

10.13: Critical Temperature and Pressure

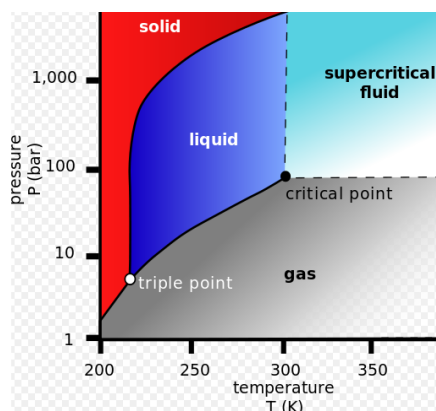
Suppose we seal a pure liquid and its vapor in a strong glass tube and heat it to a very high temperature. As we increase the temperature, the vapor pressure will rise. (It is not a good idea to heat a liquid this way unless you are sure the container can withstand the increased pressure.) The rising vapor pressure corresponds to a greater number of molecules in the limited volume of the vapor phase. In other words, the vapor becomes considerably denser. Eventually we reach a temperature at which the density of the vapor becomes the same as that of the liquid. Since liquids are usually distinguished from gases on the basis of density, at this point both have become identical. The temperature at which this occurs is called the **critical temperature**, and the pressure is called the **critical pressure**.

The accompanying videos illustrate what happens experimentally in the case of Chlorine. In the first video, as the temperature nears the critical temperature, liquid and vapor become very similar in appearance and the meniscus between them becomes difficult to distinguish. Finally, at the critical temperature the meniscus disappears completely. Above the critical temperature the sample is quite uniform and it is difficult to know whether to call it a liquid or a gas.



In the second half of the video, the flask is brought back below the critical temperature. The speed of gas molecules decreases to a point where intermolecular forces can cause a liquid phase to condense out. The meniscus reappears, and the Chlorine separates back again into a liquid and vapor phase.

Once a gas is above its critical temperature, it is *impossible* to get it to separate into a liquid layer below and a vapor layer above no matter how great a pressure is applied, as can be seen in the graph below. On the graph, once the temperature is higher than 300 K, it is not possible to revert to liquid form. Increasing the pressure only leads to the transition from gas to supercritical fluid.



Oxygen, for instance, is well above its critical temperature at room temperature. If we increase the pressure on it to a few thousand atmospheres, its density becomes so high that we are forced to classify it as a liquid. Nevertheless as we increase the pressure, there is no point at which drops of liquid suddenly appear in the gas. Instead the oxygen gradually changes from something which is obviously a gas to something which is obviously a liquid (a supercritical fluid). Conversely, if we gradually relax the pressure, there is no point at which the oxygen will start to boil.

The following table lists the critical temperatures and critical pressures for some well-known gases and liquids. Such data are often quite useful. Many gases are sold commercially in strong steel cylinders at high pressures. The behavior of the gas in such a cylinder depends on whether it is above or below the critical temperature. The critical temperature of propane, for instance, is 97°C, well above room temperature. Thus propane in a high-pressure cylinder consists of a mixture of liquid and vapor, and you can sometimes hear the liquid sloshing about inside.

Table 10.13.1 *Critical Temperatures and Pressures of Some Simple Substances.*

Critical Temperatures and Pressures of Some Simple Substances			
Name	Critical Temperature (K)	Critical Pressure (MPa)	Critical Pressure (atm)
Hydrogen (H)	33.2	1.30	12.8
Neon (Ne)	44.5	2.7	26.9
Nitrogen (N)	126.0	3.39	33.5
Carbon dioxide (CO ₂)	304.2	7.39	73.0
Propane (C ₃ H ₈)	370	4.23	41.8
Ammonia (NH ₃)	405.5	11.29	111.5
Water (H ₂ O)	647.1	22.03	217.5

The pressure of the gas in such a cylinder will be the vapor pressure of propane at namely, 9.53 atm (965.4 kPa). As long as there is some liquid left in the cylinder, the pressure will remain at 9.53 atm. Only when all the liquid has evaporated the pressure begin to drop. At that point the cylinder will be virtually empty. A very different behavior is found in the case of a cylinder of oxygen. Since oxygen is above its critical temperature at 20°C, the cylinder will contain a uniform fluid rather than a liquid-vapor mixture. As we use up the oxygen, the pressure will gradually decrease to 1 atm, at which point no more O₂ will escape from the cylinder.

The principles discussed in the preceding paragraph apply to the aerosol sprays most of us encounter every day. Such spray cans contain a small quantity of the active ingredient—hair conditioner, deodorant, shaving cream, and the like—and a large quantity of propellant. The propellant is a substance, such as propane, whose critical temperature is well above room temperature. Therefore it can be liquefied at the high pressure in the spray can.

When the valve is opened, the vapor pressure of the liquid propellant causes the active ingredient and the propellant to spray out of the can. As long as liquid propellant remains, the pressure inside the can will be constant (it will be the vapor pressure), and the spray will be reproducible. It should be obvious why such cans always bear a warning against throwing them in a fire—vapor pressure increases more rapidly at [higher temperatures](#), and so heating an enclosed liquid is far more likely to produce an explosion than heating a gas alone. (The latter case was described in an [earlier example](#).)

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