

12: The Kinetic Molecular Theory

Foundation

We assume an understanding of the atomic molecular theory postulates, including 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. Finally, we assume a knowledge of the **Ideal Gas Law**, and the observations from which it is derived.

Goals

Our continuing goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise. As simple examples, we compare the substances water, carbon dioxide, and nitrogen. Each of these is composed of molecules with few (two or three) atoms and low molecular weight. However, the physical properties of these substances are very different. Carbon dioxide and nitrogen are gases at room temperature, but it is well known that water is a liquid up to 100°C. To liquefy nitrogen, we must cool it to -196°C , so the boiling temperatures of water and nitrogen differ by about 300°C. Water is a liquid for a rather large temperature range, freezing at 0°C. In contrast, nitrogen is a liquid for a very narrow range of temperatures, freezing at -210°C . Carbon dioxide poses yet another very different set of properties. At atmospheric pressure, carbon dioxide gas cannot be liquefied at all: cooling the gas to -60°C converts it directly to solid "dry ice". As is commonly observed, warming dry ice does not produce any liquid, as the solid sublimates directly to gas.

Why should these materials, whose molecules do not seem all that different, behave so differently? What are the important characteristics of these molecules which produce these physical properties? It is important to keep in mind that these are properties of the bulk materials. At this point, it is not even clear that the concept of a molecule is useful in answering these questions about melting or boiling.

There are at least two principal questions that arise about the **Ideal Gas Law**. First, it is interesting to ask whether this law always holds true, or whether there are conditions under which the pressure of the gas cannot be calculated from $\frac{nRT}{V}$. We thus begin by considering the limitations of the validity of the **Ideal Gas Law**. We shall find that the ideal gas law is only approximately accurate and that there are variations which do depend upon the nature of the gas. Second, then, it is interesting to ask why the ideal gas law should ever hold true. In other words, why are the variations not the rule rather than the exception?

To answer these questions, we need a model which will allow us to relate the properties of bulk materials to the characteristics of individual molecules. We seek to know what happens to a gas when it is compressed into a smaller volume, and why it generates a greater resisting pressure when compressed. Perhaps most fundamentally of all, we seek to know what happens to a substance when it is heated. What property of a gas is measured by the temperature?

Observation 1: Limitations of the Validity of the Ideal Gas Law

To design a systematic test for the validity of the **Ideal Gas Law**, we note that the value of $\frac{PV}{nRT}$, calculated, from the observed values of P , V , n , and T , should always be equal to 1, exactly. Deviation of $\frac{PV}{nRT}$ from 1 indicates a violation of the **Ideal Gas Law**. We thus measure the pressure for several different gases under a variety of conditions by varying n , V , and T , and we calculate the ratio $\frac{PV}{nRT}$ for these conditions.

In Figure 12.1, the value of this ratio is plotted for several gases as a function of the "particle density" of the gas in moles, $\frac{n}{V}$. To make the analysis of this plot more convenient, the particle density is given in terms of the particle density of an ideal gas at room temperature and atmospheric pressure (i.e. the density of air), which is $0.04087 \frac{\text{mol}}{\text{L}}$. In Figure 12.1, a particle density of 10 means that the particle density of the gas is 10 times the particle density of air at room temperature. The x-axis in the figure is thus unitless.



Figure 12.1: Validity of the Ideal Gas Law

Note that $\frac{PV}{nRT}$ on the y-axis is also unitless and has value exactly 1 for an ideal gas. We observe in the data in this figure that $\frac{PV}{nRT}$ is extremely close to 1 for particle densities which are close to that of normal air. Therefore, deviations from the **Ideal Gas Law** are not expected under "normal" conditions. This is not surprising, since **Boyle's Law**, **Charles' Law**, and the **Law of Combining**

Volumes were all observed under normal conditions. Figure 12.1 also shows that, as the particle density increases above the normal range, the value of $\frac{PV}{nRT}$ starts to vary from 1, and the variation depends on the type of gas we are analyzing. However, even for particle densities 10 times greater than that of air at atmospheric pressure, the **Ideal Gas Law** is accurate to a few percent.

Thus, to observe any significant deviations from $PV = nRT$, we need to push the gas conditions to somewhat more extreme values. The results for such extreme conditions are shown in Figure 12.2. Note that the densities considered are large numbers corresponding to very high pressures. Under these conditions, we find substantial deviations from the **Ideal Gas Law**. In addition, we see that the pressure of the gas (and thus $\frac{PV}{nRT}$) does depend strongly on which type of gas we are examining. Finally, this figure shows that deviations from the **Ideal Gas Law** can generate pressures either greater than or less than that predicted by the **Ideal Gas Law**.



Figure 12.2: Deviations from the Ideal Gas Law

Observation 2: Density and Compressibility of Gas

For low densities for which the **Ideal Gas Law** is valid, the pressure of a gas is independent of the nature of the gas, and is therefore independent of the characteristics of the particles of that gas. We can build on this observation by considering the significance of a low particle density. Even at the high particle densities considered in Figure 12.2, all gases have low density in comparison to the densities of liquids. To illustrate, we note that 1 gram of liquid water at its boiling point has a volume very close to 1 milliliter. In comparison, this same 1 gram of water, once evaporated into steam, has a volume of over 1700 milliliters. How does this expansion by a factor of 1700 occur? It is not credible that the individual water molecules suddenly increase in size by this factor. The only plausible conclusion is that the distance between gas molecules has increased dramatically.

Therefore, it is a characteristic of a gas that the molecules are far apart from one another. In addition, the lower the density of the gas the farther apart the molecules must be, since the same number of molecules occupies a larger volume at lower density.

We reinforce this conclusion by noting that liquids and solids are virtually incompressible, whereas gases are easily compressed. This is easily understood if the molecules in a gas are very far apart from one another, in contrast to the liquid and solid where the molecules are so close as to be in contact with one another.

We add this conclusion to the observations in Figures 12.1 and 12.2 that the pressure exerted by a gas depends only on the number of particles in the gas and is independent of the type of particles in the gas, provided that the density is low enough. This requires that the gas particles be far enough apart. We conclude that the **Ideal Gas Law** holds true because there is sufficient distance between the gas particles that the identity of the gas particles becomes irrelevant.

Why should this large distance be required? If gas particle A were far enough away from gas particle B that they experience no electrical or magnetic interaction, then it would not matter what types of particles A and B were. Nor would it matter what the sizes of particles A and B were. Finally, then, we conclude from this reasoning that the validity of the ideal gas law rests on the presumption that there are no interactions of any type between gas particles.

Postulates of the Kinetic Molecular Theory

We recall at this point our purpose in these observations. Our primary concern in this study is attempting to relate the properties of individual atoms or molecules to the properties of mass quantities of the materials composed of these atoms or molecules. We now have extensive quantitative observations on some specific properties of gases, and we proceed with the task of relating these to the particles of these gases.

By taking an atomic molecule view of a gas, we can postulate that the pressure observed is a consequence of the collisions of the individual particles of the gas with the walls of the container. This presumes that the gas particles are in constant motion. The pressure is, by definition, the force applied per area, and there can be no other origin for a force on the walls of the container than that provided by the particles themselves. Furthermore, we observe easily that the pressure exerted by the gas is the same in all directions. Therefore, the gas particles must be moving equally in all directions, implying quite plausibly that the motions of the particles are random.

To calculate the force generated by these collisions, we must know something about the motions of the gas particles so that we know, for example, each particle's velocity upon impact with the wall. This is too much to ask: there are perhaps 10^{20} particles or

more, and following the path of each particle is out of the question. Therefore, we seek a model which permits calculation of the pressure without this information.

Based on our observations and deductions, we take as the postulates of our model:

- A gas consists of individual particles in constant and random motion
- The individual particles have negligible volume.
- The individual particles do not attract or repel one another in any way.
- The pressure of the gas is due entirely to the force of the collisions of the gas particles with the walls of the container.

This model is the **Kinetic Molecular Theory of Gases**. We now look to see where this model leads.

Derivation of Boyle's Law from the Kinetic Molecular Theory

To calculate the pressure generated by a gas of N particles contained in a volume V , we must calculate the force F generated per area A by collisions against the walls. To do so, we begin by determining the number of collisions of particles with the walls. The number of collisions we observe depends on how long we wait. Let's measure the pressure for a period of time Δt and calculate how many collisions occur in that time period. For a particle to collide with the wall within the time Δt , it must start close enough to the wall to impact it in that period of time. If the particle is traveling with speed v , then the particle must be within a distance $v\Delta t$ of the wall to hit it. Also, if we are measuring the force exerted on the area A , the particle must hit that area to contribute to our pressure measurement.

For simplicity, we can view the situation pictorially in Figure 12.3. We assume that the particles are moving perpendicularly to the walls. (This is clearly not true. However, very importantly, this assumption is only made to simplify the mathematics of our derivation. It is not necessary to make this assumption, and the result is not affected by the assumption.) In order for a particle to hit the area A marked on the wall, it must lie within the cylinder shown, which is of length $v\Delta t$ and cross-sectional area A . The volume of this cylinder is $Av\Delta t$, so the number of particles contained in the cylinder is $(Av\Delta t) \times \frac{N}{V}$.



Figure 12.3: Collision of a Particle with a Wall within time Δt

Not all of these particles collide with the wall during Δt , though, since most of them are not traveling in the correct direction. There are six directions for a particle to go, corresponding to plus or minus direction in x , y , or z . Therefore, on average, the fraction of particles moving in the correct direction should be $\frac{1}{6}$, assuming as we have that the motions are all random. Therefore, the number of particles which impact the wall in time Δt is $(Av\Delta t) \times \frac{N}{6V}$.

The force generated by these collisions is calculated from Newton's equation, $F = ma$, where a is the acceleration due to the collisions. Consider first a single particle moving directly perpendicular to a wall with velocity v as in Figure 12.3. We note that, when the particle collides with the wall, the wall does not move, so the collision must generally conserve the energy of the particle. Then the particle's velocity after the collision must be $-v$, since it is now traveling in the opposite direction. Thus, the change in velocity of the particle by the time Δt , we find that the total acceleration (change in velocity per time) is $\frac{2Avv^2}{6V}$, and the force imparted on the wall due to collisions is found by multiplying by the mass of the particles:

$$F = \frac{2ANmv^2}{6V} \quad (12.1)$$

To calculate the pressure, we divide by the area A , to find that

$$P = \frac{Nmv^2}{3V} \quad (12.2)$$

or, rearranged for comparison to **Boyle's Law**,

$$PV = \frac{Nmv^2}{3} \quad (12.3)$$

Since we have assumed that the particles travel with constant speed v , then the right side of this equation is a constant. Therefore the product of pressure times volume, PV , is a constant, in agreement with **Boyle's Law**. Furthermore, the product PV is proportional to the number of particles, also in agreement with the **Law of Combining Volumes**. Therefore, the model we have developed to describe an ideal gas is consistent with our experimental observations.

We can draw two very important conclusions from this derivation. First, the inverse relationship observed between pressure and volume and the independence of this relationship on the type of gas analyzed are both due to the lack of interactions between gas particles. Second, the lack of interactions is in turn due to the great distances between gas particles, a fact which will be true provided that the density of the gas is low.

Interpretation of Temperature

The absence of temperature in the above derivation is notable. The other gas properties have all been incorporated, yet we have derived an equation which omits temperature all together. The problem is that, as we discussed at length above, the temperature was somewhat arbitrarily defined. In fact, it is not precisely clear what has been measured by the temperature. We defined the temperature of a gas in terms of the volume of mercury in a glass tube in contact with the gas. It is perhaps then no wonder that such a quantity does not show up in a mechanical derivation of the gas properties.

On the other hand, the temperature does appear prominently in the **Ideal Gas Law**. Therefore, there must be a greater significance (and less arbitrariness) to the temperature than might have been expected. To discern this significance, we rewrite the last equation above in the form

$$PV = \frac{2}{3}N \left(\frac{1}{2}mv^2 \right) \quad (12.4)$$

The last quantity in parentheses can be recognized as the kinetic energy of an individual gas particle, and $N \left(\frac{1}{2}mv^2 \right)$ must be the total kinetic energy (KE) of the gas. Therefore

$$PV = \frac{2}{3}KE \quad (12.5)$$

Now we insert the **Ideal Gas Law** for PV to find that

$$KE = \frac{3}{2}nRT \quad (12.6)$$

This is an extremely important conclusion, for it reveals the answer to the question of what property is measured by the temperature. We see now that the temperature is a measure of the total kinetic energy of the gas. Thus, when we heat a gas, elevating its temperature, we are increasing the average kinetic energy of the gas particles, causing them to move, on average, more rapidly.

Analysis of Deviations from the Ideal Gas Law

We are at last in a position to understand the observations of deviations from the **Ideal Gas Law**. The most important assumption of our model of the behavior of an ideal gas is that the gas molecules do not interact. This allowed us to calculate the force imparted on the wall of the container due to a single particle collision without worrying about where the other particles were. In order for a gas to disobey the **Ideal Gas Law**, the conditions must be such that this assumption is violated.

What do the deviations from ideality tell us about the gas particles? Starting with very low density and increasing the density as in Figure 12.1, we find that, for many gases, the value of $\frac{PV}{nRT}$ falls below 1. One way to state this result is that, for a given value of V , n , and T , the pressure of the gas is less than it would have been for an ideal gas. This must be the result of the interactions of the gas particles. In order for the pressure to be reduced, the force of the collisions of the particles with the walls must be less than is predicted by our model of an ideal gas. Therefore, the effect of the interactions is to slow the particles as they approach the walls of the container. This means that an individual particle approaching a wall must experience a force acting to pull it back into the body of the gas. Hence, the gas particles are confined in closer proximity to one another. At this closer range, the attractions of individual particles become significant. It should not be surprising that these attractive forces depend on what the particles are. We note in Figure 12.1 that deviation from the **Ideal Gas Law** is greater for ammonia than for nitrogen, and greater for nitrogen than for helium. Therefore, the attractive interactions of ammonia molecules are greater than those of nitrogen molecules, which are in turn greater than those of helium atoms. We analyze this conclusion in more detail below.

Continuing to increase the density of the gas, we find in Figure 12.2 that the value of $\frac{PV}{nRT}$ begins to rise, eventually exceeding 1 and continuing to increase. Under these conditions, therefore, the pressure of the gas is greater than we would have expected from our model of non-interacting particles. What does this tell us? The gas particles are interacting in such a way as to increase the force of the collisions of the particles with the walls. This requires that the gas particles repel one another. As we move to higher

density, the particles are forced into closer and closer proximity. We can conclude that gas particles at very close range experience strong repulsive forces away from one another.

Our model of the behavior of gases can be summarized as follows: at low density, the gas particles are sufficiently far apart that there are no interactions between them. In this case, the pressure of the gas is independent of the nature of the gas and agrees with the **Ideal Gas Law**. At somewhat higher densities, the particles are closer together and the interaction forces between the particles are attractive. The pressure of the gas now depends on the strength of these interactions and is lower than the value predicted by the **Ideal Gas Law**. At still higher densities, the particles are excessively close together, resulting in repulsive interaction forces. The pressure of the gas under these conditions is higher than the value predicted by the **Ideal Gas Law**.

Observation 3: Boiling Points of simple hydrides

The postulates of the **Kinetic Molecular Theory** provide us a way to understand the relationship between molecular properties and the physical properties of bulk amounts of substance. As a distinct example of such an application, we now examine the boiling points of various compounds, focusing on hydrides of sixteen elements in the main group (Groups IV through VII). These are given in Table 12.1.

Table 12.1: Boiling Points of Hydrides of Groups IV to VII

	Boiling Point (°C)
CH ₄	-164
NH ₃	-33
H ₂ O	100
HF	20
SiH ₄	-111.8
PH ₃	-87.7
H ₂ S	-60.7
HCl	-85
GeH ₄	-88.5
AsH ₃	-55
H ₂ Se	-41.5
HBr	-67
SnH ₄	-52
SbH ₃	-17.1
H ₂ Te	-2.2
HI	-35

In tabular form, there are no obvious trends here, and therefore no obvious connection to the structure or bonding in the molecules. The data in the table are displayed in a suggestive form, however, in Figure 12.4; the boiling point of each hydride is plotted according to which period (row) of the periodic table the main group element belongs. For example, the Period 2 hydrides (CH₄, NH₃, H₂O, and HF) are grouped in a column to the left of the figure, followed by a column for the Period 3 hydrides (SiH₄, PH₃, H₂S, HCl), etc.

Now a few trends are more apparent. First, the lowest boiling points in each period are associated with the Group IV hydrides (CH₄, SiH₄, GeH₄, SnH₄), and the highest boiling points in each period belong to the Group VI hydrides (H₂O, H₂S, H₂Se, H₂Te). For this reason, the hydrides belonging to a single group have been connected in Figure 12.4.



Figure 12.4: Boiling Points of Main Group Hydrides

Second, we notice that, with the exceptions of NH_3 , H_2O , and HF , the boiling points of the hydrides always increase in a single group as we go down the periodic table: for example, in Group IV, the boiling points increase in the order $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$. Third, we can also say that the hydrides from Period 2 appear to have unusually high boiling points **except** for CH_4 , which as noted has the lowest boiling point of all.

We begin our analysis of these trends by assuming that there is a relationship between the boiling points of these compounds and the structure and bonding in their molecules. Recalling our kinetic molecular model of gases and liquids, we recognize that a primary difference between these two phases is that the strength of the interaction between the molecules in the liquid is much greater than that in the gas, due to the proximity of the molecules in the liquid. In order for a molecule to leave the liquid phase and enter into the gas phase, it must possess sufficient energy to overcome the interactions it has with other molecules in the liquid. Also recalling the kinetic molecular description, we recognize that, on average, the energies of molecules increase with increasing temperature. We can conclude from these two statements that a high boiling point implies that significant energy is required to overcome intermolecular interactions. Conversely, a substance with a low boiling point must have weak intermolecular interactions, surmountable even at low temperature.

In light of these conclusions, we can now look at Figure 12.4 as directly (though qualitatively) revealing the comparative strengths of intermolecular interactions of the various hydrides. For example, we can conclude that, amongst the hydrides considered here, the intermolecular interactions are greatest between H_2O molecules and weakest between CH_4 molecules. We examine the three trends in this figure, described above, in light of the strength of intermolecular forces.

First, the most dominant trend in the boiling points is that, within a single group, the boiling points of the hydrides increase as we move **down** the periodic table. This is true in all four groups in Figure 12.4; the only exceptions to this trend are NH_3 , H_2O , and HF . We can conclude that, with notable exceptions, intermolecular interactions increase with increasing atomic number of the central atom in the molecule. This is true whether the molecules of the group considered have dipole moments (as in Groups V, VI, and VII) or not (as in Group IV). We can infer that the large intermolecular attractions for molecules with large central atoms arises from the large number of charged particles in these molecules.

This type of interaction arises from forces referred to as **London forces** or **dispersion forces**. These forces are believed to arise from the instantaneous interactions of the charged particles from one molecule with the charged particles in an adjacent molecule. Although these molecules may not be polar individually, the nuclei in one molecule may attract the electrons in a second molecule, thus inducing an instantaneous dipole in the second molecule. In turn, the second molecule induces a dipole in the first. Thus, two non-polar molecules can interact as if there were dipole-dipole attractions between them, with positive and negative charges interacting and attracting. The tendency of a molecule to have an induced dipole is called the **polarizability** of the molecule. The more charged particles there are in a molecule, the more **polarizable** a molecule is and the greater the attractions arising from dispersion forces will be.

Second, we note that, without exception, the Group IV hydrides must have the weakest intermolecular interactions in each period. As noted above, these are the only hydrides that have no dipole moment. Consequently, in general, molecules without dipole moments have weaker interactions than molecules which are polar. We must qualify this carefully, however, by noting that the nonpolar SnH_4 has a higher boiling point than the polar PH_3 and HCl . We can conclude from these comparisons that the increased polarizability of molecules with heavier atoms can offset the lack of a molecular dipole.

Third, and most importantly, we note that the intermolecular attractions involving NH_3 , H_2O , and HF must be uniquely and unexpectedly large, since their boiling points are markedly out of line with those of the rest of their groups. The common feature of these molecules is that they contain small atomic number atoms which are strongly electronegative, which have lone pairs, and which are bonded to hydrogen atoms. Molecules without these features do not have unexpectedly high boiling points. We can deduce from these observations that the hydrogen atoms in each molecule are unusually strongly attracted to the lone pair electrons on the strongly electronegative atoms with the same properties in other molecules. This intermolecular attraction of a hydrogen atom to an electronegative atom is referred to as **hydrogen bonding**. It is clear from our boiling point data that hydrogen bonding interactions are much stronger than either dispersion forces or dipole-dipole attractions.

Review and Discussion Questions

Explain the significance to the development of the kinetic molecular model of the observation that the ideal gas law works well only at low pressure.

Explain the significance to the development of the kinetic molecular model of the observation that the pressure predicted by the ideal gas law is independent of the type of gas.

Sketch the value of $\frac{PV}{nRT}$ as a function of density for two gases, one with strong intermolecular attractions and one with weak intermolecular attractions but strong repulsions.

Give a brief molecular explanation for the observation that the pressure of a gas at fixed temperature increases proportionally with the density of the gas.

Give a brief molecular explanation for the observation that the pressure of a gas confined to a fixed volume increases proportionally with the temperature of the gas.

Give a brief molecular explanation for the observation that the volume of a balloon increases roughly proportionally with the temperature of the gas inside the balloon.

Explain why there is a correlation between high boiling point and strong deviation from the **Ideal Gas Law**.

Referring to Figure 12.4, explain why the hydride of the Group IV element always has the lowest boiling point in each period.

Explain why the Period 2 hydrides except CH_4 all have high boiling points, and explain why CH_4 is an exception.

Contributors and Attributions

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