

Introduction

We've talked about the empirical gas laws and kinetic theory and how well they agree. There are some assumptions in kinetic theory that don't apply for real gases under certain conditions, and it has been observed that **the empirical gas laws themselves break down at extreme conditions**. We will discuss these conditions and the reasons why the empirical gas laws fail.

Attractions and repulsions

The kinetic theory of a gas states that there are no attractive or repulsive forces affecting the molecules in a gas (postulate 3). This isn't strictly true. There **are** attractions and repulsions between molecules- even molecules in the gas phase. At conditions where molecules would be **far apart**, we can ignore these forces and the empirical gas laws hold. The empirical gas laws work best at **low to moderate** pressures, where there are fewer collisions and not much opportunity for molecules to interact with each other.

When gas molecules are already moving fast, attractions and repulsions won't have much effect on the molecules. Think of trying to catch a baseball - is it easier to stop a pop fly or a line drive? Molecules move faster at **high temperature**, so the empirical gas laws work best at high temperature.

Summarizing, gases best follow the empirical gas laws at **high temperatures** and **low pressures**. At these conditions, gases are said to be **ideal** and obey the **ideal gas equation**, $PV=nRT$.

What conditions are "ideal"?

Practically speaking, most simple gases like O_2 and N_2 are **ideal** at normal conditions - room temperature and atmospheric pressure. If you increase the pressure and decrease the temperature, the gases become less and less **ideal** until they actually stop being gases at all - they **liquefy**. In the liquid state, attractive forces hold molecules close together. Liquids, of course, do not obey the empirical gas laws!

In this course, you should assume that a gas is under **ideal conditions** unless told otherwise. You should still be aware that at very low temperatures and high pressures, the empirical gas laws. The closer to the liquid state the gas is, the less ideal it behaves.

When conditions aren't "ideal"

When gases are close to liquefying, we can no longer ignore factors like attractive forces between gas molecules. In these situations, we use alternatives to the ideal gas equation. Some of these alternatives attempt to correct the ideal gas equation and include things that the ideal gas equation ignores.

An early attempt (1873) to correct the ideal gas equation is the van der Waals equation of

state. The van der Waals equation looks a lot like $PV=nRT$...

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

... where P , V , T , n , and R are the same as the ideal gas equation and “ a ” and “ b ” are additional parameters.

The pressure and volume terms in the original ideal gas equation have been modified. The parameter “ a ” depends on **attractive forces** in the gas state, and the parameter “ b ” depends on the **size of individual gas molecules**. Both of these parameters also depend – unlike any terms in the ideal gas law – on the identity of the gas molecules. Each gas will have different values of “ a ” and “ b ”. Carbon dioxide will be different from water vapor, which will be different from helium.

We won't bother calculating gas properties with the van der Waals equation in this class, but it's worth it to look at the equation to see how you can correct for conditions where the ideal gas assumptions don't apply.

Summary

In this note pack, we've noted that real gases behave like ideal gases (i.e. they obey the gas laws) at conditions similar to the conditions you're used to living in - moderate temperatures and pressures. Gases obey the gas laws even more exactly at low pressures and high temperatures. These conditions simulate the conditions that molecules are postulated to be in by kinetic theory.