Gases that deviate from ideality are known as Real Gases, which originate from two factors: (1) First, the theory assumes that as pressure increases, the volume of a gas becomes very small and approaches zero. While it does approach a small number, it will not be zero because molecules do occupy space (i.e. have volume) and cannot be compressed. (2) Intermolecular forces do exist in gases. These become increasingly important in low temperatures, when translational (definition of translational, please) molecular motion slows down, almost to a halt. However, at high temperatures, or even normal, everyday temperatures, the intermolecular forces are very small and tend to be considered negligible.

Introduction

While the Kinetic-Molecular Theory does an excellent job explaining gases, there are a few properties it does not explain regarding its description of real gases. The theory assumes that collisions between gas molecules and the walls of a container are perfectly elastic, gas particles do not have any volume, and there are no repulsive or attractive forces between molecules. These assumptions pertain to Ideal Gases. While these assumptions generally hold true, there are circumstances where gases deviate from ideality.

Gases tend to behave ideally in two different situations. First, they behave ideally at High Temperatures! This is due to the fact that molecules are flying past each other at extremely high speeds (remember that temperature is a measure of the average kinetic energy, which is directly proportional to velocity). Second, they behave ideally at Low Pressures! This is because at low pressures, the volume of the molecules tends to become negligible in comparison to the total volume of the gas (Remember Boyle's Law, that Pressure and Volume are inversely proportional).

So, if this is when they behave ideally, when do they behave non ideally? Gases behave non ideally at cold temperatures because of the fact that at cold temperatures, molecules are moving relatively slowly past one another, allowing for the repulsive and/or attractive forces between molecules to take effect, deviating from an Ideal Gas. Gases also behave non ideally at High Pressures, because at high pressures, the volume of molecules becomes a factor.

Real gases and the molar volume

To illustrate the slight differences between the numerical properties of real and ideal gases at normal temperatures and pressures consider the following comparison. You will remember that we used the ideal gas equation to work out a value for the molar volume of an ideal gas at STP (standard temperature and pressure).

If you know the density of a gas at a particular temperature and pressure, it is very easy to work out its molar volume. For example, at 273 K and 1 atmosphere pressure, the density of helium is 0.1785 g dm$^{-3}$. That means that 0.1785 g of helium occupies 1 dm$^{3}$ at STP. It is a fairly simple sum to work out what 1 mole of helium, He, would occupy.

The mass of 1 mole of He is 4 g and would occupy

$$\frac{4}{0.1785 \;dm^3} = 22.4\; dm^3 \tag{1}$$

That's the same (at least to 3 significant figures) as the ideal gas value, suggesting that helium behaves as an ideal gas under these conditions. If you do this for a random sample of other gases, you get these values (to 3 significant figures) for the molar volume at STP (273 K and 1 atmosphere pressure).
Table 1: Molar Volume and densities of select gases

<table>
<thead>
<tr>
<th></th>
<th>density (g dm(^{-3}))</th>
<th>molar volume at stp</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.1785</td>
<td>22.4</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.2506</td>
<td>22.4</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.4290</td>
<td>22.4</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.717</td>
<td>22.3</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.977</td>
<td>22.3</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>1.260</td>
<td>22.2</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>0.769</td>
<td>22.1</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>2.926</td>
<td>21.9</td>
</tr>
</tbody>
</table>

So although for simple calculation purposes we use the value 22.4 dm\(^3\) for all gases, you can see that it isn’t exactly true. Even at ordinary temperatures and pressures, real gases can deviate slightly from the ideal value. The effect is much greater under more extreme conditions, as we will see next.

**Compression factors**

For an ideal gas, \((pV = nRT)\). If \(pV\) and \(nRT\) are the same, and you divide one by the other, then the answer will, of course, be 1. For real gases, \((pV \neq nRT)\), and so the value will be something different. Another way to think of this is by taking a look at the compressibility factor:

\[
Z = \frac{PV}{nRT} \quad \text{(2)}
\]

\(Z\) measures the deviation of a gas from its ideal state. It can be expressed as the ratio \((PV/nRT)\). By analyzing this mathematically, we can clearly see that the compressibility factor is equal to 1 in an ideal gas, because

\[
PV = nRT \quad \text{(3)}
\]

or

\[
\frac{PV}{nRT} = 1 \quad \text{(4)}
\]

However, in a real gas, as the pressure increases, \(Z\) increases to a number larger than one, distorting the ideality. The same is true for when a temperature decreases, as the compressibility factor rises above 1 again as the temperature approaches a smaller number. An ideal gas has a compressibility factor equal to one, but the compressibility factor for a real gas can vary greatly from this number. The graphs below show how this varies for nitrogen as you change the
temperature and the pressure.

![Compressibility of nitrogen](image)

**Figure 1: Compressibility of nitrogen**

If nitrogen were an ideal gas under all conditions of temperature and pressure, every one of these curves would be a horizontal straight line showing a compression factor of 1. That's obviously not true!

**Things to notice**

- At low pressures of about 1 bar (100 kPa - just a bit less than 1 atmosphere), the compression factor is close to 1. Nitrogen approximates to ideal behavior at ordinary pressures.
- The non-ideal behavior gets worse at lower temperatures. For temperatures of 300 or 400 K, the compression factor is close to 1 over quite a large pressure range. The nitrogen becomes more ideal over a greater pressure range as the temperature rises.
- The non-ideal behavior gets worse at higher pressures.
- There must be at least two different effects causing these deviations. There must be at least one effect causing the $pV / nRT$ ratio to be too low, especially at low temperatures. And there must be at least one effect causing it to get too high as pressure increases. We will explore those effects in a while.

**Other gases**

Is the same behavior shown by other gases? The next diagram shows how the compression factors vary with pressure for a variety of gases at a fixed temperature.
If you were to redo the set of original nitrogen graphs (at varying temperatures) for any of these other gases, you would find that each of them will produce a set of curves similar to the nitrogen ones. What varies is the temperature at which the different graph shapes occur. For example, if you look at the carbon dioxide graph at 273 K (Figure 2), it looks similar to the nitrogen one at 100 K from the first set of curves, although it does not increase so steeply at higher pressures.

It is easy to say that gases become less ideal at low temperatures, but what counts as a low temperature varies from gas to gas. The closer you get to the temperature at which the gas would turn into a liquid (or, in the case of carbon dioxide, a solid), the more non-ideal the gas becomes.

What causes non-ideal behavior?

In the compression factor expression, \( pV / nRT \), everything on the bottom of the expression is either known or can be measured accurately. But that's not true of pressure and volume. In the assumptions we make about ideal gases, there are two statements which say things which can't be true of a real gas, and these have an effect on both pressure and volume.

The volume problem

The kinetic theory assumes that, for an ideal gas, the volume taken up by the molecules themselves is entirely negligible compared with the volume of the container. For a real gas, that assumption isn't true. The molecules themselves do take up a proportion of the space in the container. The space in the container available for things to move around in is less than the measured volume of the container.
Figure 3:

This problem gets worse the more the gas is compressed. If the pressure is low, the volume taken up by the actual molecules is insignificant compared with the total volume of the container. But as the gas gets more compressed, the proportion of the total volume that the molecules themselves take up gets higher and higher. You could imagine compressing it so much that the molecules were actually all touching each other. At that point the volume available for them to move around in is zero!

Suppose at some high pressure, you measure the volume of the container as, say, 1000 cm$^3$, but suppose the molecules themselves occupy as much as 100 cm$^3$ of it. The ideal gas equation was worked out by doing calculations based on Kinetic Theory assumptions. The $V$ in $pV$ is assumed to be the volume which the molecules are free to move around in - but in this case, it would only be 900 cm$^3$, not 1000 cm$^3$.

If you worked out the compression factor, $pV / nRT$, by putting the total volume of the container into the formula, the answer is bound to be higher than it ought to be. It does not allow for the volume taken up by the molecules themselves. Let's just repeat one of the earlier diagrams so that you can see this effect in operation.

Figure 4:

For a real gas like nitrogen, notice how the compression factor tends to increase with pressure. For an ideal gas, the compression factor...
would be 1 over the whole pressure range. The value of the compression factor is too high at high pressures for a real gas. The reason for that is that the measured volume that you put into the expression is too high because you are not allowing for the volume taken up by the molecules. That error gets relatively worse the more compressed the gas becomes.

The pressure problem

Another key assumption of the Kinetic Theory for ideal gases is that there are no intermolecular forces between the molecules. That is wrong for every real gas. If there weren't any intermolecular forces then it would be impossible to condense the gas as a liquid. Even helium, with the weakest of all intermolecular forces, can be turned to a liquid if the temperature is low enough.

So what effect do intermolecular forces have? For a gas molecule in the middle of the gas, there is no net effect. It will be attracted to some extent to all the other molecules around it, but, on average, those attractions will cancel each other out. Attractions from behind a molecule, tending to slow it down, will be canceled out by attractions from in front of it, tending to speed it up.

![Figure 5](image)

Despite all the intermolecular forces it is experiencing, the molecule picked out in green will just continue to move in the same direction at the same speed. That's different if the molecule is just about to hit the wall of the container.

![Figure 5](image)

Now there are not any gas molecules in front of it, and the net pull is backwards into the body of the gas. The molecule will slow down just before it hits the wall. If it slows down, it will hit the wall less hard, and so exert less pressure. The overall effect of this is to make
the measured pressure less than it would be if the gas was ideal. That means that if you put the measured pressure into the expression \( \frac{pV}{nRT} \), the value of the compression factor will be less than it would be if the gas was ideal. This is why, under some conditions, graphs of compression factors drop below the ideal value of 1. Look yet again at the nitrogen curves:

This effect is most important at low temperatures. Why is that? At lower temperatures, the molecules are moving more slowly on average. Any pull they feel back into the gas will have relatively more effect on a slow moving particle than a faster one. At higher temperatures, where the molecules are moving a lot faster, any small pull back into the body of the gas is hardly going to be noticeable. At high temperatures, the effect of intermolecular forces is indeed negligible.

And there is one final effect concerning intermolecular forces which is slightly more hidden away. As pressure increases, the molecules are forced more closely together. If they are closer, the intermolecular forces will become more important. So, as pressure increases, you would expect more lowering of the compression factor relative to the ideal case. The molecules which slow down the one just about to hit the wall will be closer to it, and so more effective.

Is that what happens? Yes, up to a point. Look again at the nitrogen curve at 100 K. As the pressure increases, at first the value of the compression factor falls. But it soon starts to rise again. Why? Because at this point, the effect of the size of the molecules starts to become more important - and as the pressure is increased even more, this other effect becomes dominant.

**Which is the most ideal gas?**

You are looking for a gas with the smallest possible molecules, and the lowest possible intermolecular forces. That is helium. A helium molecule consists of a single small atom, and the van der Waals dispersion forces are as low as it is possible for them to be. Like helium, a hydrogen molecule also has two electrons, and so the intermolecular forces are going to be small - but not as small as helium. In the hydrogen molecule, you have two atoms that you can distribute the charges over. As molecules get larger, then dispersion forces will increase, and you may get other intermolecular forces such as dipole-dipole attractions as well. Gases made of molecules such as these will be much less ideal.
The van der Waals Equation

There are a large number of potential equations that can portray how real gases act, but to keep it simple, chemists stick to the van der Waals Equation because it is the easiest to portray how gases act:

\[
\left[P+\dfrac{an^2}{V^2}\right]\left[V-nb\right]=nRT \tag{5}\]

with

- \(P\) is the Pressure in atmospheres (atm)
- \(V\) is the Volume in Liters (L)
- \(n\) is the Number of moles (mol)
- \(R\) is the gas Constant and is \(0.08206 \dfrac{L*atm}{mol*K}\)
- \(T\) is the absolute Temperature in Kelvin (K)

While this looks far more intimidating than \(PV=nRT\), keep in mind that it is very similar to the ideal gas equation, but corrects for a few things. The right-hand side of the equation is the exact same as the ideal gas equation. It only changes regarding the Pressure and Volume to account for the things regarding intermolecular forces and the volume of gas molecules.

So, what about this \(\dfrac{an^2}{V^2}\)? Well, this is added to the pressure in order to account for the intermolecular forces of attraction. The \(a\) is a value that accounts for the amount of attraction between each particle. This is multiplied by the amount of moles squared, \(n^2\), as the overall amount of attractive forces is dependent on how much of the gas is there. This is then divided by \(V^2\) and added to pressure because the measured pressure is lower than expected.

The value \(b\) is the omitted volume per mole, and is related to the volume of the gas moles. This value must be included because real gases have volume. Therefore, the measured volume includes the volume of the molecules as well. In order for the equation to be accurate, the volume per mole, \(nb\), must be subtracted from the measured volume to represent the available volume within the gas.

\(a\) and \(b\) are constants for any particular gas (and even varies lightly with temperature and pressure), but they vary from gas to gas to allow for the different intermolecular forces, and molecular sizes. That means that, unfortunately, you no longer have a single equation that you can use for any gas. Fortunately, however, the ideal gas equation works well enough for most gases at ordinary pressures, as long as the temperature is reasonably high.

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