

14.3.1: Real vs. Ideal Gases

Now, we need to expand on the qualifications with which we begin this chapter. We imagine that the results of a large number of experiments are available for our analysis. Our characterization of these results has been that all gases obey the same equations—Boyle’s law, Charles’ law, and the ideal gas equation—and do so exactly. This is an oversimplification. In fact they are always approximations. They are approximately true for all gases under all “reasonable” conditions, but they are not exactly true for any real gas under any condition. It is useful to introduce the idea of hypothetical gases that obey the classical gas equations exactly. In the previous section, we call the combination of Boyle’s law and Charles’ law the ideal gas equation. We call the hypothetical substances that obey this equation *ideal gases*. Sometimes we refer to the classical gas laws collectively as the *ideal gas laws*.

At very high gas densities, the classical gas laws can be very poor approximations. As we have noted, they are better approximations the lower the density of the gas. In fact, experiments show that the pressure—volume—temperature behavior of any real gas becomes arbitrarily close to that predicted by the ideal gas equation in the limit as the pressure goes to zero. This is an important observation that we use extensively.

At any given pressure and temperature, the ideal gas laws are better approximations for a compound that has a lower boiling point than they are for a compound with a higher boiling point. Another way of saying this is that they are better approximations for molecules that are weakly attracted to one another than they are for molecules that are strongly attracted to one another.

Forces between molecules cause them to both attract and repel one another. The net effect depends on the distance between them. If we assume that there are no intermolecular forces acting between gas molecules, we can develop exact theories for the behavior of macroscopic amounts of the gas. In particular, we can show that such substances obey the ideal gas equation. (We shall see that a complete absence of repulsive forces implies that the molecules behave as point masses.) Evidently, the difference between the behavior of a real gas and the behavior it would exhibit if it were an ideal gas is just a measure of the effects of intermolecular forces.

The ideal gas equation is not the only equation that gives a useful representation for the interrelation of gas pressure—volume—temperature data. There are many such *equations of state*. They are all approximations, but each can be a particularly useful approximation in particular circumstances. We discuss *van der Waal’s equation* and the *virial equations* later in this chapter. Nevertheless, we use the ideal gas equation extensively.

We will see that much of chemical thermodynamics is based on the behavior of ideal gases. Since there are no ideal gases, this may seem odd, at best. If there are no ideal gases, why do we waste time talking about them? After all, we don’t want to slog through tedious, long-winded, pointless digressions. We want to understand how real stuff behaves! Unfortunately, this is more difficult. The charm of ideal gases is that we can understand their behavior; the ideal gas equation expresses this understanding in a mathematical model. Real gases are another story. We can reasonably say that we can best understand the behavior of a real gas by understanding how and why it is different from the behavior of a (hypothetical) ideal gas that has the same molecular structure.

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