Chemical separation (chemical engineering)

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A process used to purify substances or to isolate them from other substances. In industrial applications, the ultimate goal is the isolation of a product of given purity. Most industrial chemical processes involve a separation stage. This may involve a preliminary purification stage before the reaction process, or a final stage involving the separation of the desired product. Two well-known processes are distillation and crystallization.

Distillation and crystallization

The distillation process is based on the relative volatilities (that is, vapor pressures) of the components. It involves the heating of the feed material (which is to be separated) in a boiler. The heated vapors enter a column and partially condense on the many plates or trays. These plates have a large surface area to facilitate the equilibrium between the vapor and the liquid. The vapor in the column is richer in the more volatile (lighter) component. As the vapor travels up the column, this process of enrichment is enhanced. The final stage of the distillation process is the complete condensation of this vapor as it leaves the column. This is done by cooling the vapor to a temperature well below its boiling point. The result is a separation of a light component or components (the condensate) from heavy components left in the boiler. The overall separation achieved depends not only on the relative vapor pressures of the components but also on the number of trays in the column. In spite of the high energy demands of the distillation process, 90% of all separation processes in the chemical and petrochemical industries worldwide are distillation processes. See also: DISTILLATION; VAPOR PRESSURE.

In the crystallization process, separation is based on the relative solubilities of the components. The separation of sea salt from water is usually done by crystallization through the evaporation of the water either by heating or by using solar energy. See also: CRYSTALLIZATION.

Thermodynamics offers a proper understanding of all separation processes. Not only is it useful in quantifying the separation of components, but thermodynamic relationships are also vital in the design of industrial separation plants.
Basic theory

When an equilibrium exists between phases (solids, liquids, or gases), the chemical potential, \( \mu_i \), for species \( i \) in each phase may be expressed by Eq. (1).

\[
\mu_i(\text{solid}) = \mu_i(\text{liquid}) = \mu_i(\text{gas})
\]  

(1)

For a vapor-liquid equilibrium process (distillation) this equality results in Eq. (2),

\[
y_i / x_i = \gamma_i P_i^0 / P_{\text{(total)}}
\]

(2)

the relationship between the vapor composition \( (y_i) \) and the liquid composition \( (x_i) \) at a temperature \( T \). Here, \( \gamma_i \) is the activity coefficient of species \( i \), \( P_i^0 \) is the vapor pressure of pure \( i \) at \( T \), and \( P_{\text{(total)}} \) is the total vapor pressure of the system. It is this ratio that defines the separating efficiency and is known as the distribution coefficient. Other relationships can be derived for other phase separation processes (such as crystallization), and in every case the results will be based on Eq. (1). See also: CHEMICAL EQUILIBRIUM.

Separation processes

Industrial separation processes involve all the possible phase pairs apart from solid-solid, which is kinetically too slow for useful applications (Table 1). See also: ADSORPTION OPERATIONS.

Supercritical fluid extraction. The process of supercritical fluid extraction is a relatively new separation technique. Interest in it is based on the high solubility of some solids in the supercritical solvent, the high degree of selectivity, the ease of separating the required product, and the ease with which the solvent can be recovered. To understand the process requires an understanding of the critical point. See also: SUPERCRITICAL FLUID.

The liquid-vapor phase line (as opposed to the solid-vapor and solid-liquid phase lines) for pressure and temperature discontinues at a certain point (Fig. 1), known as the critical point. At temperatures above the critical temperature \( T_c \), it is not possible to liquefy the gas by pressure alone. In other words, it is impossible to produce a liquid meniscus from the gas phase by pressure alone. At conditions above the critical temperature and pressure \( (P_c) \), the gas is known as a supercritical fluid (Fig. 1).

For an understanding of the general process, it is best to look at the most important supercritical fluid extraction process, the decaffeination of coffee using carbon dioxide. Carbon dioxide fluid, at a pressure of 200 atm (20 megapascals) and a temperature of 50°C (122°F) [in excess of \( P_c \) (\( \text{CO}_2 \)) = 73 atm and \( T_c \) (\( \text{CO}_2 \)) = 31°C (88°F)], is pumped through the extraction cell containing the ground coffee in a mesh basket. The supercritical carbon dioxide has the unique capacity for dissolving only the caffeine and not the compounds that give coffee its taste
The carbon dioxide fluid, now containing dissolved caffeine, leaves the cell, and its pressure is reduced to below its critical value. As a result, the fluid vaporizes to a gas and the solid caffeine precipitates as it is not soluble in gaseous carbon dioxide. The coffee without caffeine is recovered and the carbon dioxide...
compressed and recycled. Apart from the simplicity of the process and the fact that it is done at a low temperature (it apparently does not affect the coffee taste or flavor), its main advantage is that the solvent is a natural substance and if any residue is left in the coffee it will be harmless. This is not true for some other decaffeination processes which use organic solvents such as methylene chloride.

Carbon dioxide is the most popular solvent used in supercritical fluid extraction. This is largely due to its relatively low critical pressure and temperature, and the ease with which the supercritical state can be achieved. It is extensively used in the perfume industry, where high temperatures would destroy the chemicals. It is used, for example, in separating oxygenated compounds (such as geranyl acetate), valuable as perfumes, from lemon oil, which consists largely of terpenes of low value, such as limonene.

Water has received much attention as a possible solvent for supercritical fluid extraction. Its critical properties are, however, too high for convenience \( P_c = 218 \text{ atm} (22.1 \text{ MPa}) \) and \( T_c = 374^\circ \text{C} (705^\circ \text{F}) \), but it does have the interesting property of dissolving nonpolar liquids such as hexane. This is not possible at ambient temperature and pressure.

**Membrane separation processes.** An important new technology uses membranes to effect separation. The membrane is usually a thin plastic film (0.1–5 micrometers) on a thick porous and inert support layer \( (100–500 \mu \text{m}) \) \[\text{Fig. 2}\]. The driving force pushing the permeate across the membrane is invariably a pressure difference between the feed mixture and the permeate. The membranes are made of synthetic polymers such as poly(vinyl alcohol), for separating water and alcohol liquids; polyurethane, for separating aromatic liquids from cycloalkane liquids; polyimides, for separating gases such as oxygen and nitrogen; and cellulose acetate, for separating pure water from seawater. *See also: Membrane separations.*
When the feed and the permeate are both gases, the process is known as gas separation. The pressure difference is usually between 10 and 100 atm (1 and 10 MPa), with the pressure of the permeate being about 1 atm (0.1 MPa). When the feed and permeate are liquids, the process is reverse osmosis, and it is best known for desalination of dilute aqueous solutions such as seawater, brackish water, and industrial wastewater. The pressure applied on the feed side is usually 80–100 atm (8–10 MPa), while the permeate is kept at ambient pressure. If the feed is a liquid under its own saturation pressure and the permeate is a gas or vapor kept at a low pressure ($5 \times 10^{-3}$ atm or 0.5–2 kPa) by a suitable vacuum pump, the process is known as pervaporation. The permeate is recovered in a cooling trap. See also: WASTEWATER REUSE; WATER DESALINATION.

Perhaps the main advantage of the membrane technique is that it is possible to tailor-make a membrane for a particular separation. Its limitations include chemical breakdown of the membrane with time and its slowness. The mechanism of the process is complex and involves properties such as the relative solubilities and relative diffusion coefficients of the feed chemicals in the membrane (Table 2).

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### Bibliography


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Additional Readings


Chemical Engineers’ Resource Page

Laboratory for Process Equipment, Delft University of Technology