hydrocarbons form a type I system with a plait point, so paraffin-free aromatics cannot be obtained by refluxing some of the solvent-free extract product.

In the lower section of the extractor, medium- and high-boiling paraffins are displaced from the extract phase by contact with a low-boiling hydrocarbon fraction prepared by distillation of the extract. Water is present in this system and forms a low-boiling azeotrope with the lighter hydrocarbons, so the distillation is actually an azeotropic distillation (see Chap. 19). Vapors from the column are condensed and separated into two phases, and the hydrocarbon phase is returned to the extractor as backwash. In the lower section of the extractor, enough stages are provided for nearly complete transfer of the medium and heavy paraffins to the raffinate phase. The extract leaves saturated with light hydrocarbons, but these are removed in the azeotropic distillation column.

Solvent is recovered in the second distillation column, which is a vacuum steam-distillation column, with reflux of the organic phase to get high-purity aromatics. The final column is a multistage extraction column, where water is used to wash the solvent from the raffinate. There is a closed cycle for water to minimize solvent loss, and a small amount of water can be tolerated in the extraction solvent.

The backwash stream is sometimes called countersolvent or reflux, but the term "reflux" should be reserved for streams having the same composition as the product. The backwash need not be a low-molecular-weight material; in one version of the Sulfolane process, the backwash is a heavy paraffinic fraction, which is easily removed from both extract and raffinate.

SUPERCRITICAL FLUID EXTRACTION

Certain compounds may be separated from solids or liquids by extraction with a solvent held at a pressure and temperature above the critical point of the solvent. Such a process, when used with either solids or liquids, is known as supercritical fluid extraction. In addition to its selective dissolving power, a supercritical fluid has several advantages over conventional liquid solvents. Its density and viscosity are low, and the diffusivities of solutes in it are high—about 100 times greater than those in ordinary liquids. Consequently, the supercritical fluid easily penetrates porous or fibrous solids. Solutes can be recovered from a supercritical fluid merely by changing the temperature or the pressure, although other ways are also used. The chief disadvantage of supercritical fluid extraction is the high pressure required.

PHASE EQUILIBRIA. A useful solvent for supercritical extraction, especially in food processing, is carbon dioxide, which has a critical point of 31.06°C and 73.8 bars (1070 $\mathrm{lb}_f/\mathrm{in.}^2$). The phase diagram for pure CO_2 (Fig. 20.16) shows the equilibrium regions of solid, liquid, and gas and the conditions under which a supercritical fluid exists. In the supercritical region there is no distinction between liquid and gas and no phase transition from one to the other; the supercritical fluid acts like a very dense gas or a light, mobile liquid.

Solubility and selectivity in a supercritical fluid are strong functions of temperature and pressure. For nearly total extraction of solutes by supercritical

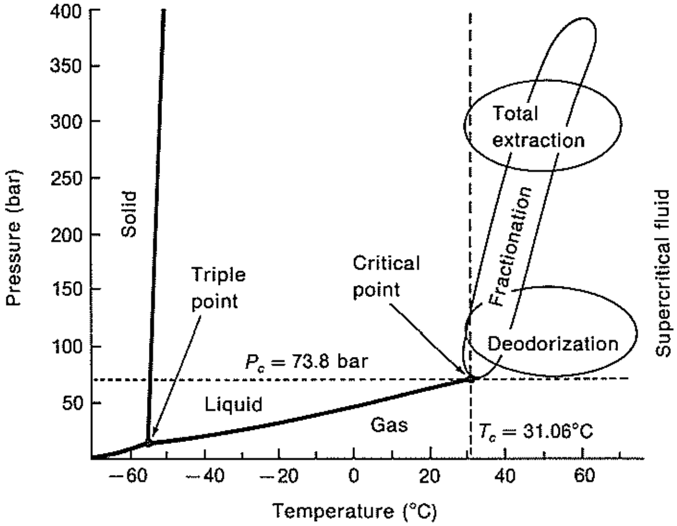

FIGURE 20.16
Phase diagram for carbon dioxide, illustrating regions useful for food-processing applications.[11]

CO_2, as indicated in Fig. 20.16, the highest pressure is used, since here the solubilities are highest. The loaded solvent may then be passed through a series of separation vessels in which the temperature or pressure is changed stepwise, to give what is called multistage fractionation. For selective removal of odor-producing volatile components conditions close to the critical point are advantageous. Here the solubilities are smaller but the selectivity for the most volatile compounds is much higher.

Equilibrium phase diagrams for one or more solutes in supercritical CO_2 and other solvents can be very complicated.[2] Relatively little equilibrium information has been published; this lack coupled with the cost of high-pressure equipment and the difficulties of scaleup have to date limited the commercial applications of supercritical fluid extraction.

COMMERCIAL PROCESS.[11] A practical example of a supercritical fluid extraction process is the decaffeination of coffee. Coffee beans are first soaked in water to make the extraction more selective and then are loaded into an extraction vessel through which supercritical CO_2 is circulated to dissolve the caffeine. In a separate scrubbing vessel the caffeine is transferred from the CO_2 to water, also at high pressure. Extraction is continued until the caffeine content of the beans, originally 0.7 to 3 percent, is reduced to less than 0.02 percent. At the end of the batch cycle the water is depressurized and distilled away from the caffeine. In an alternative process the caffeine is separated from the CO_2 by adsorption on activated carbon. In either case the supercritical fluid extraction is said not to affect the characteristic flavor and aroma of the coffee.