

2.9: Temperature and the Ideal Gas Thermometer

In [Section 2.2](#) we suppose that we have a thermometer that we can use to measure the temperature of a gas. We suppose that this thermometer uses a liquid, and we define an increase in temperature by the increase in the volume of this liquid. Our statement of Charles' law asserts that the volume of a gas is a linear function of the volume of the liquid in our thermometer, and that the same linear function is observed for any gas. As we note in [Section 2.8](#), there is a problem with this statement. Careful experiments with such thermometers produce results that deviate from Charles' law. With sufficiently accurate volume measurements, this occurs to some extent for any choice of the liquid in the thermometer. If we make sufficiently accurate measurements, the volume of a gas is not exactly proportional to the volume of any liquid (or solid) that we might choose as the working substance in our thermometer. That is, if we base our temperature scale on a liquid or solid substance, we observe deviations from Charles' law. There is a further difficulty with using a liquid as the standard fluid on which to base our temperature measurements: temperatures outside the liquid range of the chosen substance have to be measured in some other way.

Evidently, we can choose to use a gas as the working fluid in our thermometer. That is, our gas-volume measuring device is itself a thermometer. This fact proves to be very useful because of a further experimental observation. To a very good approximation, we find: If we keep the pressures in the thermometer and in some other gaseous system constant at low enough values, both gases behave as ideal gases, and we find that the volumes of the two gases are proportional to each other over any range of temperature. Moreover, this proportionality is observed for any choice of either gas. This means that we can define temperature in terms of the expansion of any constant-pressure gas that behaves ideally. In principle, we can measure the same temperature using any gas, so long as the constant operating pressure is low enough. When we do so, our device is called the **ideal gas thermometer**. In so far as any gas behaves as an ideal gas at a sufficiently low pressure, any real gas can be used in an ideal gas thermometer and to measure any temperature accurately. Of course, practical problems emerge when we attempt to make such measurements at very high and very low temperatures.

The (very nearly) direct proportionality of two low-pressure real gas volumes contrasts with what we observe for liquids and solids. In general, the volume of a given liquid (or solid) substance is not exactly proportional to the volume of a second liquid (or solid) substance over a wide range of temperatures.

In practice, the ideal-gas thermometer is not as convenient to use as other thermometers—like the mercury-in-glass thermometer. However, the ideal-gas thermometer is used to calibrate other thermometers. Of course, we have to calibrate the ideal-gas thermometer itself before we can use it.

We do this by assigning a temperature of 273.16 K to the triple point of water. (It turns out that the melting point of ice isn't sufficiently reproducible for the most precise work. Recall that the triple point is the temperature and pressure at which all three phases of water are at equilibrium with one another, with no air or other substances present. The triple-point pressure is 611 Pa or 6.03×10^{-3} atm. See [Section 6.3](#).) From both theoretical considerations and experimental observations, we are confident that no system can attain a temperature below absolute zero. Thus, the size³ of the kelvin (one degree on the Kelvin scale) is fixed by the difference in temperature between a system at the triple point of water and one at absolute zero. If our ideal gas thermometer has volume V at thermal equilibrium with some other constant-temperature system, the proportionality of V and T means that

$$\frac{T}{V} = \frac{273.16}{V_{273.16}}$$

With the triple point fixed at 273.16 K, experiments find the freezing point of air-saturated water to be 273.15 K when the system pressure is 1 atmosphere. (So the melting point of ice is 273.15 K, and the triple-point is 0.10 C. We will find two reasons for the fact that the melting point is lower than the triple point: In [Section 6.3](#) we find that the melting point of ice decreases as the pressure increases. In [Section 16.10](#) we find that solutes usually decrease the temperature at which the liquid and solid states of a substance are in phase equilibrium.)

If we could use an ideal gas in our ideal-gas thermometer, we could be confident that we had a rigorous operational definition of temperature. However, we note in [Section 2.8](#) that any real gas will exhibit departures from ideal gas behavior if we make sufficiently accurate measurements. For extremely accurate work, we need a way to correct the temperature value that we associate with a given real-gas volume. The issue here is the value of the partial derivative

$$\left(\frac{\partial V}{\partial T} \right)_P$$

For one mole of an ideal gas,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{V}{T}$$

is a constant. For a real gas, it is a function of temperature. Let us assume that we know this function. Let the molar volume of the real gas at the triple point of water be $V_{273.16}$ and its volume at thermal equilibrium with a system whose true temperature is V be V_T . We have

$$\int_{273.16}^T \left(\frac{\partial V}{\partial T}\right)_P dT = \int_{V_{273.16}}^{V_T} dV = V_T - V_{273.16}$$

When we know the integrand on the left as a function of temperature, we can do the integration and find the temperature corresponding to any measured volume, V_T .

When the working fluid in our thermometer is a real gas we make measurements to find $(\partial V/\partial T)_P$ as a function of temperature. Here we encounter a circularity: To find $(\partial V/\partial T)_P$ from pressure-volume-temperature data we must have a way to measure temperature; however, this is the very thing that we are trying to find.

In principle, we can surmount this difficulty by iteratively correcting the temperature that we associate with a given real-gas volume. As a first approximation, we use the temperatures that we measure with an uncorrected real-gas thermometer. These temperatures are a first approximation to the ideal-gas temperature scale. Using this scale, we make non-pressure-volume-temperature measurements that establish $(\partial V/\partial T)_P$ as a function of temperature for the real gas. [This function is

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V + \mu_{JT} C_P}{T}$$

where C_P is the **constant-pressure heat capacity** and μ_{JT} is the **Joule-Thomson coefficient**. Both are functions of temperature. We introduce C_P in [Section 7.9](#). We discuss the Joule-Thomson coefficient further in [Section 2.10](#) below, and in detail in [Section 10.14](#). Typically $V \gg C_P$, and the value of $(\partial V/\partial T)_P$ is well approximated by $V/T = R/P$. With $(\partial V/\partial T)_P$ established using this scale, integration yields a second-approximation to the ideal-gas temperatures. We could repeat this process until successive temperature scales converge at the number of significant figures that our experimental accuracy can support.

In practice, there are several kinds of ideal-gas thermometers, and numerous corrections are required for very accurate measurements. There are also numerous other ways to measure temperature, each of which has its own complications. Our development has considered some of the ideas that have given rise to the concept⁴ that temperature is fundamental property of nature that can be measured using a thermodynamic-temperature scale on which values begin at zero and increase to arbitrarily high values. This thermodynamic temperature scale is a creature of theory, whose real-world counterpart would be the scale established by an ideal-gas thermometer whose gas actually obeyed $PV = nRT$ at all conditions. We have seen that such an ideal-gas thermometer is itself a creature of theory.

The current real-world standard temperature scale is the **International Temperature Scale of 1990 (ITS-90)**. This defines temperature over a wide range in terms of the pressure-volume relationships of helium isotopes and the triple points of several selected elements. The triple points fix the temperature at each of several conditions up to 1357.77 K (the freezing point of copper). Needless to say, the temperatures assigned at the fixed points are the results of painstaking experiments designed to give the closest possible match to the thermodynamic scale. A variety of measuring devices—thermometers—can be used to interpolate temperature values between different pairs of fixed points.

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