

## 10.12: The Second Law and the Properties of Ideal Gases

We make extensive use of the principle that the energy of an ideal gas depends only on temperature when only pressure–volume work is possible. In Chapter 2, we consider the Joule experiment, which provides weak evidence that this principle is correct. In the Joule experiment, no temperature change is observed during the adiabatic free expansion of a gas whose behavior is approximately ideal at the initial temperature and pressure. While this observation supports the principle, the accuracy attainable in the Joule experiment is poor. Otherwise, the most compelling evidence for this principle that we have developed is the theoretical relationship between the pressure–volume product of an ideal gas model and the mean-square velocity of its molecules. We derive this relationship from the Maxwell-Boltzmann distribution law for gas velocities and use the ideal gas equation to find that the mean squared velocity depends only on temperature.

To appreciate the importance of this principle, let us review some of the important steps in our development of the second law. In Chapter 7, we observe that, since its energy depends only on temperature,  $C_V$  for an ideal gas must also depend only on temperature; this follows immediately from the definition,  $C_V = (\partial E / \partial T)_V$ . In Chapter 9, we use the conclusion that  $C_V$  depends only on temperature in our development of the relationships among the heat, work, volume, and temperature changes for an ideal gas traversing a Carnot cycle. In considering these relationships, we observe that the values of the terms  $q^{rev} / T$  for the steps in this cycle sum to zero, as required for a state function. This leads us to define entropy by the differential expression  $dS = dq^{rev} / T$  and to infer that the entropy so defined is a state function. Reasoning from the machine-based statement of the second law, we conclude that this inference is correct.

That the energy of an ideal gas depends only on temperature is therefore of central importance to the internal consistency of the thermodynamic theory we have developed. It is easy to demonstrate this internal consistency. From the ideal gas equation and the relationships developed earlier in this chapter, we can show that the quantities  $(\partial E / \partial V)_T$ ,  $(\partial E / \partial P)_T$ ,  $(\partial H / \partial V)_T$ ,  $(\partial H / \partial P)_T$ ,  $(\partial C_V / \partial V)_T$ , and  $(\partial C_P / \partial P)_T$  are all identically zero.

The fact that our theory passes this test of internal consistency is independent of the properties of real gases. However, since we want to make predictions about the behavior of real gases, we need to be able to measure these quantities for real gases. Moreover, because we want to understand the properties of real gases in terms of their molecular characteristics, we want to be able to interpret these quantities for real gases using real-gas models that explain the differences between real gas molecules and ideal gas molecules. The van der Waals equation of state provides a simple model for the effects of attractive and repulsive molecular interactions. In the next section, we first consider simple qualitative arguments about the effects of intermolecular interactions on the energy of a real gas. We then investigate these effects for a van der Waals gas. We see that the van der Waals model and our qualitative arguments are consistent.

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