoms was ignored for roughly 120 years, and the atomic molecular theory was not to be developed for another 70 years, based on mass measurements rather than pressure measurements.

Observation 2: Volume-Temperature Measurements on Gases

We have already noted the dependence of Boyle's Law on temperature. To observe a constant product of pressure and volume, the temperature must be held fixed. We next analyze what happens to the gas when the temperature is allowed to vary. An interesting first problem that might not have been expected is the question of how to measure temperature. In fact, for most purposes, we think of temperature only in the rather non-quantitative manner of "how hot or cold" something is, but then we measure temperature by examining the length of mercury in a tube, or by the electrical potential across a thermocouple in an electronic thermometer. We then briefly consider the complicated question of just what we are measuring when we measure the temperature.

Imagine that you are given a cup of water and asked to describe it as "hot" or "cold." Even without a calibrated thermometer, the experiment is simple: you put your finger in it. Only a qualitative question was asked, so there is no need for a quantitative measurement of "how hot" or "how cold." The experiment is only slightly more involved if you are given two cups of water and asked which one is hotter or colder. A simple solution is to put one finger in each cup and to directly compare the sensation. You still don't need a calibrated thermometer or even a temperature scale at all.

Finally, imagine that you are given a cup of water each day for a week at the same time and are asked to determine which day's cup contained the hottest or coldest water. Since you can no longer trust your sensory memory from day to day, you have no choice but to define a temperature scale. To do this, we make a physical measurement on the water by bringing it into contact with something else whose properties depend on the "hotness" of the water in some unspecified way. (For example, the volume of mercury in a glass tube expands when placed in hot water; certain strips of metal expand or contract when heated; some liquid crystals change color when heated; *etc.*) We assume that this property will have the same value when it is placed in contact with two objects which have the same "hotness" or temperature. Somewhat obliquely, this defines the temperature measurement.

For simplicity, we illustrate with a mercury-filled glass tube thermometer. We observe quite easily that when the tube is inserted in water we consider "hot," the volume of mercury is larger than when we insert the tube in water that we consider "cold." Therefore, the volume of mercury is a measure of how hot something is. Furthermore, we observe that, when two very different objects appear to have the same "hotness," they also give the same volume of mercury in the glass tube. This allows us to make quantitative comparisons of "hotness" or temperature based on the volume of mercury in a tube.

All that remains is to make up some numbers that define the scale for the temperature, and we can literally do this in any way that we please. This arbitrariness is what allows us to have two different, but perfectly acceptable, temperature scales, such as Fahrenheit and Centigrade. The latter scale simply assigns zero to be the temperature at which water freezes at atmospheric pressure. We then insert our mercury thermometer into freezing water, and mark the level of the mercury as "0". Another point on our scale assigns 100 to be the boiling point of water at atmospheric pressure. We insert our mercury thermometer into boiling water and mark the level of mercury as "100." Finally, we just mark off in increments of $\frac{1}{100}$ of the distance between the "0" and the "100" marks, and we have a working thermometer. Given the arbitrariness of this way of measuring temperature, it would be remarkable to find a quantitative relationship between temperature and any other physical property.

Yet that is what we now observe. We take the same syringe used in the previous section and trap in it a small sample of air at room temperature and atmospheric pressure. (From our observations above, it should be clear that the type of gas we use is irrelevant.) The experiment consists of measuring the volume of the gas sample in the syringe as we vary the temperature of the gas sample. In each measurement, the pressure of the gas is held fixed by allowing the piston in the syringe to move freely against atmospheric pressure. A sample set of data is shown in Table 1.3 and plotted **here**.

Table 1.3. Sample Data from
Volume-Temperature
Measurement

Temperature (°C)	Volume (ml)
11	95.3
25	100.0
47	107.4
73	116.1
159	145.0

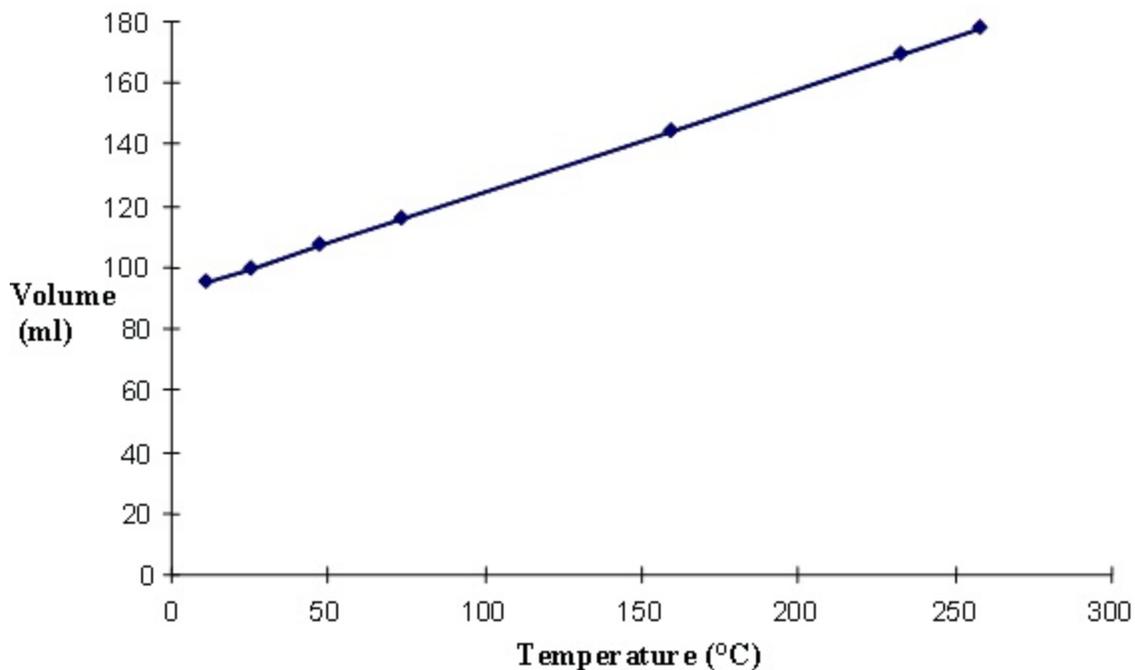|	
233	169.8
258	178.1

Figure 1.3. Volume vs. Temperature of a Gas

We find that there is a simple linear (straight line) relationship between the volume of a gas and its temperature as measured by a mercury thermometer. We can express this in the form of an equation for a line:

$$V = \alpha t + \beta \tag{1.5}$$

where V is the volume and t is the temperature in °C. α and β are the slope and intercept of the line, and in this case, $\alpha = 0.335$ and, $\beta = 91.7$. We can rewrite this equation in a slightly different form:

$$V = \alpha \left(t + \frac{\beta}{\alpha} \right) \tag{1.6}$$

This is the same equation, except that it reveals that the quantity $\frac{\beta}{\alpha}$ must be a temperature, since we can add it to a temperature. This is a particularly important quantity: if we were to set the temperature of the gas equal to $-\left(\frac{\beta}{\alpha} \right) = -273°C$, we would find that the volume of the gas would be exactly 0! (This assumes that this equation can be extrapolated to that temperature. This is quite an optimistic extrapolation, since we haven't made any measurements near to -273°C. In fact, our gas sample would condense to a liquid or solid before we ever reached that low temperature.)

Since the volume depends on the pressure and the amount of gas (Boyle's Law), then the values of α and β also depend on the pressure and amount of gas and carry no particular significance. However, when we repeat our observations for many values of the amount of gas and the fixed

pressure, we find that the **ratio** $-\left(\frac{\beta}{\alpha}\right) = -273°C$ does not vary from one sample to the next. Although we do not know the physical significance of this temperature at this point, we can assert that it is a true constant, independent of any choice of the conditions of the experiment. We refer to this temperature as **absolute zero**, since a temperature below this value would be predicted to produce a negative gas volume. Evidently, then, we cannot expect to lower the temperature of any gas below this temperature.

This provides us an "absolute temperature scale" with a zero which is not arbitrarily defined. This we define by adding 273 (the value of $\frac{\beta}{\alpha}$) to temperatures measured in °C, and we define this scale to be in units of degrees Kelvin (K). The data in Table 1.3 are now recalibrated to the absolute temperature scale in Table 1.4 and plotted **here**.

Table 1.4. Analysis of Volume-Temperature Data

Temperature (°C)	Temperature (K)	Volume (ml)
11	284	95.3
25	298	100.0
47	320	107.4
73	350	116.1
159	432	145.0
233	506	169.8
258	531	178.1

Figure 1.4. Volume vs. Absolute Temperature of a Gas
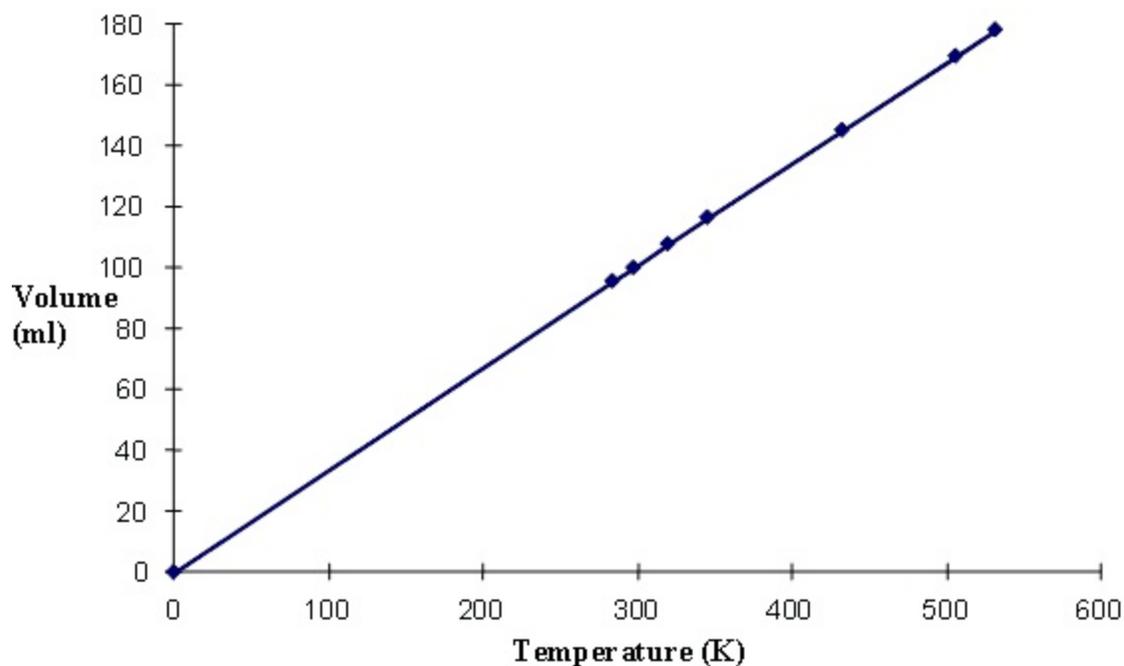
Note that **the volume is proportional to the absolute temperature** in degrees Kelvin,

$$V=kT \tag{1.7}$$

provided that the pressure and amount of gas are held constant. This result is known as **Charles' Law**, dating to 1787.

As with Boyle's Law, we must now note that the "constant" k is not really constant, since the volume also depends on the pressure and quantity of gas. Also as with Boyle's Law, we note that Charles' Law does not depend on the **type** of gas on which we make the measurements, but rather depends only the number of particles of gas. Therefore, we slightly rewrite Charles' Law to explicit indicate the dependence of k on the pressure and number of particles of gas

$$V=k(N, P)T \tag{1.8}$$

The Ideal Gas Law

We have been measuring four properties of gases: pressure, volume, temperature, and "amount", which we have assumed above to be the number of particles. The results of three observations relate these four properties pairwise. Boyle's Law relates the pressure and volume at constant temperature and amount of gas:

$$(P \times V)=k_1(N, T) \tag{1.9}$$

Charles' Law relates the volume and temperature at constant pressure and amount of gas:

$$V=k_2(N, P)T \tag{1.10}$$

The Law of Combining Volumes leads to Avogadro's Hypothesis that the volume of a gas is proportional to the number of particles (N) provided that the temperature and pressure are held constant. We can express this as

$$V=k_3(P, T)N \tag{1.11}$$

We will demonstrate below that these three relationships can be combined into a single equation relating P, V, T, and N. Jumping to the conclusion, however, we can more easily show that these three relationships can be considered as special cases of the more general equation known as the **Ideal Gas Law**:

$$PV=nRT \tag{1.12}$$

where R is a constant, n is the number of moles of gas, related to the number of particles N by Avogadro's number, N_A

$$n = \frac{N}{N_A}$$

(1.13)

In Boyle's Law, we examine the relationship of P and V when n (or N) and T are fixed. In the Ideal Gas Law, when n and T are constant, $\mathbf{nRT}$ is constant, so the product $\mathbf{PV}$ is also constant. Therefore, Boyle's Law is a special case of the Ideal Gas Law. If n and P are fixed in the Ideal Gas Law, then $v = \frac{nR}{P}T$ and $\frac{nR}{P}$ is a constant. Therefore, Charles' Law is also a special case of the Ideal Gas Law. Finally, if P and T are constant, then in the Ideal Gas Law, $v = \frac{RT}{P}n$ and the volume is proportional the number of moles or particles. Hence, Avogadro's hypothesis is a special case of the Ideal Gas Law.

We have now shown that the each of our experimental observations is consistent with the Ideal Gas Law. We might ask, though, how did we get the Ideal Gas Law? We would like to derive the Ideal Gas Law from the three experimental observations. To do so, we need to learn about the functions $k_1(N, T)$, $k_2(N, P)$, $k_3(P, T)$.

We begin by examining Boyle's Law in more detail: if we hold N and P fixed in Boyle's Law and allow T to vary, the volume must increase with the temperature in agreement with Charles' Law. In other words, with N and P fixed, the volume must be proportional to T. Therefore, k_1 in Boyle's Law must be proportional to T:

$$k_1(N, T) = (k_4(N) \times T)$$

(1.14)

where k_4 is a new function which depends only on N. Equation 1.9 then becomes

$$(P \times V) = k_4(N)T$$

(1.15)

Avogadro's Hypothesis tells us that, at constant pressure and temperature, the volume is proportional to the number of particles. Therefore k_4 must also increase proportionally with the number of particles:

$$k_4(N) = (k \times N)$$

(1.16)

where k is yet another new constant. In this case, however, there are no variables left, and k is truly a constant. Combining Equation 1.15 and Equation 1.16 gives

$$(P \times V) = (k \times N \times T)$$

(1.17)

This is very close to the Ideal Gas Law, except that we have the number of particles, N, instead of the number of the number of moles, n. We put this result in the more familiar form by expressing

the number of particles in terms of the number of moles, n, by dividing the number of particles by Avogadro's number, N_A, from Equation 1.13. Then, from Equation 1.17,

$$(P \times V) = (k \times N_A \times n \times T) \tag{1.18}$$

The two constants, k and N_A, can be combined into a single constant, which is commonly called R, the gas constant. This produces the familiar conclusion of Equation 1.12.

Observation 3: Partial Pressures

We referred briefly above to the pressure of mixtures of gases, noting in our measurements leading to Boyle's Law that the total pressure of the mixture depends only on the number of moles of gas, regardless of the types and amounts of gases in the mixture. The Ideal Gas Law reveals that the pressure exerted by a mole of molecules does not depend on what those molecules are, and our earlier observation about gas mixtures is consistent with that conclusion.

We now examine the actual process of mixing two gases together and measuring the total pressure. Consider a container of fixed volume 25.0L. We inject into that container 0.78 moles of N_2 gas at 298K. From the Ideal Gas Law, we can easily calculate the measured pressure of the nitrogen gas to be 0.763 atm. We now take an identical container of fixed volume 25.0L, and we inject into that container 0.22 moles of O_2 gas at 298K. The measured pressure of the oxygen gas is 0.215 atm. As a third measurement, we inject 0.22 moles of O_2 gas at 298K into the **first** container which already has 0.78 moles of N_2. (Note that the mixture of gases we have prepared is very similar to that of air.) The measured pressure in this container is now found to be 0.975 atm.

We note now that the **total** pressure of the mixture of N_2 and O_2 in the container is equal to the sum of the pressures of the N_2 and O_2 samples taken separately. We now define the **partial pressure** of each gas in the mixture to be the pressure of each gas as if it were the only gas present. Our measurements tell us that the partial pressure of N_2, P_{N_2}, is 0.763 atm, and the partial pressure of O_2, P_{O_2}, is 0.215 atm.

With this definition, we can now summarize our observation by saying that the total pressure of the mixture of oxygen and nitrogen is equal to the sum of the partial pressures of the two gases. This is a general result: **Dalton's Law of Partial Pressures**.

Law 1.1.

The total pressure of a mixture of gases is the sum of the partial pressures of the component gases in the mixture

Review and Discussion Questions

Exercise 1.

Sketch a graph with two curves showing Pressure vs. Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise 2.

Sketch a graph with two curves showing Pressure vs. 1/Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise 3.

Sketch a graph with two curves showing Volume vs. Temperature for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same pressure. Explain the comparison of the two curves.

Exercise 4.

Sketch a graph with two curves showing Volume vs Temperature for two different values of the pressure of the gas, with $P_2 > P_1$, both for the same number of moles. Explain the comparison of the two curves.

Exercise 5.

Explain the significance of the fact that, in the volume-temperature experiments, $\frac{\beta}{\alpha}$ is observed to have the same value, independent of the quantity of gas studied and the type of gas studied. What is the significance of the quantity $\frac{\beta}{\alpha}$? Why is it more significant than either β or α?

Exercise 6.

Amonton's Law says that the pressure of a gas is proportional to the absolute temperature for a fixed quantity of gas in a fixed volume. Thus, $P = k(N, V)T$. Demonstrate that Amonton's Law can be derived by combining Boyle's Law and Charles' Law.

Exercise 7.

Using Boyle's Law in your reasoning, demonstrate that the "constant" in Charles' Law, *i.e.* $k_2(N, P)$, is inversely proportional to P.

Exercise 8.

Explain how Boyle's Law and Charles' Law may be combined to the general result that, for constant quantity of gas, $(P \times V)=kT$.

Exercise 9.

Using Dalton's Law and the Ideal Gas Law, show that the partial pressure of a component of a gas mixture can be calculated from

$$P_i=PX_i \tag{1.19}$$

Where P is the total pressure of the gas mixture and X_i is the **mole fraction** of component i, defined by

$$X_i = \frac{n_i}{n_{total}} \tag{1.20}$$

Exercise 10.

Dry air is 78.084% nitrogen, 20.946% oxygen, 0.934% argon, and 0.033% carbon dioxide. Determine the mole fractions and partial pressures of the components of dry air at standard pressure.

Exercise 11.

Assess the accuracy of the following statement:

"Boyle's Law states that $PV=k_1$, where k_1 is a constant. Charles' Law states that $V=k_2T$, where k_2 is a constant. Inserting V from Charles' Law into Boyle's Law results in $Pk_2T=k_1$. We can rearrange this to read $PT = \frac{k_1}{k_2} = a\ constant$. Therefore, the pressure of a gas is inversely proportional to the temperature of the gas."

In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

Solutions

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