

PV diagram

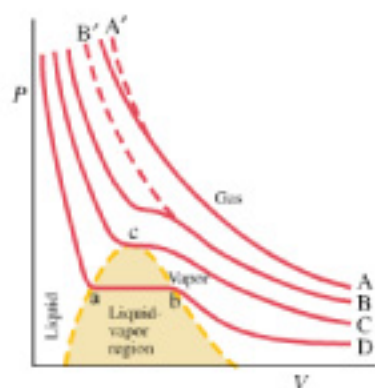


FIGURE 13-19 PV diagram for a real substance. Curves A, B, C, and D represent the same gas at different fixed temperatures ($T_A > T_B > T_C > T_D$).

Let us look at a graph of pressure plotted against volume for a given amount of gas. On such a “PV diagram,” Fig. 13-19, each point represents an equilibrium state of the given substance. The various curves (labeled A, B, C, and D) show how the pressure varies as the volume is changed at constant temperature for several different values of the temperature. The dashed curve A' represents the behavior of a gas as predicted by the ideal gas law; that is, $PV = \text{constant}$. The solid curve A represents the behavior of a real gas at the same temperature. Notice that at high pressure, the volume of a real gas is less than that predicted by the ideal gas law. The curves B and C in Fig. 13-19 represent the gas at successively lower temperatures, and we see that the behavior deviates even more from the curves predicted by the ideal gas law (for example, B'), and the deviation is greater the closer the gas is to liquefying.

To explain this, we note that at higher pressure we expect the molecules to be closer together. And, particularly at lower temperatures, the potential energy associated with the attractive forces between the molecules (which we ignored before) is no longer negligible compared to the now reduced kinetic energy of the molecules. These attractive forces tend to pull the molecules closer together so at a given pressure, the volume is less than expected from the ideal gas law. At still lower temperatures, these forces cause liquefaction, and the molecules become very close together.

Curve D represents the situation when liquefaction occurs. At low pressure on curve D (on the right in Fig. 13-19), the substance is a gas and occupies a large volume. As the pressure is increased, the volume decreases until point b is reached. Beyond b, the volume decreases with no change in pressure; the substance is gradually changing from the gas to the liquid phase. At point a, all of the substance has changed to liquid. Further increase in pressure reduces the volume only slightly—liquids are nearly incompressible—so on the left the curve is very steep as shown. The shaded area under the dashed line represents the region where the gas and liquid phases exist together in equilibrium.

Curve C in Fig. 13-19 represents the behavior of the substance at its **critical temperature**; the point c (the one point where this curve is horizontal) is called the **critical point**. At temperatures less than the critical temperature (and this is the definition of the term), a gas will change to the liquid phase if sufficient pressure is applied. Above the critical temperature, no amount of pressure can cause a gas to change phase and become a liquid: no liquid surface forms. The critical temperatures for various gases are given in Table 13-2. Scientists tried for many years to liquefy oxygen without success. Only after the discovery of the critical point was it realized that oxygen can be liquefied only if first cooled below its critical temperature of -118°C .

Often a distinction is made between the terms “gas” and “vapor”: a substance below its critical temperature in the gaseous state is called a **vapor**; above the critical temperature, it is called a **gas**.

The behavior of a substance can be diagrammed not only on a PV diagram but also on a PT diagram. A PT diagram, often called a **phase diagram**, is

Critical point

Vapor vs. gas

Phase diagram (PT)

TABLE 13-2 Critical Temperatures and Pressures

Substance	Critical Temperature		Critical Pressure (atm)
	$^\circ\text{C}$	K	
Water	374	647	218
CO ₂	31	304	72.8
Oxygen	-118	155	50
Nitrogen	-147	126	33.5
Hydrogen	-239.9	33.3	12.8
Helium	-267.9	5.3	2.3