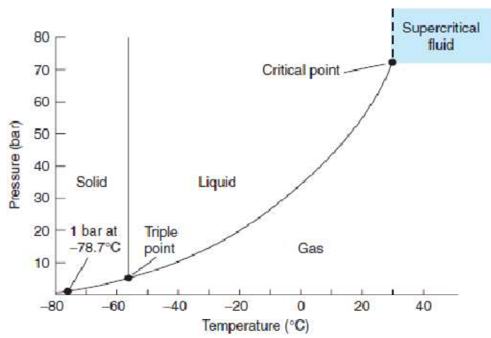
18th Week

BOX 24-3 "Green" Technology: Supercritical Fluid Chromatography

In the phase diagram for carbon dioxide, solid CO_2 (Dry Ice) is in equilibrium with gaseous CO_2 at a temperature of −78.7°C and a pressure of 1.00 bar. The solid *sublimes* without turning into liquid. Above the *triple point* at −56.6°C, liquid and vapor coexist as separate phases. For example, at 0°C, liquid is in equilibrium with gas at 34.9 bar. Moving up the liquid-gas boundary, we see that two phases always exist until the *critical point* is reached at 31.3°C and 73.9 bar. *Above this temperature, only one phase exists, no matter what the pressure.* We call this phase a **supercritical fluid** (Color Plate 29). Its density and viscosity are between those of the gas and liquid, as is its ability to act as a solvent.



Phase diagram for CO_2.

An interesting supercritical fluid to demonstrate is SF_6.[16] The photographs at the right show different changes as fluid is warmed and cooled through its supercritical temperature.

Supercritical fluid chromatography with a mixture of CO_2 and organic solvent is a "green" technology that reduces organic solvent use by up to 90% for the separation of kilograms of compounds and enantiomers in the pharmaceutical industry.[17] The low viscosity of the supercritical fluid also permits faster flow to increase productivity. Though CO_2 is a weak solvent by itself, when mixed with some organic solvent, it is capable of dissolving a variety of compounds.

Supercritical fluid chromatography provides increased speed and resolution, relative to liquid chromatography, because of higher diffusion coefficients of solutes in supercritical fluids. Unlike gases, supercritical fluids can dissolve nonvolatile solutes. When pressure is released, the solvent turns to gas, leaving the solute in the gas phase for easy detection. Carbon dioxide is the supercritical fluid of choice for chromatography because it is compatible with flame ionization and ultraviolet detectors, it has a low critical temperature, and it is nontoxic.

Equipment for supercritical fluid chromatography is similar to that for HPLC with packed columns or open tubular columns. Eluent strength is increased in HPLC by gradient elution and in gas chromatography by raising the temperature. In supercritical fluid chromatography, eluent strength is increased by making the solvent *denser* by increasing the pressure. The chromatogram shows a density-gradient elution.

Critical constants

Compound	Critical temperature (°C)	Critical pressure (bar)	Critical density (g/mL)
Argon	−122.5	47	0.53
Carbon dioxide	31.3	73.9	0.448
Sulfur hexafluoride	45.6	37.0	0.755
Ammonia	132.2	113.0	0.24
Diethyl ether	193.6	36.8	0.267
Methanol	240.5	79.9	0.272
Water	374.4	229.8	0.344