10

Distillation

Of all the unit operations discussed, distillation is the one most unique to chemical engineering. It is the most widely used unit operation in the oil and petrochemical industries and is used in virtually any chemical process where liquids of differing compositions must be separated, solvent must be recovered, and hydrocarbon feedstocks such as crude oil and natural gas liquids must be separated into useful components for further processing.

The basic concepts of distillation are quite simple. It is a means of separating two or more liquids based upon their differences in boiling point and vapor pressure. Every liquid has a boiling point at a given pressure. For example, water boils at 100°C at atmospheric pressure. Between 0°C and 100°C, its vapor pressure increases until it equals the atmospheric pressure, at which point it boils. The temperature at which this happens will be a function of pressure. Each liquid has a vapor pressure curve that shows the relationship between the vapor pressure of a liquid and its temperature. Figure 10.1 shows vapor pressure curves for a number of different liquid compounds. "Normal" boiling points are normally referred to as the boiling point at atmospheric pressure. Pressure will affect the boiling point of any liquid.

The vapor pressure curve data for water is shown in Figure 10.2.

These graphs also illustrate a few additional physical property characteristics that exist for water and may exist with other liquids. Water has what is called a "triple point." This is a pressure and temperature at which all three phases (solid, liquid, and gas) can coexist. For water, this is around 4 mm absolute pressure. The "critical point" is where the vapor pressure of the material will not allow its condensation.

Figure 10.3 shows the vapor pressure information for ethanol (C_2H_5OH) at atmospheric pressure.

Since there is a difference in vapor pressure and boiling point, it is conceivable that we could use distillation to separate these two materials. How? Since the shape of the curves is different and there is a difference in boiling point (ethanol boils at a lower temperature (78°C) than water (100°C)), we would

Chemical Engineering for Non-Chemical Engineers, First Edition. Jack Hipple.

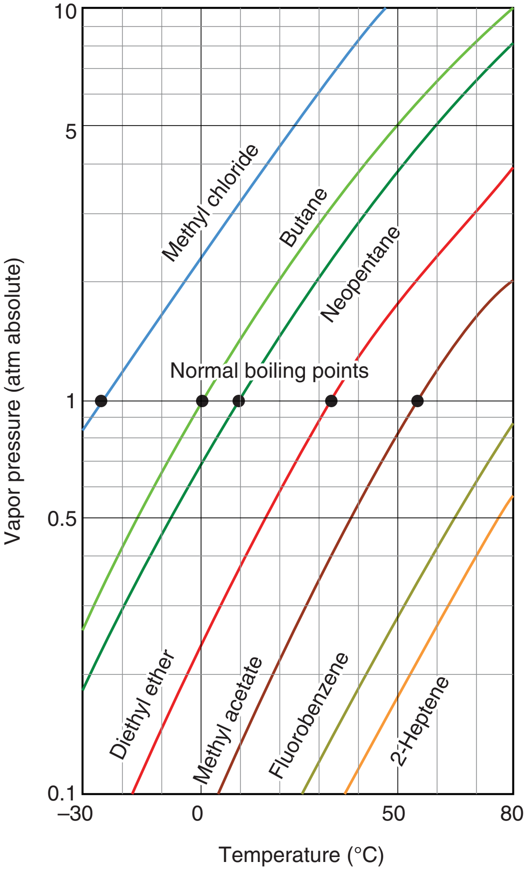


Figure 10.1 Boiling points of organic compounds. Source: Cmglee, https://commons.wikimedia.org/wiki/File:Vapor_pressure_chart.svg. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

expect that if we took a mixture of ethanol and water and heated it, the overhead vapors would contain more ethanol than water. That's exactly what happens. If we were to then condense this vapor mixture, we would now have a liquid mixture with a higher concentration of ethanol than we started with. If we then boiled this mixture again, the overhead vapor would be still richer in ethanol. Condensing and reboiling would continue this progression toward a nearly pure ethanol overhead stream. Conversely, the remaining liquid would become enriched (i.e., a higher concentration) with water, eventually producing a nearly pure water stream. This is the basic concept of distillation—boil, condense; boil, condense; boil, condense, etc. Done a sufficient number of times, we should be able to produce a nearly pure overhead stream of the lower

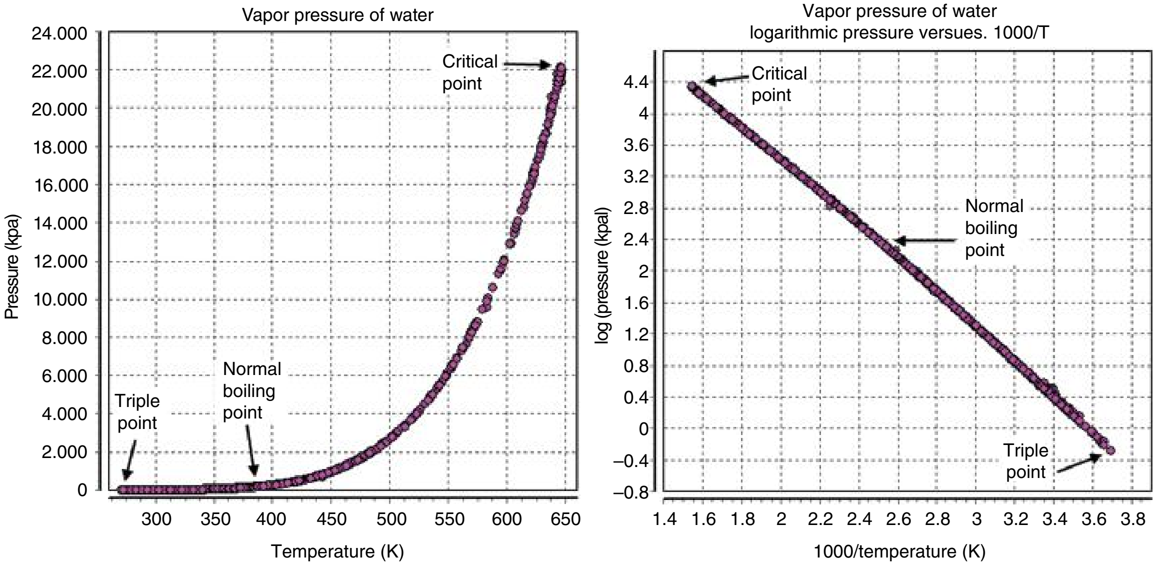


Figure 10.2 Water vapor pressure. Source: Wilfried, https://commons.wikimedia.org/wiki/File:Vapor_Pressure_of_Water.png. Used under CC BY 3.0, https://creativecommons.org/licenses/by/3.0/deed.en. ©Wikipedia.

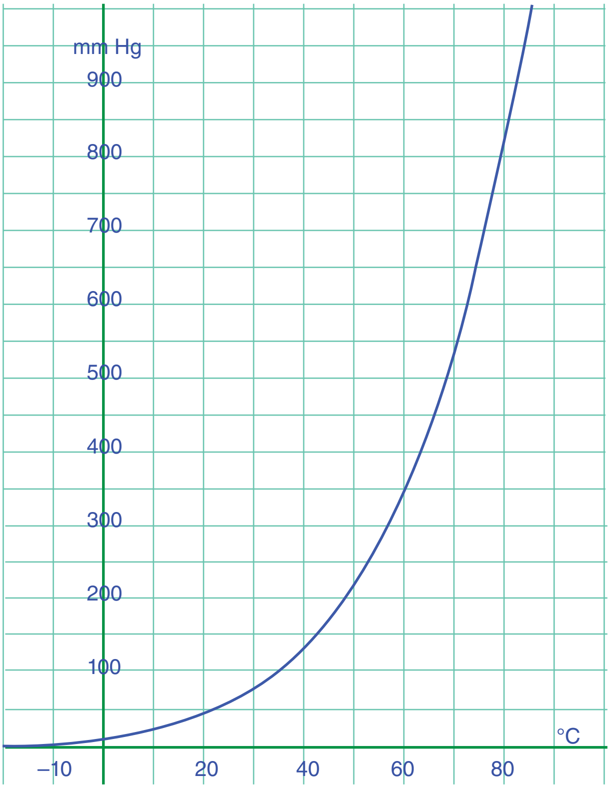


Figure 10.3 Vapor pressure of ethanol versus temperature.

boiling component and a nearly pure bottom stream of the higher boiling component as a "residue." In concept, two liquids with any difference in boiling point can be separated by distillation, but as we will see, it is frequently not that simple, although the basic concept is the same.

We can display this process as follows (the energy input is not shown, only the concentration changes), shown in Figure 10.4.

Now in order for this concept to be practical, more than one "stage" is needed, requiring the need to condense the more concentrated overhead vapor we have produced, condense it again (liquefy it), reboil it, and so on as many times as necessary to get the purity of the more volatile that we desire. We do this in a *distillation column*, which incorporates the vaporization and condensation in one process unit as shown in Figure 10.5.

Let's now discuss some of the fundamentals of distillation, the effect of physical properties, and some of the fundamental design parameters that are involved.

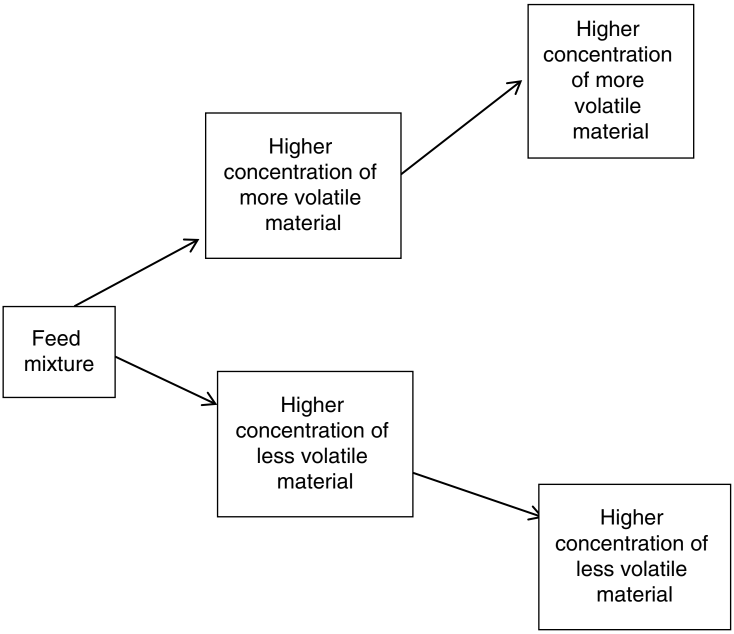
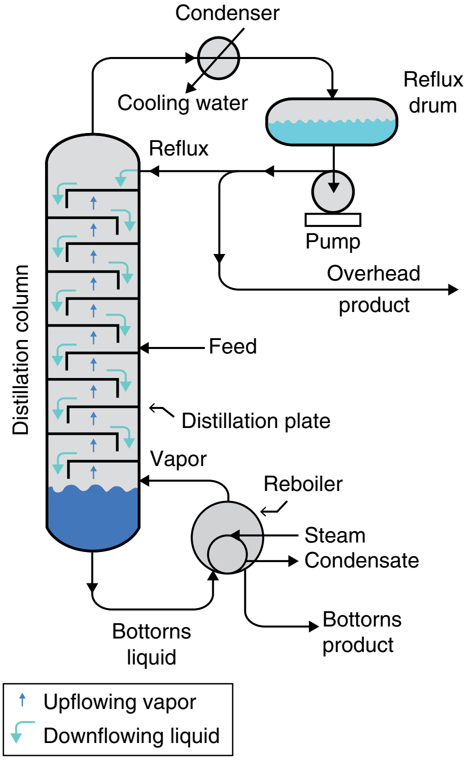


Figure 10.4 Concentrating by boiling and condensing.

Figure 10.5 Typical distillation system. Source: Sponk https://commons.wikimedia.org/wiki/File:Continuous_Binary_Fractional_Distillation.PNG. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.



Raoult's Law

Let's assume that we have one or more liquids in solution. How do we decide how much volatility (vapor pressure) is above the liquid for any of the components? For an ideal solution, we use Raoult's law:

$$P_a = x_a P^0$$

where P_a is the partial pressure or mole fraction in the vapor space above the solution, P^0 is the vapor pressure of "a" by itself (at the temperature of concern), and x_a is the mole fraction of component "a" in the solution. This equation applies only to ideal solutions (i.e., hydrocarbon mixtures) and not to solutions with significant molecular interaction (alcohols, aldehydes, ketones, etc.). In many cases, the data must be gathered with laboratory work or found in the literature.

Regardless of whether the solution is ideal or not, the sum of the component partial pressures ($P_a + P_b + P_c + \ldots.$), when boiling, must equal the total pressure in the system. If the sum does not equal, then there is inaccuracy with the data or measurements of concentration, temperature, or pressure.

With insoluble liquids such as CCl_4 and water, the principle still applies; the sum of the partial pressures must equal the total pressure in the system.

We can visualize Raoult's law on this graph, for a three-component system (this equation is valid regardless of whether the solution is ideal or not) as shown in Figure 10.6.

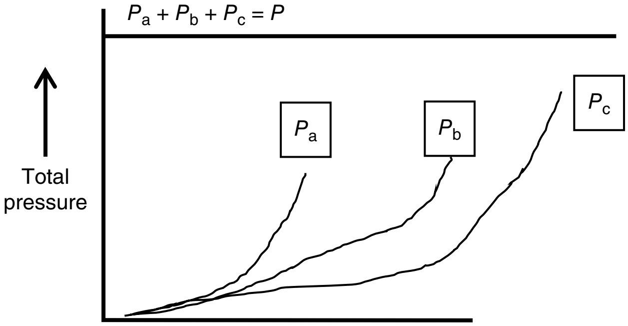


Figure 10.6 Raoult's law: total pressure = sum of partial pressures.

Another way of expressing this is that when the sum of all the partial pressures of the individual components in the mixture or solution equals the total pressure, the system will boil. The total pressure of the system will have a great effect on the boiling temperature.

Some other terms that we use to describe a volatile liquid system are the following:

Volatility is the ratio of the partial pressure of the component in the mixture divided by its mole fraction in the liquid. We can express this as

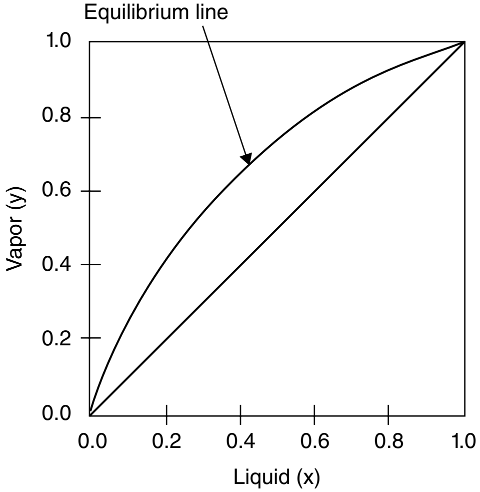
$$V_a = \frac{P_a}{X_a}$$

where V_a is the volatility of compound "a."

Relative volatility, "α," is the ratio of one component's volatility to another and is one of the key measures of how difficult it is to separate a mixture by distillation. This number tells us how difficult a distillation separation might be. If α is low, there is not much difference in the volatility of the compounds, and separation by distillation will be costly, but not necessarily impossible. If α is high, then distillation will be an economical choice, involving fewer trays (less tall column) and less energy.

We can visualize the volatility of a given compound on a simple y versus x graph, where y is the mole fraction of the component in the vapor phase versus the mole fraction in the liquid phase as shown in Figure 10.7.

Figure 10.7 Vapor–liquid equilibrium line.



The 45° line in this graph is simply a reference line showing where y and x have the same values. The larger the distance between the equilibrium line and this reference line, the greater the volatility (y/x) of the compound.

If we go back to the original description of distillation (boil, condense; boil, condense; boil, condense), we can visualize some equipment approaches to using the difference in volatility to increase the purity of the more volatile component while at the same time increasing the concentration of the less volatile component.

Batch Distillation

This would describe a batch process where a charge of a liquid mixture is charged into a vessel with a means for supplying heat (coils or jacket). As heat increases the temperature of the mixture, the more volatile component will come over in the vapor at a much greater concentration, proportional to the α of the mixture. As the more volatile component distills over, its concentration in the charge vessel will decrease and more of the less volatile component will distill over, reducing the purity of the overhead product. At some point, the specification for the overhead product will drop below specification, and the distillation will need to be stopped. This type of distillation is frequently used to remove a solvent from a batch-reaction process. (If a solvent is the only component coming overhead, this type of operation would be more appropriately called an evaporator, to be discussed later). The overhead vapor is condensed in a condenser/heat exchanger. An example of such a process is shown in Figure 10.8.

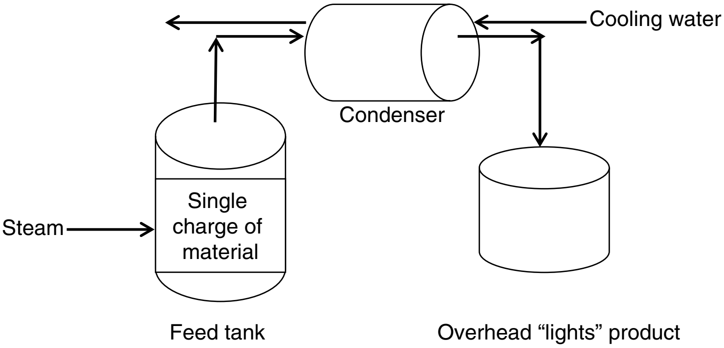


Figure 10.8 Batch distillation.

This process uses only one stage of "boil/condense" and so is suitable only for systems with a large relative volatility difference.

Flash Distillation

This is a continuous one-stage distillation process. The feed is continuous and product removals (top and bottom) are both done continuously. A simple flow sheet of this type of process is shown in Figure 10.9.

It is also likely that the feed to such a continuous one-stage flash distillation may be preheated, and it is also possible, in either of these cases, that vacuum may be used to reduce the boiling point of the solution.

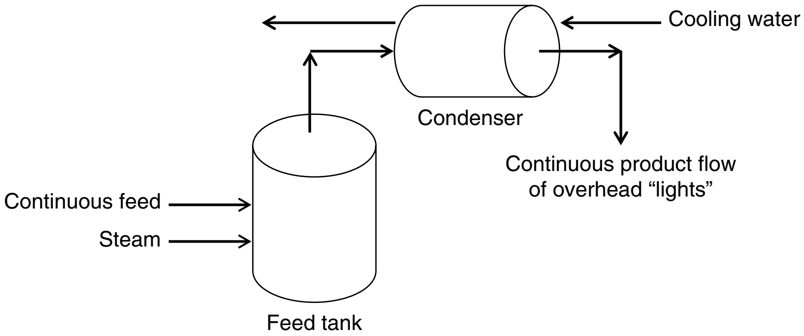


Figure 10.9 Continuous flash distillation.

Continuous Multistage Distillation

An example of a process diagram of a distillation column is shown in Figure 10.10.

As we can see, there are numerous design variables that need to be chosen. These include the method of contacting between vapor and liquid (this diagram shows what is known as a sieve tray), the internals within the column, the amount of reflux returned to the column (a reminder that unless we have reflux, we have no method for producing the "condense" mechanism to achieve more than one stage of separation), the nature and size of the heat exchangers (both top and bottom), and the height and diameter of the column.

Let's look at each of these in more detail:

1) Amount of reflux returned to the column to provide the necessary "condensing" part of the process. This will also directly affect the amount of reboiling at the bottom of the column. The choice of this ratio will affect what we call the "operating line" for the column, which is in effect, the line that graphically shows the mass balance and actual compositions of the liquid and gas flows at any particular point in the column. This is normally referred to as the *reflux ratio*, or the ratio of moles of material returned to the column divided by the moles taken off as product. We will see examples of this graphical display in the next section.
2) Method of contacting between the liquid and gas flows in the column. This can be either a tray or packings (the previous diagram shows a particular type of type). The packing material can be ceramic, plastic, or an inserted structure inside the column.
3) Nature of heat exchangers required at the top and bottom of the column. One will be a condenser (at the top, to produce product and generate reflux) and the other a reboiler (to provide the energy to boil mixtures prior to condensing).

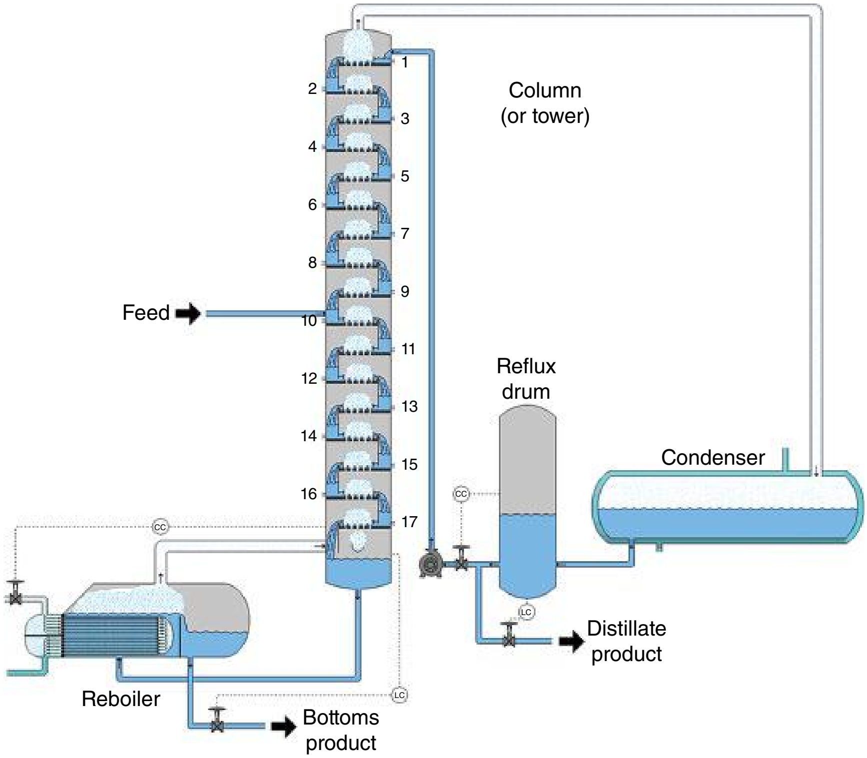


Figure 10.10 Traditional distillation process. Source: Guzman, https://commons.wikimedia.org/wiki/File:Distillation_Column_(Tower).png. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

4) Diameter of the column. This will be affected by the liquid and vapor flow rates, densities and viscosities of these streams, and the ratio of liquid to gas flow rates.
5) Height of the column. This will be primarily determined by the relative volatility of the materials being distilled, the purity of the overhead or bottoms stream required, and the reflux ratio.
6) Efficiency of contacting between the liquid and vapor flows in the column. This is affected by numerous variables including the design of the contacting system and the physical properties of the liquid and vapor, including density, surface tension, and viscosity.

Reflux Ratio and Operating Line

Recall why we need reflux at all. If we did not do this and took the overhead vapor off and then condensed it as the product, this would be the equivalent of a one-stage distillation. The amount we return to the column directly affects the number of trays or height of packing required. The more we return to the column, the more "boil/condense" we do and the shorter the column needs to be. At the same time, the higher flows used require the column to be wider in diameter, and/or a larger pressure drop is seen (high liquid and gas flows = higher pressure drop). The less we return, the less "boil/condense" we get (per stage of contact), thus requiring a taller column. There is a chemical engineering optimization between the capital cost of the column, its height and diameter, the cost of the heat exchangers, and the water and steam usage. There is no one correct design for a column; it will depend on the trade-off of cost and capital, energy and cooling water demands, required purity of the top and bottoms product, and occasionally height limitations within a building.

Though most all distillation column design is done via software programs, it is useful to envision what is going on inside the column via graphical analysis, which is how columns were designed prior to software program availability.

The operating line is a graphical display of the mass balance (the liquid and vapor compositions) versus height in the column. Its slope will change based on the reflux ratio within the column as well as whether we are describing the top (rectifying) section of the column (above the feed input location in Figure 10.10) or the bottom (stripping) section of the column (below the feed input location in Figure 10.10), as shown in Figure 10.11.

The upper operating line is basically a material balance line above the feed point and into the column and the product taken off the top. The lower operating line is the material balance between the feed and bottom product from the column. The slopes of these lines and where they intersect are determined by the amount of reflux, the reboiled vapor rate at the bottom, and the temperature of the feed into the column. The junction of the two lines is where the feed is introduced into the column. If the column is operated under total reflux (all the product is returned to the column), the two lines move downward to the 45° reference line until they intersect. The distance between the operating lines and the vapor–liquid equilibrium line gives us a feel for the number of

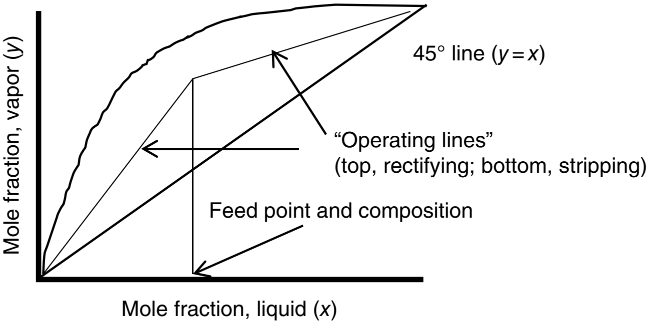


Figure 10.11 Graphical representation of distillation.

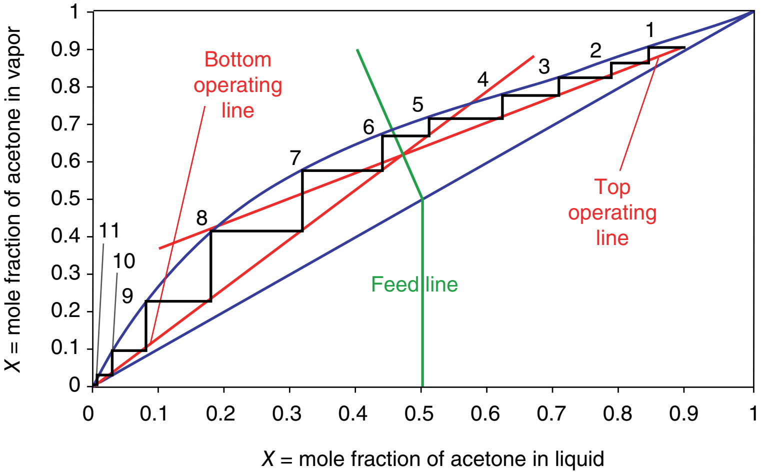


Figure 10.12 McCabe–Thiele diagram for acetone–ethanol distillation. Source: Chemical Engineering Progress, 3/12, pp. 35–41 and 6/13, pp. 27–35. Reproduced with permission of American Institute of Chemical Engineers.

stages (boil/condense) we need to produce the desired product purity at the top and the desired composition at the bottom of the column.

Such a column diagram for the separation of acetone and ethanol is shown in Figure 10.12. This type of diagram is known as a McCabe–Thiele diagram and is the best way to visualize what is occurring inside a distillation column.

At the other end of the spectrum, we could greatly increase the reflux, minimizing the number of trays and decreasing the height. However, the energy costs will go up and the column will need to be larger in diameter. The diagram for this choice is shown in Figure 10.13.

We have a trade-off between operating cost and capital to which there is no one answer. The design will be a choice based on the cost factors as viewed by the user of the column.

At the end of this extreme would be total reflux of the overhead product back to the column with no product taken off. This is frequently a start-up test done on a column during start-up and tells us the best performance the column will achieve at the same pressure. This condition maximizes the distance between the vapor–liquid equilibrium line and the “operating line,” which shows the actual compositions that should exist in the column at any stage or tray. At total reflux, the operating line overlaps exactly with the 45° reference line we discussed earlier.

This optimization of reflux ratio and height of column (number of contacting devices or amount of packing) can be represented as seen in Figure 10.14.

The extremes at each end of the curve represent the minimum reflux ratio that can be used to accomplish the separation (at maximum number of trays) and the minimum number of trays required. The shape of this curve will be a strong function of the relative volatility (α) discussed at the beginning of this unit.

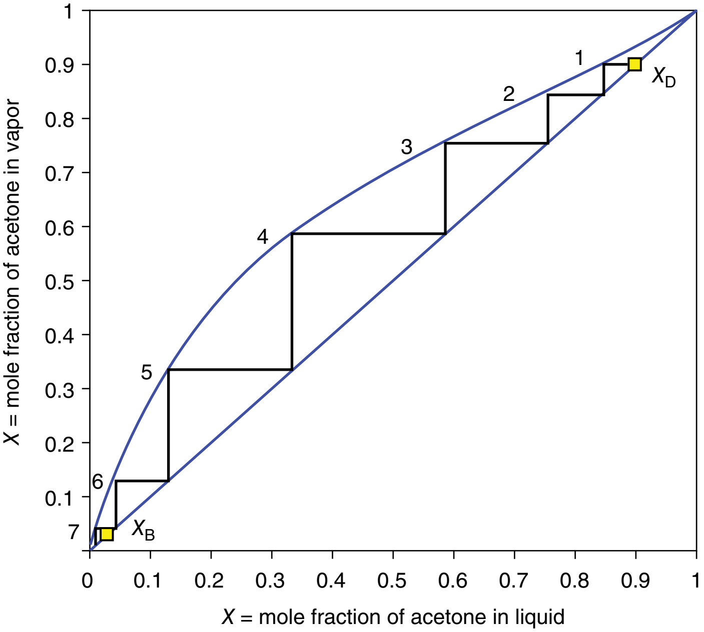


Figure 10.13 High reflux in distillation. Source: Chemical Engineering Progress, 3/12, pp. 35–41 and 6/13, pp. 27–35. Reproduced with permission of American Institute of Chemical Engineers.

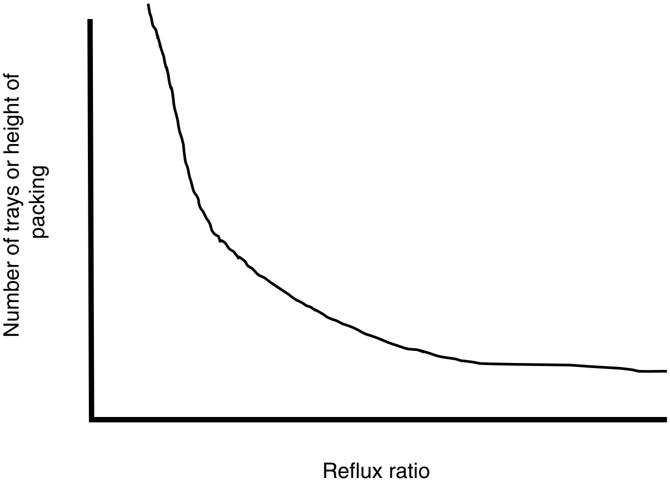


Figure 10.14 Number of trays versus reflux ratio in distillation.

Pinch Point

There is an interesting limitation at the low reflux extreme of column design. If the reflux rate is low enough, the operating/material balance line will intersect the vapor–liquid equilibrium curve as shown in Figure 10.15. Under these conditions, the column will produce no separation or change in composition as there is no driving force of composition difference. The reflux ratio, L/V ratio, vapor–liquid equilibrium data, and number of trays (or height of packing) are all connected and interact with each other in a design sense to produce a distillation column design.

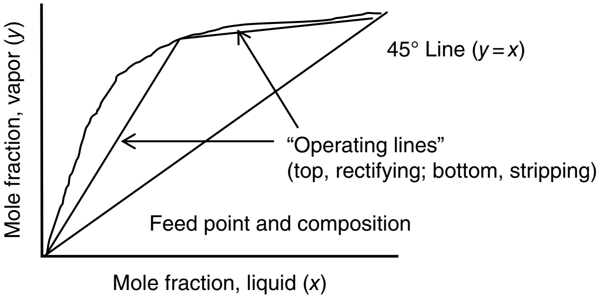


Figure 10.15 Graphical representation of a distillation pinch point.

The intersection of the lower and upper column operating lines at the vapor equilibrium line eliminates the driving force for separation. This graph represents the opposite of total reflux, where we don't reflux enough material back into the column to provide a driving force between the operating line and the vapor–liquid equilibrium line. The column becomes inoperable (but uses minimal energy and water to condense) in the same sense that a column on total reflux produces no product but uses the shortest tower.

Feed Plate Location

It is always best to introduce the feed into the column at a point where we calculate that composition to exist when the column is operating. This minimizes the energy and capital cost of "re-equilibrating" the feed to the conditions in the tower.

Column Internals and Efficiency

In all the discussions up until now, we have assumed that if the graphical design shows a certain number of trays, then that's the number we install. The real world is different. We are basically contacting liquids and gases in counter current flow using some kind of physical contacting mechanism. The efficiency of this contacting is affected by a large number of process and property variables:

1) Physical Properties. It is easy to visualize how differences in density and viscosity of the gases and liquids could affect how efficiently and completely a liquid and a gas would mix on a plate or within the voids of a packed bed. These properties may vary significantly from top to bottom of the column due to temperature gradients from top to bottom (recall the effect of temperature on viscosity discussed earlier). The density difference between the gas and the liquid, including those from top to bottom, will also affect the speed of mixing and equilibration. The graphs shown previously assume that perfect equilibrium is achieved at each stage prior to the next stage of contacting.
2) Column Internals. We can specify a certain number of trays or height of packing on the assumption that we get excellent and complete contacting between gas and liquid, but there are a number of reasons why this does not happen. These include plugging of holes in trays or plates with process contaminants and flow restrictions in any hydraulic or gas pathways. Also of concern is slow degradation in any support equipment holding trays, and packing in place.
3) Column Efficiency Measurements. The measurement of column efficiency can be done in a variety of ways. The first would be overall plate efficiency. We measure the actual performance in a pilot plant, and compare it to the predicted performance from previous calculations. For example, if the graphs or calculations show that 7 trays should be needed and 10 are actually needed, we can say that the overall tray efficiency is 70% and use this as a design factor for similar systems using similar materials. Another is to try to determine the actual efficiency of each individual plate or height of packing. This is much more appropriate if we expect large differences in density, viscosity, and liquid/gas ratio over the entire height of the column. This efficiency, known as the Murphree plate efficiency, would be integrated over the entire column height to determine the actual number of required trays.

We have mentioned occasionally the use of loose packing instead of trays. We will discuss this further, but another type of efficiency measurement is called the height equivalent to a theoretical plate (HETP). This is in effect a statement that x number of feet of packing provides the same degree of contact as one physically distinct tray.

Unique Forms of Distillation

There are several unique types of distillation used for various reasons:

1) Steam Distillation. Occasionally, an overhead product is desired that decomposes close to or below its normal boiling point that would exist at the top of a distillation column. If the product is not water soluble, steam can be introduced as a diluent, artificially lowering its boiling point.
2) Vacuum Distillations. Operating a distillation under vacuum will lower the boiling points and vapor pressures within the column. A vacuum distillation can produce the same effect as a steam distillation. With steam, there is an energy cost, increased capital costs, and a need to separate the product from the overhead steam. The vapor piping systems are also larger and more costly. Vacuum systems also cost more than atmospheric or pressure distillations.
3) Azeotropes and Azeotropic Distillation. Most of the time, azeotropes are considered barriers to achieving a high purity material, but if an azeotrope is identified that can withdraw an undesired compound (this is what is done by adding benzene to the 95% ethanol/water azeotrope) to a sufficient degree, then this can be a way around a limitation to achieving a desired purity of the product. A typical y versus x or vapor–liquid equilibrium diagram for two liquids has a diagram similar to what we have already seen (as in Figure 10.16).

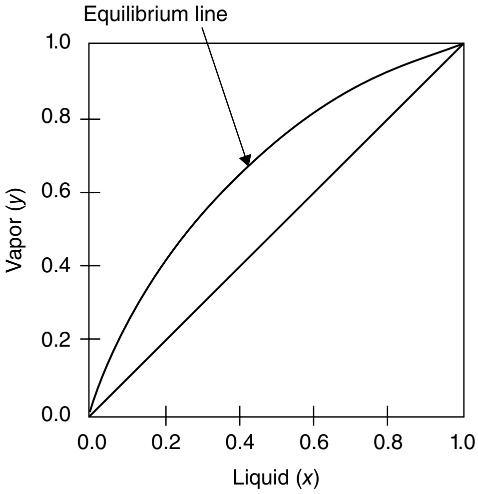


Figure 10.16 Vapor–liquid equilibrium for an ideal solution.

An *azeotrope* is a composition point where the boiled vapor has the same concentration as the liquid. This can occur when there are strong molecular interactions between liquid components. Combinations of polar compounds (water, alcohols, ketones, aldehydes) are most likely to exhibit this behavior. For normal hydrocarbons this is unlikely. It is best, however, not to assume anything and look up azeotropic compositions in available literature references. When an azeotrope occurs, it is not possible to obtain further change in composition, beyond this point, by boiling and condensing since the liquid and vapor have the same composition. In other words the y and x on the mole fraction diagrams we have displayed so far have the same value.

Azeotropes are, in effect, significant deviation from Raoult's law. The deviations can be either "positive" (the total component vapor pressure is more than calculated from Raoult's law) or "negative." If Raoult's law was represented as a straight line, then azeotropes would be represented as seen in Figure 10.17.

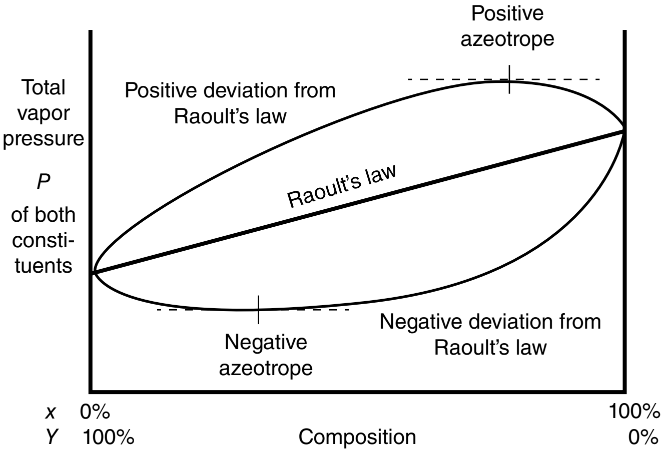


Figure 10.17 Azeotropic compositions: positive and negative. Source: Karlhahn, https://commons.wikimedia.org/w/index.php?curid=2685348. © Wikipedia.

An illustration of such a system, propanol–water, is shown in Figure 10.18. The azeotropic composition is around 70 mole%.

A similar azeotrope is seen for ethanol and water at 95.5% ethanol (Figure 10.19). A maximum boiling azeotrope will have a boiling point higher than predicted from Raoult's law and a minimum boiling azeotrope will have a boiling part lower than predicted. We can see this as we plot the boiling point of azeotropic mixtures versus composition. We will see either a positive deviation (higher BP) or negative deviation (lower BP) from an ideal solution calculation as shown in Figures 10.20 and 10.21.

Very frequently we will find that commercial products, such as ethanol and nitric acid, are sold and shipped at their azeotropic composition points (95.5% and 68%, respectively), since further changing the concentrations will involve added cost and complexity.

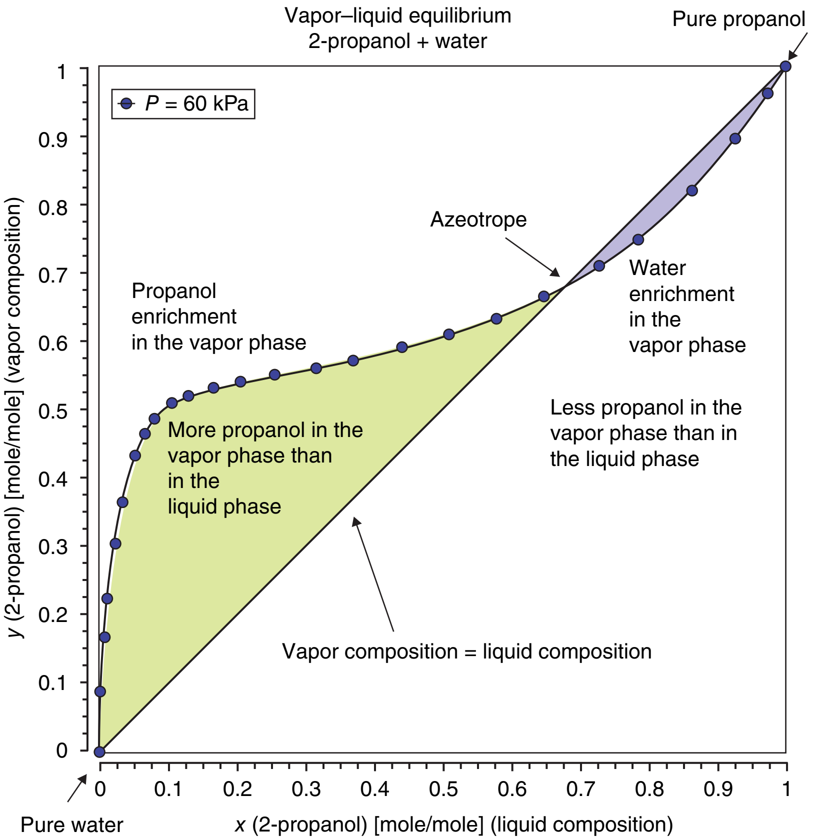


Figure 10.18 Azeotropic composition for a nonideal system. Source: Wilfried, https://commons.wikimedia.org/w/index.php?curid=9788841. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

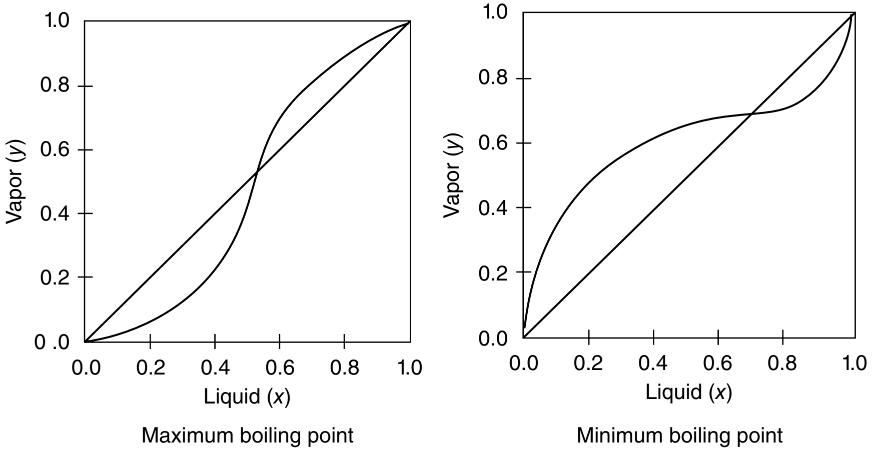


Figure 10.19 Maximum and minimum boiling azeotropes.

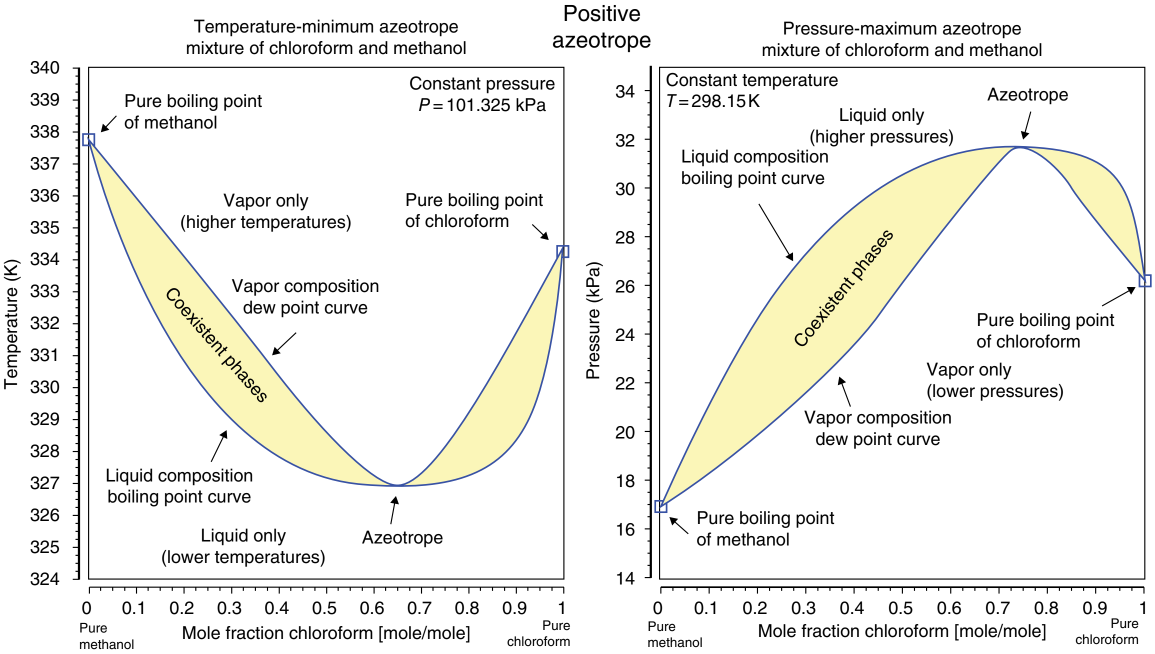


Figure 10.20 Positive azeotropes *T*–*x*–*y* diagram. Source: Wilfried, https://commons.wikimedia.org/w/index.php?curid=7437968. Used under CC BY-SA 3.0 https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

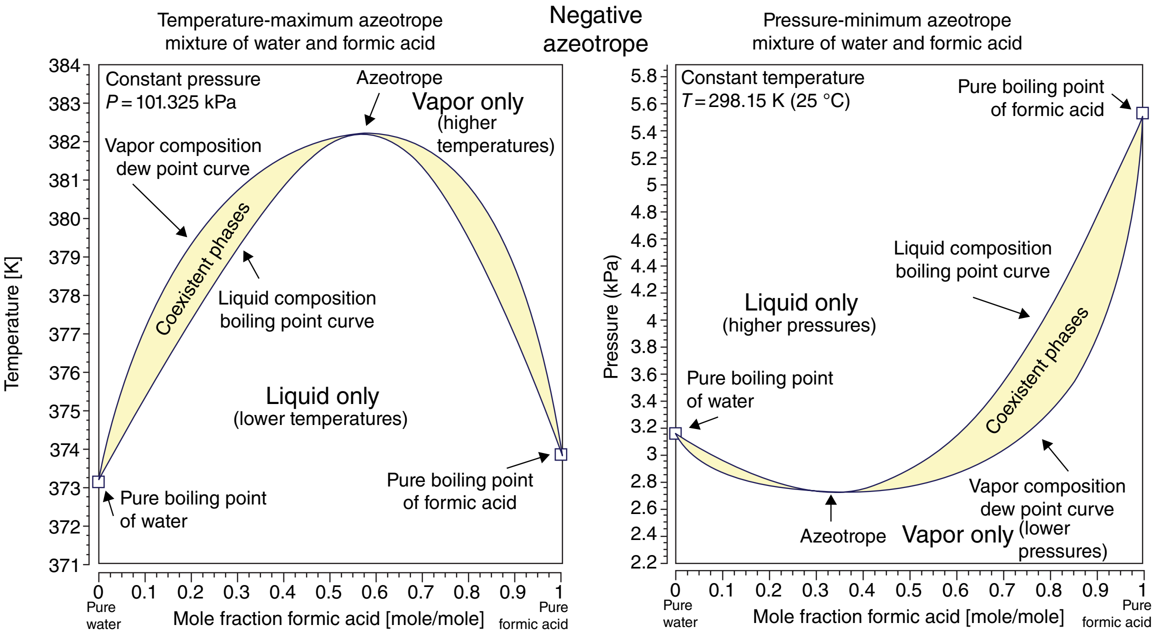


Figure 10.21 Minimum boiling azeotropes *T–x–y* diagram. Source: Wilfried, https://commons.wikimedia.org/wiki/File:Negative_Azeotrope.png. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

A way of dealing with an azeotropic system, if it is desired to produce a product beyond this composition, when the lighter boiling component is the limiting factor is to change the pressure in what is known as "pressure swing" distillation. In this situation, we change the pressure (moving toward either vacuum or pressure) to change the boiling point of the mixture, allowing the azeotropic point to be changed.

An example of such a process is shown in Figure 10.22.

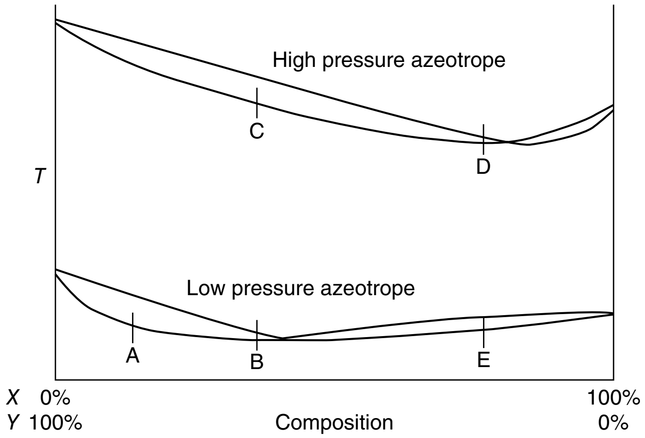


Figure 10.22 Using pressure change to break an azeotrope.

The separation of the 95–5% water azeotrope is a commercial example of the use of this technique, varying the pressure between atmosphere and 8 atmospheres to "jump" over the normal atmospheric azeotrope at 95%. Another approach to the azeotrope challenge, when one of the components is water, is to add salt to the water, raising its boiling point.

Another interesting way of using azeotropes is in a positive way, that is, introduce a third component that forms a multiple component azeotrope to remove a component from a binary mixture that is difficult to separate. Acetic acid and water have very close boiling points, and the introduction of ethanol to deliberately form the water/ethanol azeotrope discussed earlier removes the water and makes it easier to produce pure acetic acid.

Multiple Desired Products

In many cases, there is a feed mixture that needs to be separated into multiple streams of pure products. There are two basic approaches to this. One is, with sufficient knowledge of the vapor pressures as a function of composition, to withdraw side products at various heights within the column. This concept is used in separating the basic components of crude oil as illustrated in Figure 10.23. This illustration shows not only the distillation but also the uses for the various products. As we would expect, the lower boiling components are in the upper section of the column (LPGs, hydrocarbon feedstocks, gasoline) and the higher boiling components in the bottom half (diesel fuel, lubricants, asphalt factions, etc.).

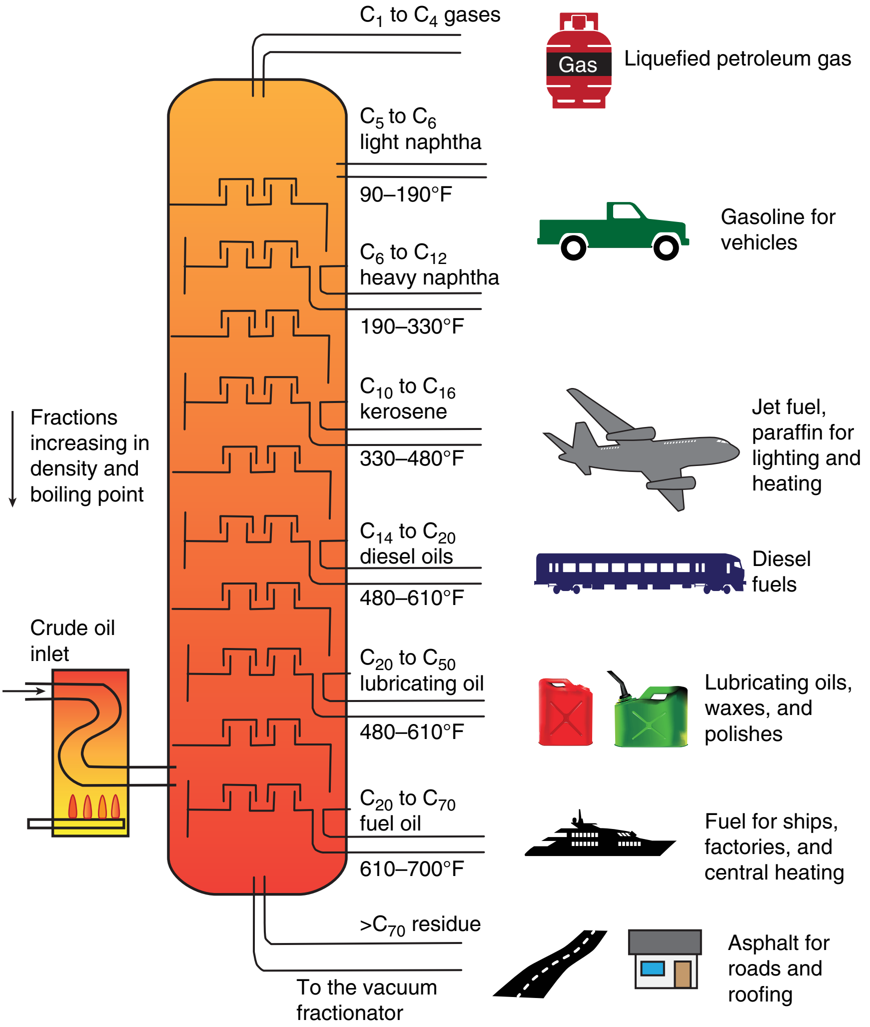


Figure 10.23 Crude oil distillation. Source: Chemical Engineering Progress, 11/12, pp. 32–38. Reproduced with permission of American Institute of Chemical Engineers.

Though not as well known by the public, the separation of air into its components such as oxygen, nitrogen, argon, carbon dioxide, and rare gases such as krypton is done in the same way, although the operating temperatures in the columns are several hundred degrees below zero and large amounts of insulation are used around process equipment.

Column Internals and Efficiencies

Regardless of what kind of distillation we are running, decisions about the type and method of contacting need to be made. As mentioned several times already, there is rarely one choice but a decision based on cost and practical aspects relating to the fluids and vapors being distilled, separated, and collected. The contacting can be done via trays or loose fill packing.

Tray Contacting Systems

There are basically three types of contacting trays: bubble cap, valve, and sieve:

1) Bubble cap trays are probably the oldest commercially used trays and allow the vapor rising up the column to "bubble through" the downflowing liquid to create the contacting, as shown in Figure 10.24.

   This type of tray provides intimate mixing but can be costly to fabricate. With dirty or high viscosity fluids, the ability of the cap to float up and down can be hindered, and cleaning can be a major challenge. If a cap is plugged off in some way, the vapor pressure drop will increase across the tray as we have the same amount of vapor trying to rise through fewer holes. Raising the pressure or pressure drop will affect the vapor–liquid equilibrium for the column as well as peripheral equipment performance. One excellent performance characteristic of these types of trays is their ability to minimize "weeping." This refers to the liquid on the tray to "weep" down into the tray below. Anything that promotes mixing between the trays defeats the whole purpose of distillation, which is to separate the vapor and liquid in distinct stages
2) Another type of tray is a sieve tray, which is basically a plate with holes in it, designed to have both the downcoming liquid and rising vapor go through the same hole, creating intimate mixing. This type of tray, shown in Figure 10.25, due to its low cost and ease of maintenance, has become the workhorse of the chemical industry.

   The major operating issue with sieve trays is the potential for weeping. Since there is no mechanical barrier to liquid downflow, as in the bubble cap design, there is greater possibility of plate-to-plate mixing, lowering the

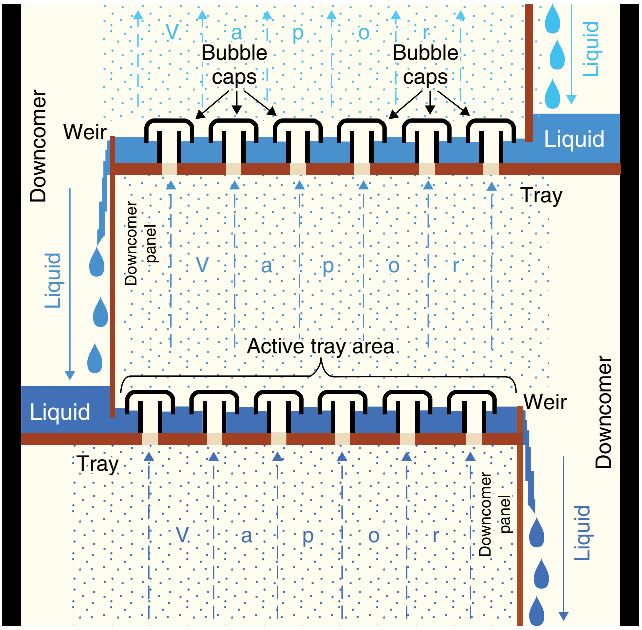


Figure 10.24 Bubble cap trays. Source: Pedlackes, https://commons.wikimedia.org/wiki/File:Bubble_Cap_Trays.PNG. Used under CC BY-SA 2.5, https://creativecommons.org/licenses/by-sa/2.5/deed.en. © Wikipedia.

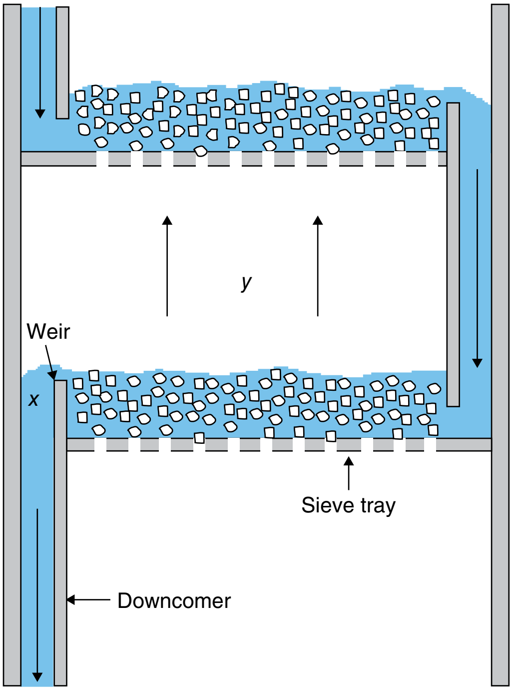


Figure 10.25 Sieve tray. Source: Reproduced with permission of Brigham Young University.

efficiency of the column's separation capability. Weeping is a much greater possibility at low operating rates as there may be insufficient upward vapor flow to maintain a liquid level on the tray.

Design variables for this type of tray include the spacing between trays, the height of the weir, the hole size, and the geometry of the downcomer. These will be affected by liquid and gas properties (density, viscosity) and the surface tension and tendency to foam. To repeat, any operating factor that causes mixing between trays defeats the entire purpose of the process, which is to separate the boiling and condensing aspects.

Another type of tray design is the valve tray, a hybrid between the bubble cap and sieve tray. Here the sieve tray holes have a mechanical sealing device internal to the tray, performing somewhat the same function as a bubble cap but in a less costly way to manufacture (see Figure 10.26).

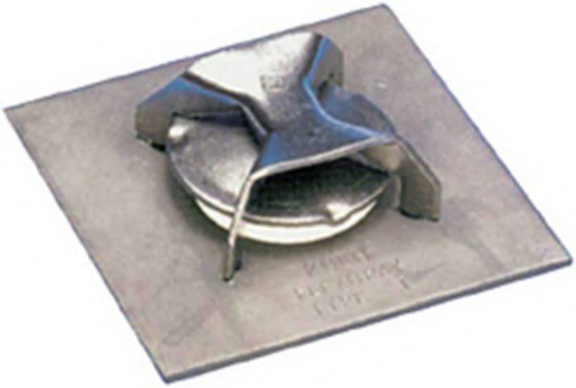


Figure 10.26 Valve tray. Source: Chemical Engineering Progress, 11/12, pp. 32–38. Reproduced with permission of American Institute of Chemical Engineers.

The "weeping" that would allow liquid to drop down through a tray opening and mix with the tray below can be influenced by a variety of fluid and process variables including vapor velocity, liquid density, liquid depth on the tray, and the differences in liquid and gas properties such as density and viscosity.

Another type of tray is a dual flow tray, which is usually angularly designed to allow gas and liquid to go through the same holes.

Packed Towers in Distillation

Instead of a discrete separation of gas/liquid contacting, it is also possible to have the gas and liquid flowing up and down the tower in a continuous way by filling the tower with loose fill packing. Examples of such packings are both random and structured. Random packings include Raschig rings, Pall rings, Intalox™ saddles, and a wide variety of other preformed ceramic, metal, and plastic shapes.

Figure 10.27 Tower packings. Source: Used with permission of Sulzer AG.

Packed towers used for distillation can have several advantages:

1) Lower Pressure Drop. This can mean easier separation of close boiling components and minimize the need for vacuum to separate heat-sensitive materials. This can also minimize the cost of vacuum equipment.
2) Materials from which loose fill packing can be manufactured, in combination with a corrosion resistant lined column, can better handle corrosive chemical systems.

There are a few disadvantages as well. With the large surface area, there is a tendency for liquid coming down the column to tend to gravitate toward the walls, so it is usually necessary to provide redistribution every 10–20 ft. down the column. The liquid is collected from the walls and redistributed to the center of the column. The degree to which this happens will be affected by density, viscosity, and surface tension of the liquid. Second, if ceramic packing is used, it is critical that, during start-up, the boxes in which this type of packing is normally shipped be gently dropped via a rope and gently tipped over. Ceramics are very brittle materials and, if dropped from a significant height, will shatter upon reaching the bottom of the column, resulting in small pieces that can clog support trays at the bottom of the column and cause excessive pressure drop.

Figure 10.28 Structured packing. Source: Used with permission of Sulzer AG.

Structured packing is a way of inserting fixed geometric shapes within the diameter of a column, as shown in Figure 10.28. These types of packing inserts have extremely low pressure drop and are highly efficient but also are more expensive than either tray or loose fill packed towers for distillation. Given their high efficiency and low pressure drop, they can provide separation capability in situations where very low relative volatilities exist, height limitations on columns may exist, or product decomposition is of concern.

We have mentioned pressure drop across tower packings a number of times. Pressure drop across distillation towers, from large to small, would be:

1) Bubble cap
2) Valve and dual flow
3) Sieve trays
4) Loose packing
5) Structured packing

There are some practical issues in the operation and design of packed towers, both for distillation as well as absorption and stripping (to be discussed in Chapter 11):

Plumb tests must be done during start-up. This is more important with a packed tower than a tray tower. With the much higher surface area, there is a tendency for the downflowing liquid to gravitate toward the walls vs. the direction it first starts. This is also why occasional redistribution of liquid flow is required in a packed tower.

Leveling tests should also be done on tray towers for the same reason.

Support plates for packed towers must be unobstructed to avoid high pressure drop. With ceramic packings, due to their inherent brittleness, installation must be done carefully by gently tipping over the typical several cubic feet boxes at the bottom (or their next layer) and dump them from the top of the tower.

Distillation reboilers We have already reviewed the basics of heat transfer and heat exchangers. At the bottom of a distillation tower, heat input is required to boil up the heavy liquid and provide the "boil" part of the boil/condense distillation mechanism. A general diagram of this type of exchanger is seen in Figure 10.29.

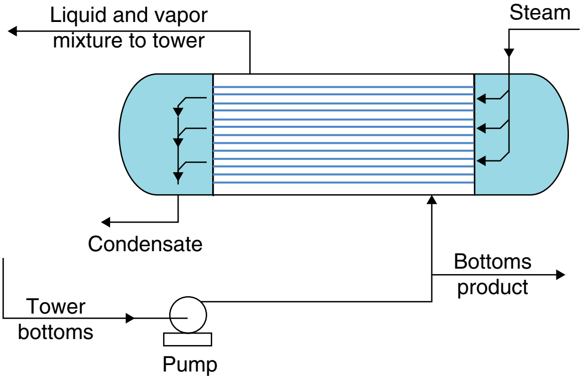


Figure 10.29 Reboiler configuration. Source: Mbeychok, https://commons.wikimedia.org/wiki/File:ForcedCirculation.png. Used under CC BY-SA 3.0, https://creativecommons.org/licenses/by-sa/3.0/deed.en. © Wikipedia.

It may also be possible, with a low heat requirement, to supply the reboiling needed with a jacket around the bottom of the distillation column or by tubes inserted into the bottom of the column. The design of these types of heat exchangers is fundamentally no different than we discussed earlier.

Summary

Distillation is a unique unit operation that allows us to separate liquids based on their differences in vapor pressure and boiling points. There is a wide range of design choices, both in the types of internals and contacting devices, as well as an optimization of the physical and geometric parameters of the column. Exact choices will be affected by capital and energy cost variables, geometric limitations, and the current and future quality specification requirements for the various products we can produce via this chemical engineering unit operation.

Coffee Brewing and Distillation
The way we normally brew coffee does not involve distillation processes in any way, so we'll come back to this example in the next chapter.

Discussion Questions

1 How many distillation processes are run in your complex? What is their purpose? How many are run with varying compositions of feed material? How is the operation varied in response to these changes?

2 How is the reflux ratio determined and controlled? How do limitations in cooling water affect the operation of overhead condensers?

3 What are the specifications on the overhead and bottoms products? How tightly must they be controlled? How are the reflux ratio and feed rates varied to stay within specifications? What opportunities might be presented if a higher purity overhead product could be produced?

4 How was the current mechanical design (tray type, packing, condenser, and reboiler types) determined? Have these decisions been reevaluated over time?

5 Is the minimum reflux ratio known?

6 What are the impacts of changing utility pressures and temperatures?

Review Questions (Answers in Appendix with Explanations)

1 Distillation is a unit operation based on differences in:
A __Solubility
B __Density
C __Vapor pressure
D __Crystallinity

2 A material, solution, or mixture boils when:
A __The solution is rolling around and bubbling violently
B __The sum of all the partial pressures equals the total pressure
C __It's mad
D __The partial pressures exceed the external pressure by 10%

3 The key determinant in how easy it is to separate a mixture by distillation is the:
A __Volatility of the relatives of the mixture
B __Whether the relatives want to be separated
C __Ability to heat selectively the most volatile component
D __Relative volatility of its various components

4 On a graphical plot of a distillation system, the 45° line represents:
A __The vapor phase and liquid phase having the same composition
B __All phases are created equal
C __One component has 45% more volatility than another
D __One component has 45% less volatility than another

5 In a two-component distillation system where the relative volatility is displayed on a y–x graph, a higher relative volatility will be displayed, versus a 45° line, as:
A __No difference in the lines
B __A small difference in the lines
C __A large difference between the lines
D __Price of company, suppliers, and customer stocks that change minute by minute

6 In a batch distillation system, the maximum number of stages of separation possible is:
A __One
B __Depends on relative volatility
C __A function of heating rate
D __A function of the batch size

7 In a conventional continuous distillation system, the top of the column will always contain:
A __A higher concentration of the less volatile component
B __A higher concentration of the more volatile component
C __A higher concentration of the less dense material
D __A higher concentration of the material desired by the customer

8 Returning reflux to a distillation column allows:
A __More energy to be wasted
B __More cooling water to be wasted
C __Multiple vaporizations and condensations, yielding purer top and bottom products
D __More capital expenditures to be wasted on a reboiler and condenser

9 Increasing reflux to a distillation column results in:
A __Higher pressure drop
B __Purer overhead product
C __More cooling water to be used
D __All of the above

10 Decreasing reflux to a distillation column results in all except:
A __Less cooling water and reboiler steam use
B __Lower overhead purity
C __Less intensive process control
D __Pressure drop across the column decreases

11 The "operating line" of a distillation column represents a graphical display of:
A __The line drawn by the process operators when the process computers are offline
B __The mass balance within the column
C __The line of code that operates the column
D __The line that no one on the operating floor is allowed to cross

12 Varying the reflux ratio in a distillation column allows us to:
A __Adjust the quality of overhead and bottom products
B __React to changes in feed compositions
C __Allow process adjustments to upstream and downstream processes
D __All of the above

13 Vacuum distillation can result in all but:
A __Increased energy use
B __Separation of azeotropes
C __Separation of high boiling components
D __Smaller distillation columns

14 Azeotropes are:
A __Special mixtures of chemicals that come from the tropics
B __Mixtures of chemicals with close boiling points
C __Mixtures of materials whose vapor composition when boiled is the same as the starting liquid
D __Impossible to separate

15 Ways of separating azeotropes include:
A __Changing pressure
B __Using an alternative separation technique
C __Adding a third component that shifts the vapor–liquid equilibrium
D __All of the above

16 Bubble cap trays in distillation columns have this key advantage:
A __They trap bubbles
B __Prevent liquid from dropping down on to a lower tray without contacting vapor
C __Relatively expensive
D __High pressure drop

17 Sieve trays have this disadvantage:
A __Low pressure drop
B __Inexpensive and easy to fabricate
C __Can allow weeping and mixing between stages
D __Can allow low molecular weight materials to leak through

18 Loose packings used in place of trays:
A __Will usually have lower pressure drop
B __Can be more corrosion resistant
C __Are more likely to breakup due to mechanical shock
D __All of the above

Additional Resources

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Hagan, M. and Kruglov, V. (2010) "Understanding Heat Flux Limitations in Reboiler Design" *Chemical Engineering Progress*, 11, pp. 24–31.

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http://www.separationprocesses.com/Distillation/DT_Chp04n.htm (accessed on August 31, 2016).

11

Other Separation Processes

Absorption, Stripping, Adsorption, Chromatography, Membranes

These mass transfer operations are also a key part of the chemical engineering tool kit for specific applications. Absorption and stripping are opposites of each other, while extraction, membranes, chromatography, adsorption, and leaching are more specialty processes typically used for unique separation needs.

Absorption

Absorption is defined as the transfer of a gas into a liquid. This is done to recover a valuable component in a gas stream for reuse or sale or the removal of a component in a gas stream to eliminate an environmental discharge. If the purpose of the absorption is to remove an air contaminant prior to discharge of an airstream into the atmosphere, the absorption process may be referred to as "scrubbing," implying the need to remove something prior to discharge. A general diagram of such a process would be as shown in Figure 11.1.

Figure 11.1 shows the use of packing (as designated with an "X" across the diameter of the tower), as opposed to trays, but either can be used. Packing, frequently made from ceramic materials, is very commonly seen in this unit operation because many of the gases that require absorption or scrubbing tend to be acidic gases such as SO_2 and HCl. Spray towers, without internal packing, can also be used for highly soluble gases.

One of the key design parameters is the solubility of the gas in the absorption or scrubbing liquid (frequently water, but another absorbent or solvent could also be used such as an alkali or oil). This is a physical property variable known as Henry's law constant ("H"). "H" is the ratio of the gas concentration divided by the concentration of that same gas in the absorbing/scrubbing fluid. H frequently uses the units of atm/mole fraction. It is a valid equation only for

Chemical Engineering for Non-Chemical Engineers, First Edition. Jack Hipple.

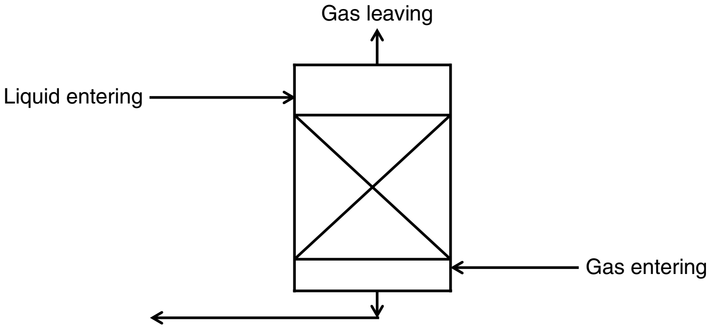

Figure 11.1 Absorption tower.

extremely dilute solutions and that is the context we will use in this chapter. In equation form, we can express the partial pressure of the gas (p) as a function of its concentration in the liquid, c, times Henry's law constant (H), that is, $p = Hc$.

At high concentrations, this relationship is not linear as it is with low concentrations.

Here are some of these values for the gases CO_2, CO, and H_2S (atm/mole fraction):

Table 11.1 Henry's law constants.

T, °C	CO_2	CO	H_2S
0	728	35 200	26 800
5	876	39 600	31 500
10	1040	44 200	36 700
15	1220	48 900	42 300
20	1420	53 600	48 300
25	1640	58 000	54 500
30	1860	62 000	60 900
35	2090	65 900	67 600
40	2330	69 600	74 500
45	2570	72 900	81 400
50	2830	76 100	88 400
60	3410	82 100	103 000

Source: Average of public information.

The following are a few points about the data in Table 11.1:

1) The Henry's law constant is very sensitive to temperature.
2) Gas solubility *decreases* dramatically with temperature. (The hotter the fluid, the less capability it has to absorb or hold the gas.) We see this every day when watching what happens to a carbonated beverage when left out in the kitchen after it has been in the refrigerator for days. It loses its "fizz," which is the carbon dioxide (CO_2) coming out of solution as the temperature rises. In chemical engineering terms, its Henry's law constant has risen by a factor of 2–4.
3) The varying slopes of these Henry's law constant values are different. H_2S is more soluble than CO at 0°C, but less soluble at 40°C. It would be a mistake to take data for two different gases, showing one more soluble than another, and assume that this difference in solubility applied at all temperatures.
4) Many gases, especially in the acid gas category such as HCl, have significant heats of absorption when they dissolve in water. It is important to calculate a heat balance on the system and estimate the temperature rise that may occur during absorption. Any increase in temperature will decrease the gas solubility.

We use a similar graphical technique to analyze a gas absorber/scrubber as we did in distillation, with the exception that there is no condensation of the overhead product (the clean gas). Instead of "plates" we frequently use the term "transfer units" to describe how tall an absorption/scrubber tower needs to be. This is a way of generalizing the number of feet of packing representing the equivalent of one contact tray. We have some of the same type of limitations we had in distillation:

1) We need to provide absorption/scrubbing fluid rates, at a minimum, above the solubility of the gas in the liquid.
2) We need to take into account the temperature rise that may occur when doing this, due to heat of absorption of the gas into the liquid.
3) There is a balance or optimization between the diameter of the column (it will increase as we increase liquid and gas velocities) and height of the column (it will decrease with higher liquid rates). As in distillation, there is no one answer but an optimization based on energy, capital, and possibly water availability and disposal costs.

Figure 11.2 shows a graphical representation of an absorber/scrubber unit with "*Y*" referring to the gas phase concentration and "*X*" referring to the liquid phase composition.

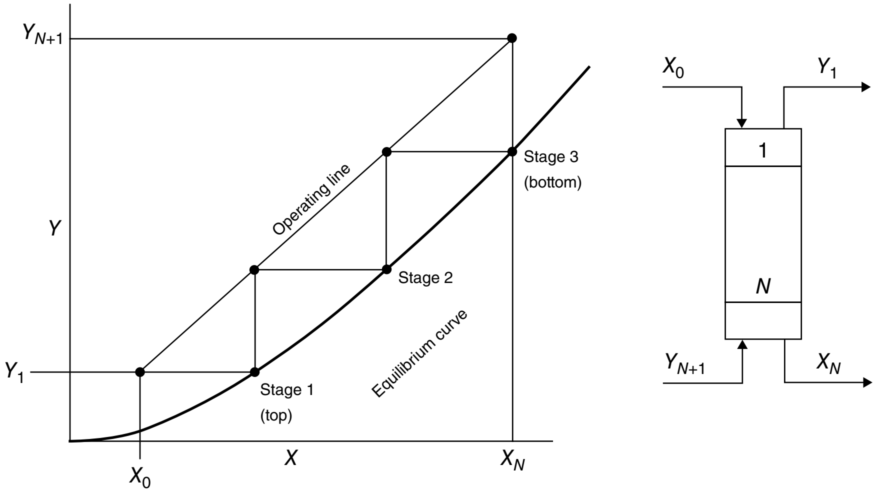

Figure 11.2 Analysis of an absorber.

The equilibrium curve shown in Figure 11.2 is basically a plot of Henry's law constant from the top to bottom of the column, indicating the amount of gas (mole fraction) that can be absorbed. The "operating line" is the same as in a distillation column, a line plotting the mass balance in the column. Since we want a component in the gas stream to move into the liquid, there must be a driving force to accomplish this. The greater the amount of absorbing/scrubbing fluid, the greater the distance between the two lines, and the number of "stages" required is fewer. In gas absorption, we generally use the phrase "transfer units" as opposed to stages; however, if we were to use a tray column to do the absorption, then we would use the same terminology. If we were to use a lower absorber fluid rate to accomplish the same degree of absorption, the tower would be taller, or we would need a more efficient packing. In the use of loose packings, vendors (or internal company experience) supply "height of a transfer unit" (HTU) equivalents, that is, 3 ft of packing type "A" is equivalent to 1 HTU. This value will vary with flow conditions and the nature of the fluid and gas properties.

Packing vendors will usually supply much of this information, but proprietary information in large corporations is also common.

We mentioned earlier the potential effect of a significant heat of solution when a gas dissolves in the absorption fluid. If we have such a situation, the equilibrium line will not be a straight line (meaning constant temperature), but will curve as its temperature increases, as shown in Figure 11.3.

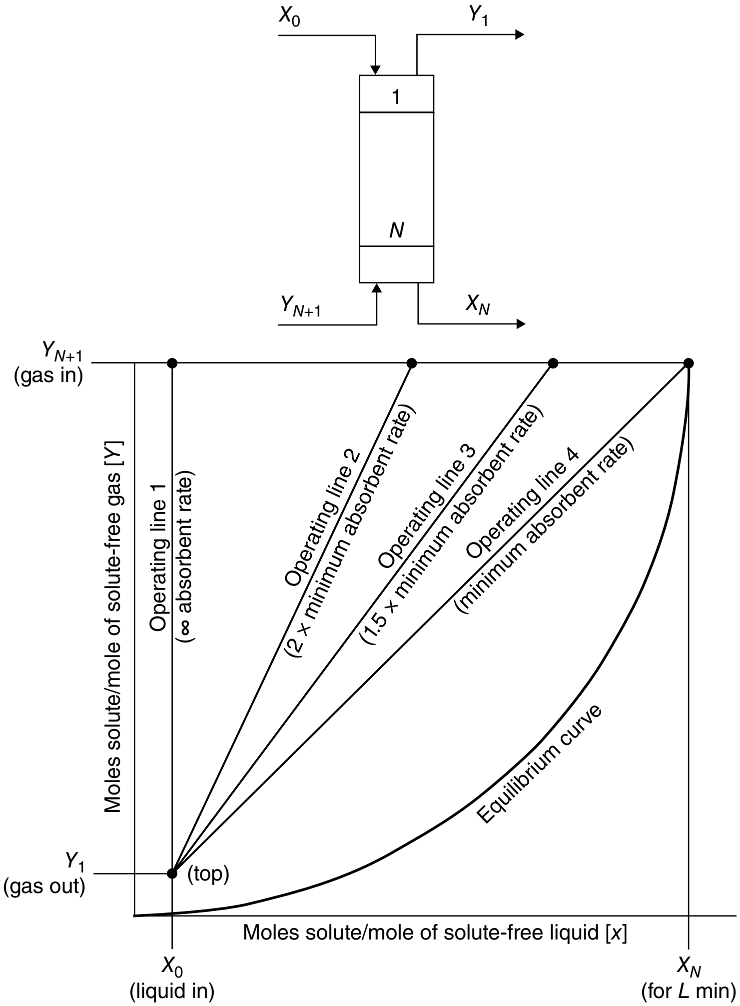

Figure 11.3 Effect of temperature on absorption.

In this type of case, a colder fluid may be needed to do the absorption required, internal cooling within the column supplied, or a taller tower required to achieve the same absorption efficiency.

Since any particular material will have a different solubility in an absorption fluid, another use of this process is to selectively remove or recover one of multiple components from a gas stream. One use of this technique is to use a hydrocarbon stream, such as a lean oil, to selectively recover low boiling hydrocarbons such as ethane, propane, butane, and pentane. If one or more of these compounds has significantly more solubility than another, it can be selectively removed or recovered.

There are occasions where the solubility of the gas may be high enough that it is not necessary to have multistage contact, and we can use what is known as a spray tower. The absorption fluid may also be a slurry of suspended solids as is often done with spray towers used in the power industry to recover sulfur dioxide (SO_2) from a power plant stack into lime ($Ca(OH)_2$) slurry.

Stripping/Desorption

This is the exact opposite of absorption or scrubbing. In this case, we have a component in the liquid (possibly material dissolved in water that cannot flow into a public waterway or company waste treatment facility) that must be removed. It is also possible that there may be a solvent in a discharge stream that has enough value to warrant recovery. In this case, the diagram for the process is exactly the same as the absorption/scrubbing process, but in these cases, the incoming liquid contains the material to be removed or recovered and the gas leaving is not clean, but now contains the material "stripped" from the liquid.

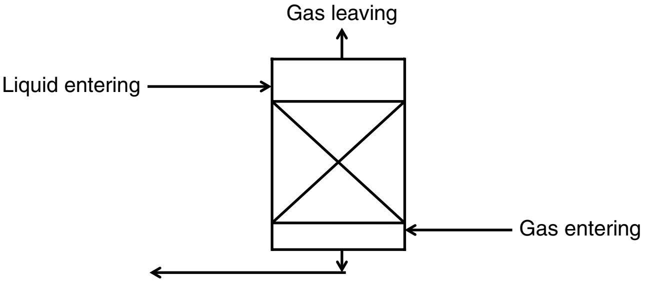

Figure 11.4 Stripping tower.

Auxiliary equipment choices are important in the design of absorbers and strippers. We have already discussed support plates and the importance, especially in packed towers, of an exact vertical installation. With stripping we have an additional concern in that we do not want fine mist of liquid being transported out the top of the column, both from an economic and environmental standpoint. We use *demisters* to accomplish this. A demister or mist eliminator is a mechanical device with very fine wire diameter that allows small liquid particles to coalesce into large enough particle size to drain back into the stripping vessel:

Figure 11.5 Typical demister. Source: Courtesy of Sulzer AG.

A widely used process in the natural gas industry illustrates both absorption and stripping. Much of the natural gas supply in the world contains not only hydrocarbons such as methane (CH_4) but also impurities such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). These two impurities not only dilute the fuel value of the natural gas but also, in the case of H_2S, cause a safety hazard due to the toxicity of this gas. However, it can be used as a feedstock for the manufacture of elemental sulfur. A class of compounds, alkanolamines, has great affinity for these two compounds. There are many different classes of these compounds (refer back to Figure 4.7 for a few examples). These compounds are used, in a combination of absorption and stripping, to produce "sweet" (non-H_2S- and CO_2-containing) natural gas that is used by both industrial and homeowners to heat their building and houses. Figure 11.6 shows an overview of this process.

In this process, sour gas is contacted with an amine that "absorbs" the sour gas impurities, H_2S and CO_2, producing a clean natural gas stream that can be utilized as a fuel. The amine, which has absorbed these impurities, frequently referred to in this industry as a "rich" amine, now needs to be "stripped" of these impurities so that it can be reused. This is done in the second tower seen in this flow sheet, producing a concentrated stream of H_2S and CO_2. This concentrated gas stream can now be used as a feedstock to a sulfur plant or a sodium hydrosulfide plant. Note that the pressures and temperatures and pressures in this process will vary greatly depending upon the temperature and pressure of the feed gas, the type of amine absorption fluid used, the level of impurities in the sour gas feed, and the intended use of the removed sour gas components.

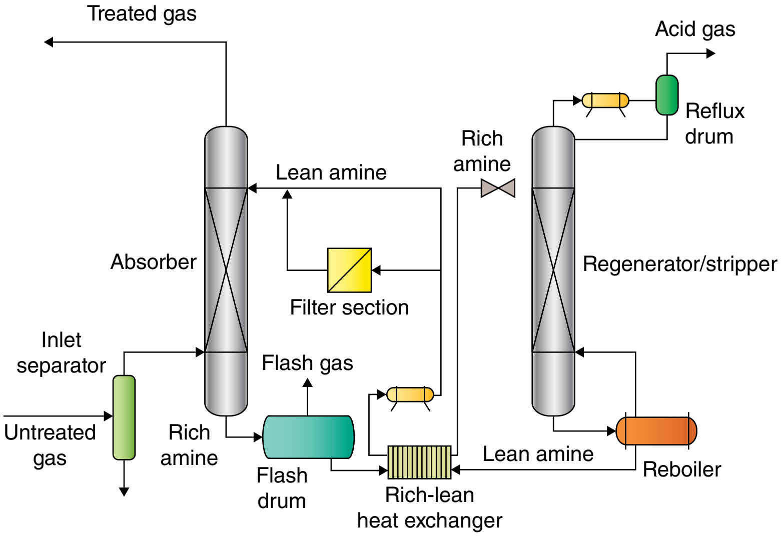

Figure 11.6 Combined absorption and stripping in purifying sour natural gas. Source: Chemical Engineering Progress, 4/13, pp. 33–40. Reproduced with permission of American Institute of Chemical Engineers.

Adsorption

In absorption, we contacted a gas with a liquid to remove or recover a component in the gas. In *adsorption*, we use a solid material to do the same thing. Adsorption can also be a liquid–solid unit operation to use a solid adsorbent to separate one liquid component from another or to remove an impurity as liquid or gas stream. The use of activated carbon to remove impurities from home drinking water is a common everyday example. Another example of this would be the use of an adsorbent to "break" an azeotrope by selectively removing one of the components via a mechanism different than vapor pressure difference. This unit operation can be used for the same purposes for which we considered absorption, but for a variety of reasons, we do not wish the recovered material to be in a solution form. The most well-known use of this technology is in the analytical chemistry area where we use the differences in adsorption preference to separate components in what is typically referred to as "gas chromatography" (GC).

This same approach can be used to separate or recover components in a gas stream on an industrial scale. Any gaseous material will have a degree of affinity for a solid surface in the same sense that it has an affinity to be absorbed into a liquid stream. We can measure this in the same sense we measure vapor–liquid equilibrium or Henry's law constants. In the area of adsorption, we call this an adsorption isotherm, and a typical example is shown in Figure 11.7, where we are plotting the amount of material adsorbed versus pressure at constant temperature.

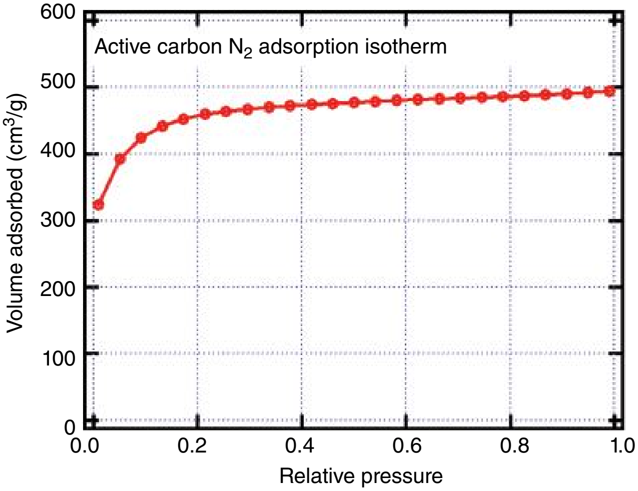

Figure 11.7 Adsorption isotherm. Source: Nandobike, https://en.wikipedia.org/wiki/File:Demac_isoth.jpg. Used under CC BY-SA 3.0 https://creativecommons.org/licenses/by-sa/3.0/. © Wikipedia.

Unless a process gas stream contains only one component that can adsorb, there will be a variety of adsorption curves, depending upon the affinity each material has for the solid adsorbent. A general equation that describes adsorption is called the Freundlich adsorption isotherm and has an equation of the following form:

$$\frac{x}{m} = Kp^{1/n}$$

where

x is the mass of the adsorbate (material adsorbed)
m is the mass of the adsorbent (material on to which the material is adsorbed)
K and n are empirical constants based on the nature of a particular adsorbent
p is the equilibrium pressure

A graphical representation of such a curve would look like that shown in Figure 11.8. This particular curve represents a material with a "K" of 4 and an "n" of 1/6.

The units in this graph are a bit different but demonstrate the same concept. "q" is in moles/kg and c is in moles/l.

A key difference between absorption and adsorption is that, in adsorption, the adsorbed material concentrates on the surface of the adsorbent as opposed to dissolving in a bulk liquid phase.

There are a number of adsorbent materials used in this unit operation, including activated carbon, zeolites, and silica gel. Their surface chemistry,

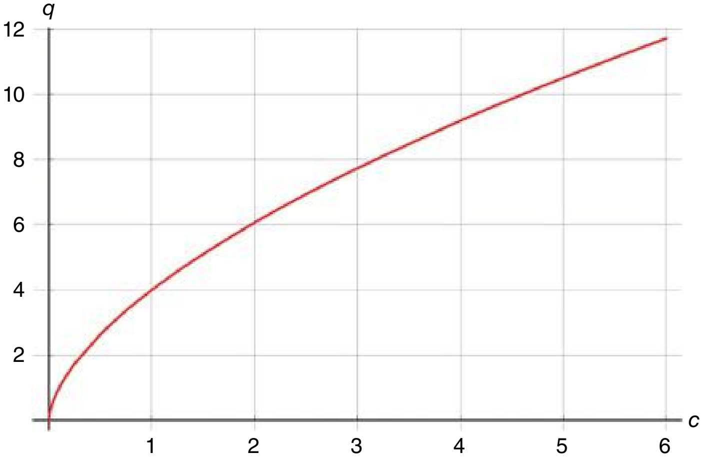

Figure 11.8 Adsorption isotherm. Source: Rosentod, https://commons.wikimedia.org/wiki/File:Freundlich_sorption_isotherm.svg. © Wikipedia.

pore size, and pore size distribution are controlled to maximize the adsorption of certain materials in preference to others. In the case of zeolites, the chemistry of preparation is so precise that the size of the pore opening is the primary controlling mechanism for what molecules are adsorbed and which ones pass through, as shown in Figure 11.9.

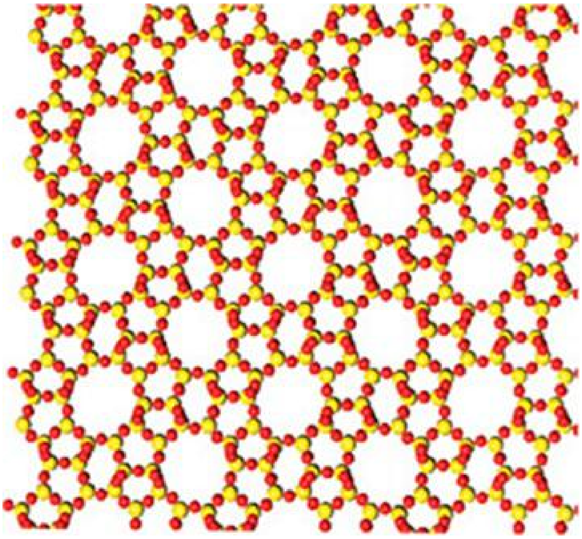

Figure 11.9 Example of a zeolite structure. Source: Prashant, http://www.nature.com/ncomms/2015/150511/ncomms8128/full/ncomms8128.html. Used under CC BY-SA 4.0 https://creativecommons.org/licenses/by/4.0/

A range of curves showing strongly adsorbed (i.e., irreversible) to non-adsorbed is shown in Figure 11.10.

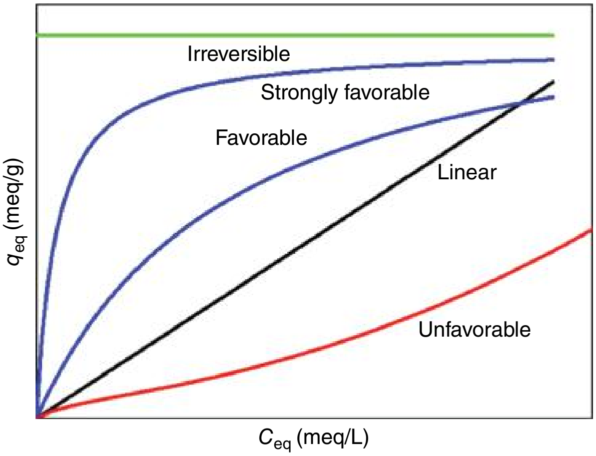

Figure 11.10 Strength of solid affinity and effect on adsorption.

In this graph, the concentration ratios are expressed in different units—another reminder how important it is to check units before comparing, sharing, or interpreting data.

We can also view adsorption as equilibrium between a gas phase component and a complex that it forms with the surface of the solid:

$$A + B \leftrightarrow AB$$

If we envision an adsorption process with a material (A) that has some reasonable ability to be adsorbed by the adsorbent (B), when the process starts, there will be no "A" leaving the column. As the adsorbent spaces are filled with adsorbate, eventually some of the adsorbate will leave the column. This can be seen in Figure 11.11.

The point at which the adsorbate begins to leave the adsorption column is called the breakthrough time and will be influenced by a number of process variables such as flow rate, pressure, temperature, and the presence of additional adsorbates. An acceptable breakthrough concentration is a function of quality specifications or environmental discharge limitations. The "AB" surface interaction mentioned previously can be complicated by the presence of more than one compound in the adsorbate as there can be additional surface chemistry interactions between the compounds on the surface after they have been adsorbed. This is why it is critical, when scaling up such a process, to use actual process stream concentrations and not single component streams, mathematically averaging the results.

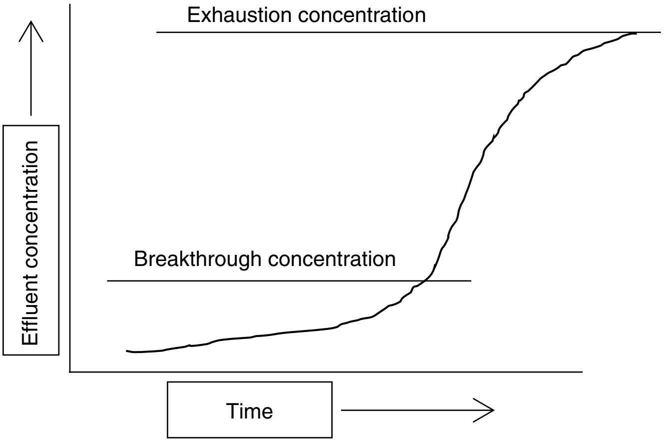

Figure 11.11 Adsorption versus time.

If we look inside the adsorbent column as a function of time, we would see something similar to that shown in Figure 11.12.

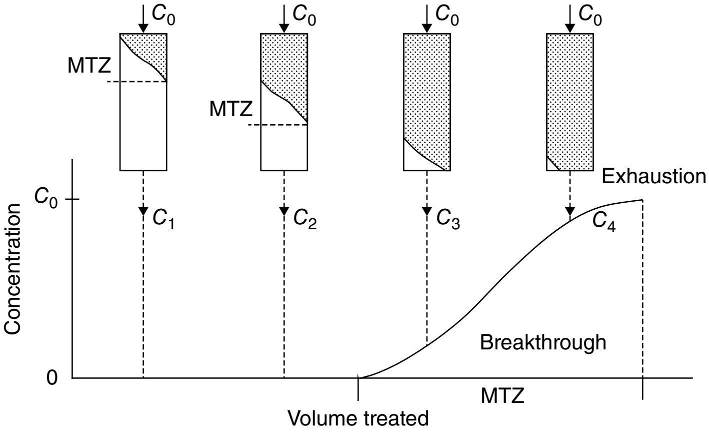

Figure 11.12 Adsorption breakthroughs.

The shape of the curve and the rate at which the adsorbate begins to leave the column will depend on the "*K*" and "*n*" of the adsorbent and the velocity of the flow.

The adsorbate (material removed from the gas or liquid) is removed from the adsorbent in a number of different ways. One is to flow an inert gas at a higher temperature than the original adsorption was done, as shown in Figure 11.13.

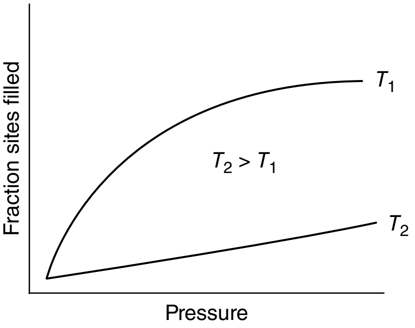

Figure 11.13 Effect of pressure and temperature on adsorption.

Another approach is to reduce the pressure and a third is to use a solvent that has a greater affinity for the adsorbate than the adsorbent.

These types of processes, since they are inherently semicontinuous, will not provide a constant flow of clean stream that contained the adsorbate. If a continuous flow of product leaving this kind of unit operation is desired, then there must be a parallel process running “out of phase,” which will start as the other unit is being regenerated.

Adsorbents having a large affinity for water can be used to “break” the ethanol–water azeotrope discussed earlier by removing water and leaving pure ethanol behind.

Practical considerations in the design of such process equipment include the following:

1) Humidity of the adsorbate stream. Water can be adsorbed on material such as carbon as well as other adsorbents. If the humidity level is less than 30%, this is not normally a problem. Adsorbed water can also cause surface interactions between different adsorbates that were not planned.
2) Auxiliary process equipment such as fans and blowers will be affected by the particle size and particle size distribution of the adsorbent.

Ion Exchange

In this separation unit operation, we introduce polarity of different types and strengths to recover or remove materials from a liquid (most frequently water) and then use a desorption process similar to what we used in adsorption reversal to recover what we have removed and return the bed to its original state. As with adsorption, this is typically a semicontinuous process where a fluid stream is passed over/through an ion exchange resin bed to remove a specific ionic species and then “regenerated” to remove the adsorbed species, dispose of it, and then "recharge" the resin bed. A home water softener is the most common consumer use of such technology. A water softening resin bed removes the Ca^{++} ion in "hard" water while at the same time displacing and releasing Na^{+} ion (already chemically attached on the resin surface) into the water. At some point in time, the resin becomes saturated in Ca^{++} ion, and the bed is "regenerated" by flushing a strong NaCl solution through the bed. The solution is made up indirectly by the homeowner when bags of salt are placed in a storage tank. Water is run through the salt tank, producing the salt solution. The displaced Ca^{++} ion (in the form of $CaCl_2$) is discharged into the sewer pipe of the homeowner.

Ion exchange polymer beads are typically cross-linked (to maintain some rigidity) polymers (styrene-divinylbenzene is a primary example) formed in the shape of round beads. The degree of cross-linking affects to what degree the polymer beads swell when in use and when being regenerated. Typical ion exchange resins/beads are shown in Figure 11.14.

The ionic chemistry on the surface of these beads can be positive ($Ca^{++}/K^{+}/(CH_3)_3NH_4^{+}$)) or negative ($OH^{-}/SO_4^{2-}/HSO_4^{-}/COOH^{-}$) depending upon the nature of the component that is being removed from the liquid stream passing through the bed. In addition to calcium, carbonates, silica, and charged organics can be removed with this type of process.

An industrial ion exchange process will have a number of tanks for processing, storage of effluent, and storage of regenerant in addition to the ion exchange unit itself.

From a chemical engineering standpoint, there are challenges in the design of such a process:

1) Pressure drop. The size and size distribution of the beads and the flow rate and liquid viscosity will all have significant effects on the pressure drop across an ion exchange bed. Ten-fold increases in viscosity can

Figure 11.14 Typical ion exchange polymer bead. Source: Bugman, https://commons.wikimedia.org/wiki/File:Ion_exchange_resin_beads.jpg. © Wikipedia.

double the pressure drop through an ion exchange bed operating at 1–6 m/h linear flow rate.

2) These types of resin beads can swell as their "raw" chemistry is changed into their replaced form. This swelling can be as much as 150% by volume. It is important that sufficient free volume be available in the tanks to accommodate this swelling. If a homeowner were to look at the tank in their water softening system, they would see a very small percentage of the tank volume actually occupied by the resin, as it needs volume to expand when regenerated.

Reverse Osmosis

Reverse osmosis is a general term referring to the use of films of various porosities to allow water to flow through and reject solids, dissolved salts, ions, and biological materials such as bacteria and viruses. Osmotic pressure refers to the pressure developed across a membrane when it is placed between a salt solution and pure water, as shown in Figure 11.15.

What this means from a practical and engineering point of view is that if we want to separate water from the small molecules dissolved in it, we need to overcome this osmotic pressure in order to force water through the membrane.

This is the basis for the brackish and seawater desalinization plants around the world, which produce drinking water from water that is too salty to drink. Figure 11.16 illustrates a picture of the largest water desalinization plant in the United States using this type of technology to supply 10% of the drinking water to the city of Tampa, Florida.

Commercial membranes can be a spiral wound or of a hollow fiber type. The holes within the membranes are typically extremely small polymer tubes as seen in Figure 11.17, illustrating a seawater membrane.

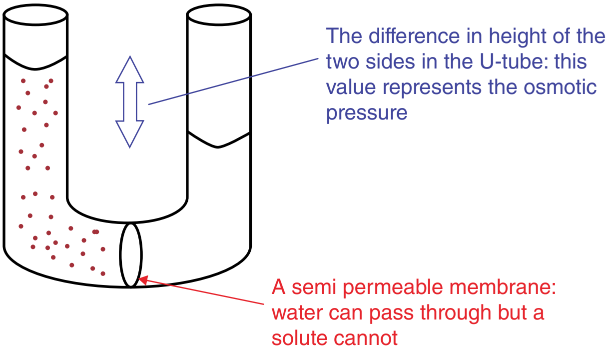

Figure 11.15 Osmotic pressure. Source: http://creativecommons.org/licenses/by-sa/4.0/. © Wikipedia.

Figure 11.16 Tampa, FL water desalinization plant. Source: http://www.chem1.com/acad/webtext/solut/solut-4.html.

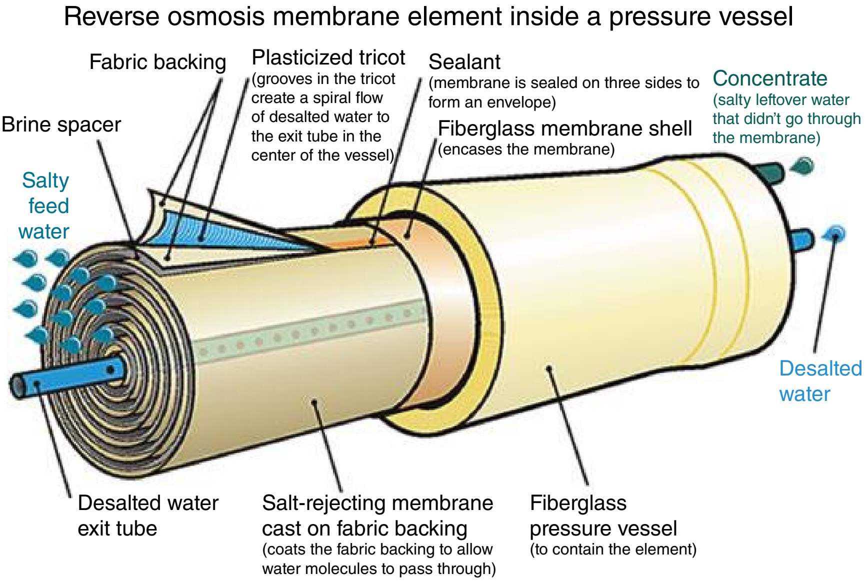

Figure 11.17 Reverse osmosis element detail. Source: http://www.chem1.com/acad/webtext/solut/solut-4.html.

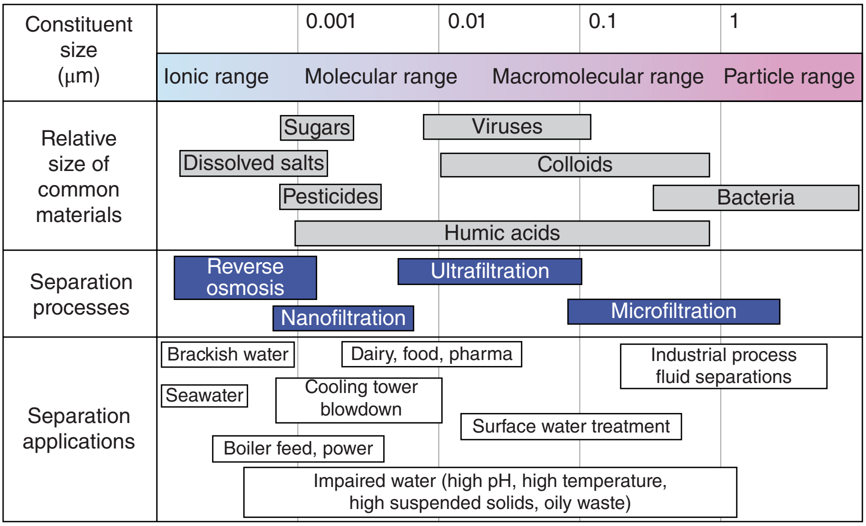

Figure 11.18 Differing separation capabilities of membrane systems. Source: Chemical Engineering Progress, 4/13, pp. 33–40. Reproduced with permission of American Institute of Chemical Engineers.

The ability of a given membrane design to filter and reject certain size molecules (primarily based on their molecular weight (MW) and size classifies the membranes as reverse osmosis, nanofiltration, ultrafiltration, or microfiltration) is illustrated in Figure 11.18.

Flow rates of fluids through membranes increase significantly with temperature as viscosity drops. Membrane systems must be cleaned frequently. High pressure reverse flow cleaning and chemical system cleaning are both used.

Gas Separation Membranes

Gases have different permeation rates through polymer materials and membranes. For example, most commercial food wraps sold in grocery stores are based on polyethylene. When wrapped in such a film, water does not permeate rapidly, so they can keep food moist and fresh. However some vegetable products need oxygen to avoid spoilage, and polyethylene's resistance to oxygen flow causes spoilage. A copolymer of vinyl/vinylidene chloride (commonly known as Saran™, a registered trademark of S.C. Johnson and Son, Inc.) controls both oxygen and water transmission. Some of these food wrap films are based on polyvinyl chloride polymer films.

Figure 11.19 Gas separation membrane. Source: Used with permission of Air Products.

The same kind of difference in gas permeability can be used to separate gases, as shown in Figure 11.19.

There are many situations in which it would be desirable to have an oxygen/nitrogen ratio different than the normal 79/21% (not counting rare gases). For example, in a combustion process, it might be desirable to have a higher oxygen/fuel ratio to raise the temperature of the flame. As opposed to building and operating a cryogenic air separation plant to produce liquid oxygen, a membrane that could separate the nitrogen and oxygen in air via a membrane system would have value. Nitrogen and oxygen have different permeation rates (oxygen normally higher), so in concept it should be possible to purify either one via a membrane process. In a recent example of a commercial application of this concept, a commercial gas separation membrane process has been developed that is sold to auto and tire stores to enable them more economically produce nitrogen at a given site, in order to use nitrogen as a tire filling gas versus using a compressed air process. This is shown in Figure 11.20.

This type of technology also has potential in flammability control if a way to produce nearly pure nitrogen can be developed, allowing a less expensive way to control the "oxygen" part of the fire triangle. It could also provide an enriched stream of oxygen for medical or oxidation processes vs. the purchase of liquified oxygen or oxygen cylinders.

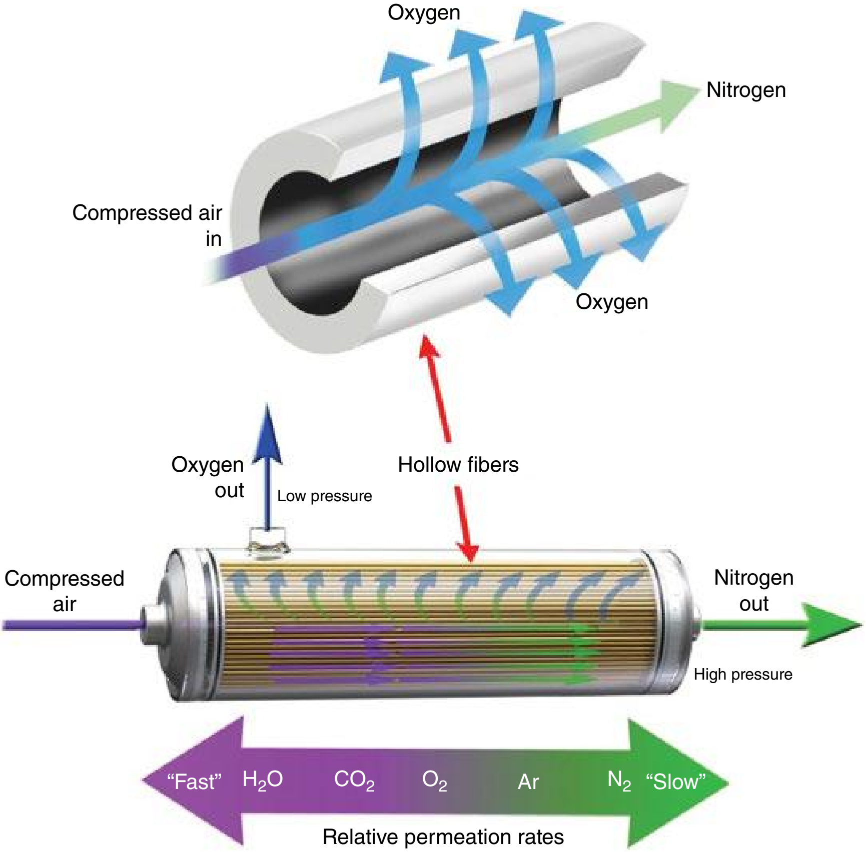

Figure 11.20 Air separation membrane. Source: Reproduced with permission of Air Products.

Leaching

A leaching operation refers to recovery of a valuable material from a solid ore or deposit through the use of a liquid, passed through the solid, and referred to as a leaching agent. Many minerals are recovered from ores in this fashion, including gold. Leaching can be done with an ore on the surface, possibly mined and brought to the surface, or "in situ" on an underground deposit.

The chemistry used in these types of operations will depend upon finding a complexing/leaching agent that can specifically attach to the mineral of interest. In the case of gold (Au is the chemical symbol for gold) mining, cyanide is such a material:

$$Au^+ + 2CN^- \rightarrow Au(CN_2)^-$$

The complexed gold is released by contacting with zinc (Zn) and displacing the leached gold:

$$2\mathrm{Au}(\mathrm{CN}_2)^- + \mathrm{Zn} \rightarrow \mathrm{Au} + \mathrm{Zn}(\mathrm{CN})_4^-$$

In addition to "in-place" leaching, there are a variety of mechanical liquid–solid contacting devices used in leaching.

Chemical engineering design variables in all of these processes will include:

1) Particle size and particle size distribution of the ore from which the valuable material is being recovered. These will greatly affect the fluid flow rate.
2) Flow rate, flow distribution, density, and viscosity of the leaching fluid
3) Depth of the ore bed
4) Particle degradation during any process using active grinding equipment
5) Downstream treatment of the leached material to achieve the desired purity

The leaching of tea from a tea bag or the brewing of coffee are common household analogies to this industrial process. The particle size and particle size distribution of the tea or coffee particles inside the bag, the temperature and flow rate of hot water, and how evenly the hot water leaching liquid is distributed or contacted will all affect the taste and concentration of the resulting beverage.

Liquid–Liquid Extraction

Liquid–liquid extraction is a unit operation where a mixture of liquids, usually in one phase, is contacted with a third liquid in which one of the components in the starting material is "extracted" into the third liquid due to enhanced solubility in this third liquid. We previously mentioned the concept of azeotropes that exist in some liquid–vapor systems that limits our ability to separate the components based on vapor pressure differences. One of the alternatives to deal with this situation is to identify another liquid in which one of the components of the azeotrope is preferentially soluble, leaving behind the desired component. This requires the identification of a solvent that is insoluble in the starting mixture but has a much greater affinity for one of the components in the starting mixture. This extracted mixture must then be treated in another separate process to be able to reuse the solvent being used as an extractant. The material removed (i.e., water in the case of the ethanol/water azeotrope) must also be recovered and treated for use or disposal. These extra steps are what make liquid–liquid extraction an inherently more complex and expensive unit operation.

The solvent is the material we are adding to extract the desired or undesired material. The "extract" is the phase containing whatever material we are

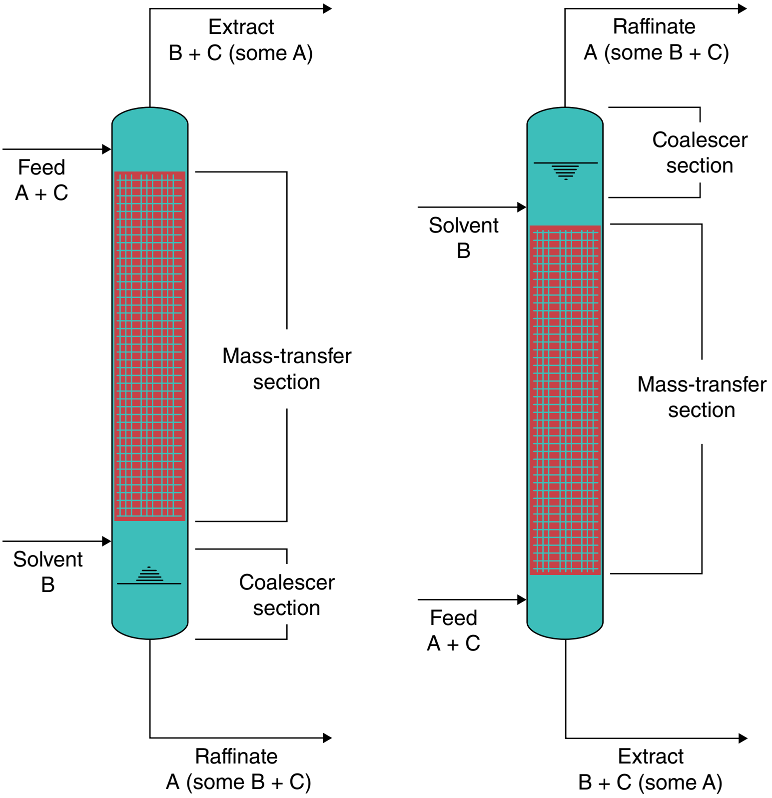

Figure 11.21 Continuous liquid–liquid extraction process. Source: Chemical Engineering Progress, 12/04, pp. 22–25. Reproduced with permission of American Institute of Chemical Engineers.

trying to extract from the initial mixture, and what is called the *raffinate* is the residual material that then must be further treated (Figure 11.22 shows the extract to be of a lower density than the raffinate phase, but this is not necessarily the case).

Liquid–liquid extraction can be done in a batch manner, but can also be done continuously as shown in Figure 11.21.

There are a number of possible configurations of such a column depending upon liquid density differences. The trays basically function as a series of tanks. The same thing could be accomplished in a series of batch tank operations.

Other approaches to continuous operations of this type include columns with a rotating shaft with the two liquids moving up and down, respectively, or columns with a vertical shaft movement as shown in Figure 11.22.

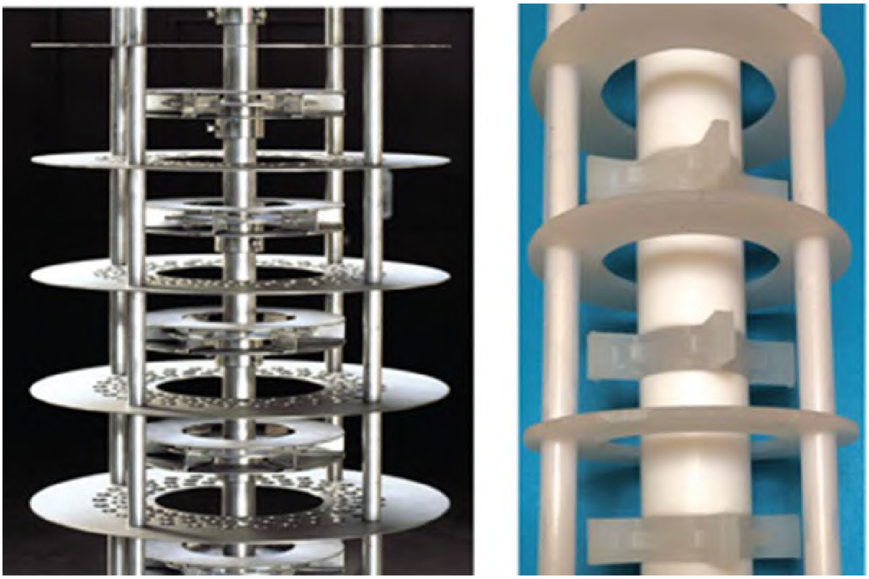

Figure 11.22 Agitated extraction columns. Source: Chemical Engineering Progress, 12/10, pp. 27–31. Reproduced with permission of American Institute of Chemical Engineers.

These types of devices usually have a variable speed drive for the internal shaft, allowing the turbulence of liquid–liquid contacting to be varied as a function of liquid physical properties such as density, viscosity, and surface tension.

Some of the process variables that can be manipulated and controlled are:

1) Ratio of solvent to feed
2) Type of physical contacting device
3) Temperatures of feed and solvent
4) Degree of agitation within the contacting column (or tank if a batch operation is used)

Surface tension, which we have not discussed previously, can affect the wetting of the process contacting surfaces as well as the tendency of the process liquids to foam when agitated. Defoaming agents may need to be evaluated and considered in such situations. Surface tensions (measured in dynes/cm) can vary from 2 to 8 for short-chain alcohols to as much as 45–50 for low MW alkanes.

The equilibrium data for a three-phase system must be available or measured in order to determine the number of contacting stages needed in a liquid–liquid extraction process. This type of data is normally shown in the form of a triangular phase diagram as shown in Figure 11.23.

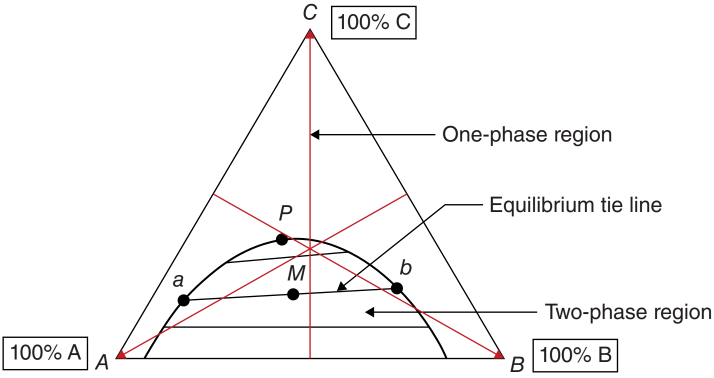

Figure 11.23 Ternary liquid equilibrium phase diagram.

In this illustration of a three-phase system, the concentrations of A, B, and C, which have been measured in laboratory studies, are shown. When the end of the line is at "A," the composition is 100% A, and it is similar with the two other components. Superimposed on this general diagram is solubility data relating to solubilities of these three liquids in each other. In the one-phase region, all three components are mutually soluble. At what is known as the "Plaitt Point" (P in the diagram), the solution "splits" into distinct phases (area labeled "M"), where we may have added "A" to the starting mixture, wanting to separate "B" from "C." If we separate these phases and add additional "A," the mixture will split again according to the tie lines in the diagram. We can envision this process as shown in Figure 11.24:

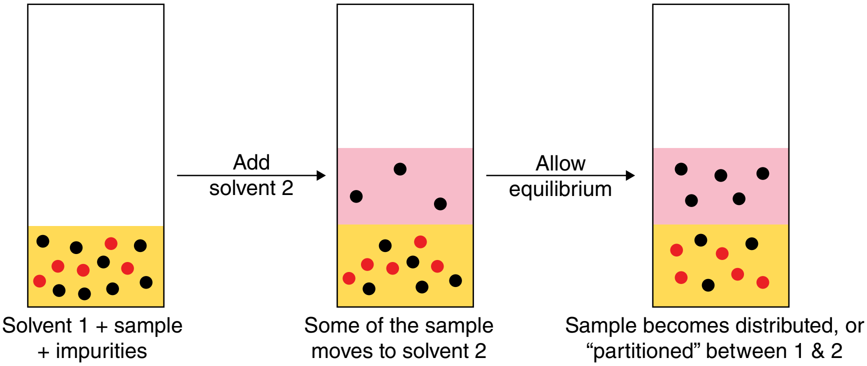

Figure 11.24 Liquid–liquid extraction in stages. Source: Reproduced with permission of American Institute of Chemical Engineers.

The composition of each phase is calculated with a mass balance calculation, summing the totals of A, B, and C.

This is analogous to the boil and condense analogy in distillation. The number of times this must be done will be a function of the solubilities of the liquid components in each other which will also be a function of temperature. A mass balance, using the compositions for each phase, will determine the final composition after each stage of contact. The number of stages of contact required to reach the final desired composition will determine the number of tanks or the height of the extraction tower.

The "tie lines" shown in Figure 11.24 are the equivalent of vapor–liquid equilibrium lines in a distillation system except that in a liquid–liquid extraction process we are viewing the data for two different *liquid* phases. The contact/separate concept here is analogous to the boil/condense model in distillation.

These kinds of diagrams are also used in solid–solid systems such as ceramics and gas–liquid–solid systems relating to systems such as the removal of caffeine from coffee beans with carbon dioxide.

It is also possible to diagram a liquid–liquid extraction process in a way similar to what we did in distillation, illustrating the analysis of how many contacting stages might be required (see Figure 11.25).

As with distillation or other mass transfer operations, the efficiency of the contacting at each stage will be a function of numerous process and physical property values (density, viscosity, and surface tension differences), and the number of stages actually required will be more than we might calculate from such a diagram.

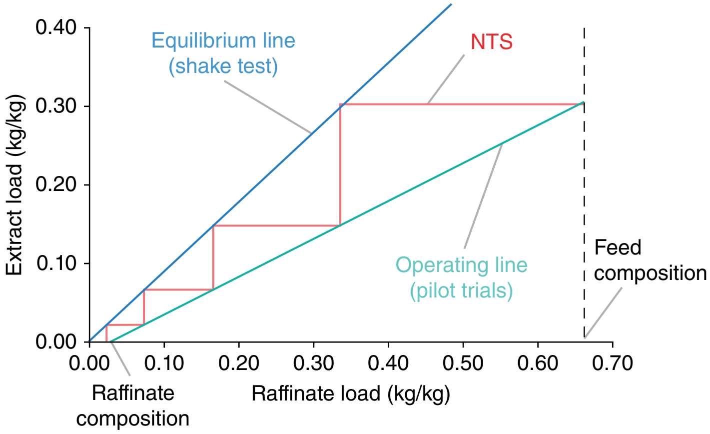

Figure 11.25 Liquid–liquid extraction stage diagram. Source: Chemical Engineering Progress, 11/15. Reproduced with permission of American Institute of Chemical Engineers.

Summary

There are a number of separation processes based on physical properties other than relative vapor pressure differences, which we used in distillation. Solubility differences can be used to recover gases into liquids. Differences in solid surface affinity and pore sizes in solids can be used to selectively recover or separate materials from liquids and gases via adsorption. Differences in liquid miscibility can be used to selectively recover or separate via liquid–liquid extraction. In many cases, several of these more specialty unit operations may be applicable to a given separation or recovery goal. The operating cost of each process, the value of the material being recovered or removed, and the capital costs of each will need to be compared to make the best choice.

Coffee Brewing

Coffee beans, either in whole or ground form, have a small percentage of actual coffee flavor ingredients with the rest being inert, as far as the coffee drinker is concerned, ingredients. In order to produce a cup of coffee, these flavor ingredients must be "leached" into water, away from the grounds. This is done by a home version of a leaching process. The beans are ground to varying degrees. A "course" grind will have a lower surface area than a "fine" grind. Everything else being equal, the fine grind will produce a stronger tasting coffee. Hot water is either percolated through or dripped through the grounds, leaching out the flavor ingredients to varying degrees. We can also assume that the geometry of the leaching mechanism and the temperature of the water (viscosity and solubility effects) will also affect the flavor of the coffee produced in this process.

The rate and temperature of the water will both affect the amount of flavor (and non-flavor) ingredients leached from the "pod" or the bed of coffee.

Discussion Questions

1. If any of these specialty unit operations are being used in your processes, are their function and design parameters well understood? What was the basis for their original choice?

2. What is the effect of changes in water temperature, viscosity, and density on their operation?

3. If less sophisticated unit operations are currently being used, is there a potential advantage in terms of cost or quality through the use of adsorption, leaching, membranes, etc.?

4 Conversely, if the choice of a specialty separation was made based on cost or lack of feasibility of a more common unit operation, have those economics changed requiring reevaluation? Could membrane quality gases replace purchased cryogenic liquids?

5 Would higher purity water have an advantage if used in your processes?

Review Questions (Answers in Appendix with Explanations)

1 Absorption is the process for recovering a gas into a:
A __Solid
B __Another gas
C __Liquid
D __Any of the above

2 Stripping is removal of a gas from:
A __Liquid
B __A reactor
C __A tank truck
D __Any of the above

3 The key variable that is used in designing an absorber or a stripper is the:
A __Temperature of the liquid
B __Temperature of the gas
C __Henry's law constant
D __External temperature

4 Henry's law constant represents:
A __The ratio of gas partial pressure to gas concentration dissolved in the liquid
B __The inverse of Henry's law variable
C __The approval of Henry to the gas solubility data generated in the lab
D __How much more gas will dissolve in a liquid if the pressure is increased

5 In an absorber, the gas enters at the:
A __End
B __Top
C __Bottom
D __Middle

6 In a stripper, the liquid enters at the:
A __End
B __Top
C __Bottom
D __Middle

7 In designing an absorber it is important to take into account:
A __Proper distribution of inlet gas across the bottom of the tower
B __Proper distribution of liquid over the cross sectional area of the tower
C __Potential temperature rise due to heat of gas dissolution
D __All of the above

8 Demisters may be required at the top of a stripper due to:
A __Fill in void space
B __Control of possible liquid carryover
C __Operators are sad when seeing material being removed from a liquid
D __To supply pressure drop

9 Adsorption is the process for recovering a component from a fluid or gas onto a:
A __Solid
B __Membrane
C __Liquid
D __Any of the above

10 The efficiency of adsorption is governed by:
A __What kind of carbon is used
B __Affinity of the gas for the solid
C __Pore size of the adsorbent
D __All of the above

11 Variables that can affect the efficiency and selectivity of adsorption include:
A __Temperature
B __Pressure
C __Adsorption isotherms
D __All of the above

12 Adsorption beds can be regenerated by all of these techniques except:
A __Change in pressure
B __Change in temperature
C __Seriously wishing
D __Purging with a large amount of gas to displace the adsorbed material

13 Liquid chromatography is a unit operation that utilizes_____to recover and/or separate liquid components:

A __Molecular size
B __Surface charge
C __Liquid–solid surface chemistry
D __Any of the above

14 Ion exchange processes use what functionality bound to a polymer surface to achieve separation:

A __Ionic charge
B __Pore size
C __Differing molecular weight polymer additions
D __Surface roughness

15 Ion exchange beds are regenerated through the use of:

A __Change in pressure
B __Change in temperature
C __Large volumes of the opposite original charge solutions
D __Purging with a large amount of gas to displace the exchanged material

16 A serious practical issue when regenerating ion exchange beds is:

A __Using the wrong regenerant solution
B __Hydraulic expansion
C __Noise created
D __Regenerating the wrong bed

17 Liquid–liquid extraction is a unit operation involving the use of a material's preference to be dissolved in:

A __One liquid close to its boiling point versus another liquid at room temperature
B __One liquid close to its freezing point versus another liquid at room temperature
C __One liquid close to its critical point versus another liquid near its boiling point
D __One liquid versus another liquid

18 To design a liquid–liquid extraction process, the following is needed:

A __A ternary phase diagram
B __Knowledge of densities and density differences
C __Surface tension of process fluids
D __All of the above

19 Operating and design variables for a liquid–liquid extraction operation include:
A __Temperature
B __Contact time
C __Liquid physical properties
D __All of the above

20 Leaching is a unit operation used to:
A __Go back to the days of the gold rush
B __Recover money from a stingy relative
C __Recover a material from a solid via liquid contact
D __Recover a material from a solid via gas contact

21 Membranes separate materials based on the difference in their:
A __Molecular weight and size
B __Desire to go through a very small hole
C __Value and price
D __Cost

Additional Resources

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12

Evaporation and Crystallization

Let's now look at two unit operations that are used to do two things:

1) Increase the concentration of a solution containing one or more dissolved materials. A simple example would be a salt solution (NaCl, KCl, $CaCl_2$, etc.). Though the most common use of this unit operation is in concentrating salt solutions, the principles are equally applicable to concentrating a material in an organic solvent, such as a drug from an organic solvent.
2) Precipitate a material, which has value, from a solution. It is to be noted that evaporation can do this as well, but evaporation is the term usually used to describe a process with heat input and a crystallization process used to describe one that is using cooling. Again, this can refer to either a water-based solution or an organic solvent-based system.

Evaporation

In evaporation, we start with a solution of one or more solid materials, which are dissolved in a solvent. A common example would be salt in water. It could also refer to a pharmaceutical product dissolved in an organic solvent. This unit operation refers to the vaporization of the solvent and increasing the concentration of the "solute" (the material dissolved in the solvent). Evaporation, carried to its extreme, would leave only a solid behind. Usually the valuable material is what is dissolved in solution.

Evaporation is a specialized form of heat transfer, which we discussed in Chapter 8. We supply steam, or some other hot heating medium, to a heat exchanger, and this heat input boils the solvent, increasing the concentration of the solute. Since the steam is condensing and the solution is boiling under turbulence on the other side of the heat exchanger, heat transfer coefficients tend to be higher than those seen in conventional liquid–liquid shell and tube heat exchangers. The mechanical design of such a heat exchanger can be of several different types.

Chemical Engineering for Non-Chemical Engineers, First Edition. Jack Hipple.

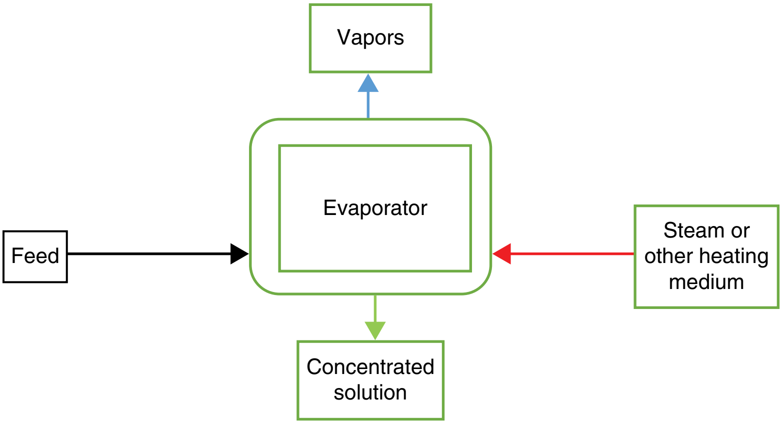

Figure 12.1 Evaporation process.

Horizontal or vertical tubes, inserted into process vessels, with the vapor coming off the top of the evaporator are condensed or disposed of. There are many different mechanical configurations of these types of evaporators depending upon liquid properties, type of heat source being used, and nature of the final product. A general diagram of a simple evaporation process is shown in Figure 12.1.

The details of the evaporator design can vary greatly, depending upon the nature (density, viscosity) of the feed, its boiling point versus pressure, the concentration desired, and the sensitivity of the concentrate to higher temperature. This last point is very important in the food and drug industry.

Regardless of the details, the overall design of the evaporator (it is just another form of a heat exchanger we discussed previously) will follow the general overall heat exchange formula we reviewed before:

$$Q = UA\Delta T$$

Q will be the total amount of energy required (BTU/h. or kcal/h.) to boil a certain number of pounds of water or solvent times its heat of vaporization plus any sensible heat necessary to reach the solution's boiling point plus any external heat losses from the process vessels. A will be the heat transfer surface area available, which could be a combination of heat transfer coils inserted into the evaporator and heat transfer area on the jacket of the evaporator. As we discussed earlier, U is the overall heat transfer coefficient and in a turbulent boiling situation will typically be higher than a normal liquid–liquid or liquid–gas heat exchanger.

There are three practical issues that often cause an evaporator to not perform as designed:

1) Level control in the evaporator must be sufficient to cover all of the tubes (assuming that all the tube area was used in the design). We have not discussed process control up to this point, but suffice it to say that if the level in the evaporator is not high enough to cover all of the tubes, the performance will not be what is expected.
2) Fouling can reduce the heat transfer coefficient over time. This would normally be seen as a slow decline in performance over time, and some degree of overdesign in the area that would be used to compensate for this. The comments made earlier in the chapter on heat exchanger apply equally to evaporators.
3) Boiling point rise. This is a subtle design mistake that is possible to make. In the basic equation mentioned earlier, the ΔT should be the difference between the temperature of the heating medium (steam, hot oil, etc.) and the temperature of the *product* solution at its boiling point. If there is a salt solution that is being evaporated, its boiling point will rise with a rise in concentration. (This would not usually be the case with an organic solvent being evaporated.) If the boiling point is underestimated, the ΔT will be lower and thus the driving force for heat transfer less, requiring more heat transfer area to achieve the desired result.

This rise in boiling point with salt solutions is characterized by what is known as a Duhring plot, where the boiling point of a particular solution is shown graphically against the boiling point of water. These diagrams can be readily found in the literature.

Operational Issues with Evaporators

Some practical issues in the operation of evaporators include the following:

1) Steam Condensate Removal. The steam typically used in an evaporator condenses into hot condensate and is either returned to an internal power plant via a steam trap system or is disposed of to public waterways, usually after having been cooled in a pond or a cooling tower. If the path for steam condensate flow is blocked in any way, hot liquid condensate can build up in the steam chest of the evaporator, reducing the heat transfer coefficient. Steam–liquid heat transfer is greater than liquid–liquid heat transfer.
2) Buildup of Non-condensables. If the steam being used is coming from a water supply that has not been vacuum degassed, there is the possibility that very small amounts of inerts in the boiler feedwater (nitrogen, oxygen) will

very slowly build up in the steam chest of an evaporator. Over a period of time, this will reduce the partial pressure of the steam and lower the heat transfer rate.

3) Entrainment and Foaming. Salt solutions tend to have high surface tension values, making it possible to create stable foams and froth during boiling. This problem can be addressed in a number of ways. First, antifoam agents can be added to the solution, assuming that the addition of these materials does not interfere with quality specifications or downstream use. Second, the vent line leaving the evaporator can be greatly enlarged in diameter (compared to the evaporator itself) to lower the gas velocity leaving the evaporator, making coalescence and condensing back into the evaporator easier. Another approach sometimes used is to use a direct steam nozzle into the overhead vapors, accelerating coalescence of drops into a liquid stream that will drain back into the evaporator.

We have discussed physical properties several times already, and this is another area where we need to remember these fundamentals and make sure we know the data for the materials we are handling. As salt solution (calcium chloride in the graph) concentration rises in an evaporator, its viscosity will increase as shown in Figure 12.2.

In Chapter 8, we discussed the heat transfer coefficient being proportional to the Reynolds number to the 0.8 power. Since the Reynolds number is $DV\rho/\mu$

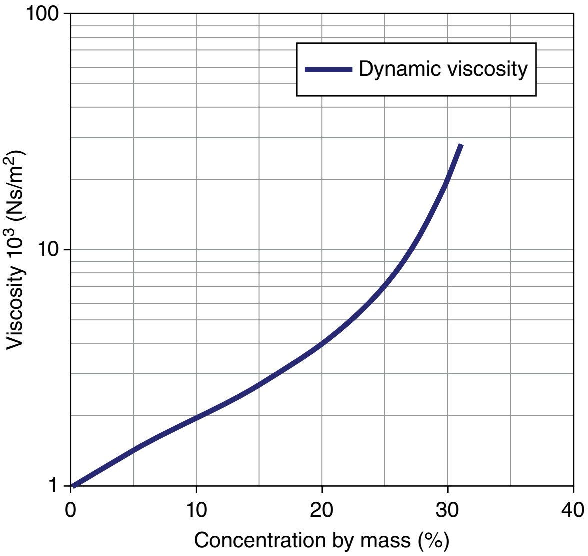

Figure 12.2 Increase in viscosity as salt concentration rises. Source: Reproduced with permission of Engineering Toolbox.

(μ is viscosity), the Reynolds number will decrease as the viscosity increases. We need to make sure when designing the evaporator that we are using the actual physical properties inside the evaporator and not the feed going into the evaporator. Viscosities typically increase as salt concentration increases.

There a number of different evaporator configurations used in different industries based on the unique characteristics of the materials being concentrated. This is especially true in the food industry.

Vacuum and Multi-effect Evaporators

Evaporators do not need to be run at atmospheric pressure. If we raise the pressure, the boiling point of the solution will rise; if we increase the pressure of steam feeding an evaporator the ΔT between the heating medium and the boiling point will increase. If we run the evaporation under vacuum, the boiling point of the solution will drop below its value at atmospheric pressure, again increasing the ΔT and the rate of heat transfer. The choice between atmospheric and non-atmospheric pressures for evaporation will depend upon a number of factors. Again, in many areas of chemical engineering, there is no right or wrong, but choices.

1) In general, vacuum is a more energy intensive process than pressure. Vacuum can be produced by a steam-driven vacuum jet or a mechanical compressor. Steam jets, though having no moving parts, produce a waste water stream, which must be treated and/or disposed of.
2) Evaporation with higher pressure steam will not only increase the ΔT but will also increase the capital cost of the evaporator.
3) Using high pressure steam in combination with vacuum on the solution side will not only provide the highest ΔT but will also require the highest capital with the lowest steam use. There is a trade-off between cost and capital, as is usually the case in all "optimization" of chemical engineering unit operations.

A multi-effect evaporator is one that uses the evaporated water from the first stage to provide the energy input to the second stage in the following fashion, showing a two-stage multi-effect evaporation system (Figure 12.3).

The feed (1 in the diagram) is heated and evaporated (in heat exchanger A1 with steam entering at point 3). The output from this first step enters a separation tank (B1). The hot, partially concentrated solution is sent to the second stage, while the vapor from the first stage (leaving the top of B1) is used to further evaporate the solution. This can only be accomplished if the pressure is reduced to lower the boiling point. The final product (2) leaves the bottom of the second stage (B2), and #4 indicates the flow of vapor to a vacuum system, which has created the vacuum necessary.

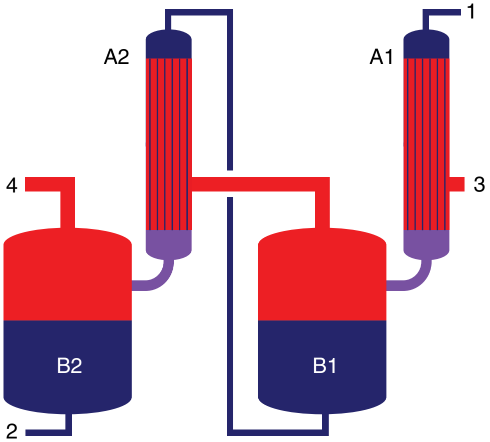

Figure 12.3 Multi-effect evaporator. Source: https://commons.wikimedia.org/wiki/File:Double_effect_evaporator.PNG. Used under CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=214928. © Wikipedia.

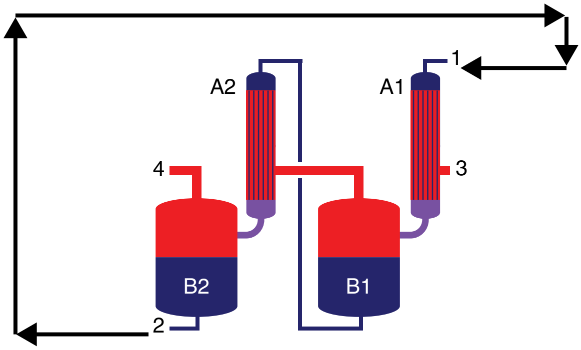

Figure 12.4 Use of vapor recompression in evaporation. Source: CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=214928

Another option used when electrical costs are relatively low compared with capital costs is vacuum recompression, where we take the off-gas from the evaporator under vacuum and then recompress it to be the primary energy source. This would effectively take the steam leaving the second stage (#4) and reusing it as the feed to the first stage, as shown in Figure 12.4.

Multiple effect evaporation can also be used to produce drinking water from seawater, as opposed to the membrane separation processes discussed earlier. The choice is a function of energy and capital costs.

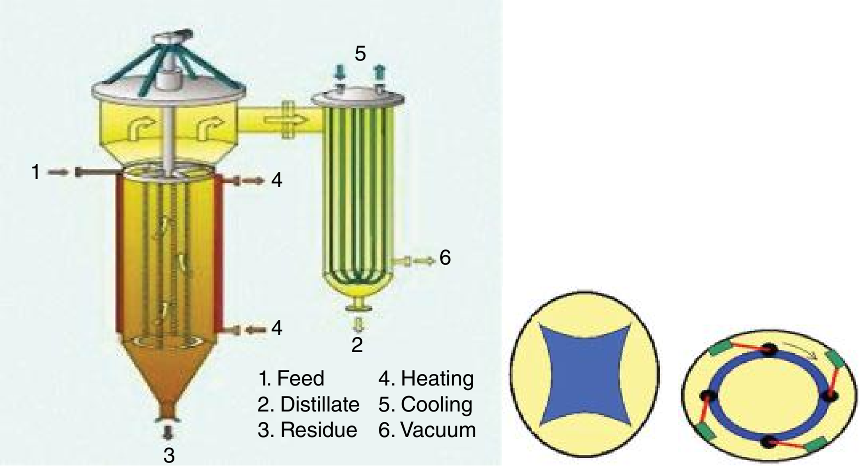

Figure 12.5 Wiped film evaporator mechanisms for viscous solutions. Source: Reproduced with permission of Sulzer.

If the viscosity of the fluid being concentrated increases rapidly during the evaporation process, it may be necessary, in a tube-type evaporator, to wipe the tubes continuously to prevent plugging of the evaporator tubes. Figure 12.5 shows an illustration of this type of evaporator/concentrator as well as some of the mechanical design choices used in scraping the walls as the evaporation takes place.

As we have discussed previously, there is no one right answer to an evaporator design choice as there was no one answer to a distillation column design. The costs of capital and energy will be key decision input data along with physical building restrictions and of course the physical properties of the solution being evaporated or concentrated.

Crystallization

In crystallization, we are normally referring to precipitating a solid from a solution by lowering its temperature. Since most materials' (but there are exceptions!) solubility in water, or other solvents, increases with temperature, one way of recovering a solid from a solution is to cool it and some of the solids will drop out of solution ("precipitate") to follow a solubility curve. Such curves for several common salts are shown in Figure 12.6.

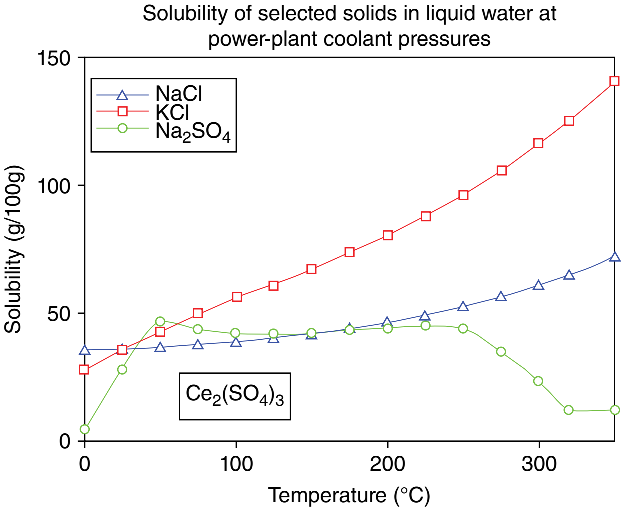

Figure 12.6 Selective salt solubilities versus temperature. Source: From public literature sources.

There are several important things to notice in this graph:

1) Two of the salts (NaCl, (common table salt); and KCl) consistently increase in solubility (shown in g/100 g in this figure) as the temperature is raised, but the slopes of these curves vary significantly. Potassium chloride (KCl) increases in solubility at a far greater rate than ordinary table salt (NaCl) as the temperature is raised.
2) Sodium sulfate's (Na_2SO_4) solubility also increases up to about 60°C, then levels out, and finally *decreases* in solubility beyond 220°C. This is due, in part, to the interaction of the sulfate molecules with the water solvent in a way that would not happen with the chloride salts. We would not necessarily expect to see this same kind of deviation in a nonpolar solvent, and it would be a great mistake to make that assumption.
3) Cesium sulfate ($Ce_2(SO_4)_3$) and other salts in the calcium family *decrease* in solubility as temperature is raised. This behavior is the root cause of hard water deposition on clothes being washed in hot water.

One approach to crystallization is to use what is known as *evaporative crystallization*. In this case, we evaporate the solution to the point where solids precipitate out when their solubility limits have been exceeded.

This type of crystallizer is similar to an evaporator, except that the solution is boiled beyond the solubility point and a solid slurry product is produced. This wet slurry then needs to be processed further.

Crystallization is inherently a more complicated process than evaporation as the usual focus is not a more concentrated solution, but recovery of a component in the liquid phase that has value. Part of this value may be in the shape, size, particle size, and particle size distribution of the crystals. Crystallizers are usually agitated, in order to better control particle size and particle size distribution, adding another process variable. Another factor is that crystal shape and particle size distribution are usually part of the design criteria in a crystallizer. Many salts, especially simple inorganic chemical salts, can have multiple states in conjunction with waters of hydration, each of which has a different crystal shape. Crystallizers are frequently used to produce drugs and food products. The shape, average particle size, and particle size distribution of these products are critical to their biological function in terms of dissolution and uptake rates.

Considering the details of an agitated crystallizer, there are a number of mechanisms going on in parallel:

1) Precipitation of material
2) Growing the size of a crystal through deposition of new material on the surface of previously precipitated material
3) Existing crystals being broken up by the agitator
4) Impurities or crystallization solution (frequently referred to as "mother liquor") being trapped inside the precipitating and growing crystals

Crystallization processes can be run under many different conditions:

1) Batch, vacuum. The feed solution is loaded into a vessel followed by pulling vacuum on the vessel, reducing the boiling point of the solution. The solution boils and material precipitates out, producing slurry for further processing, as shown in Figure 12.7. "Mother liquor" is a term used to describe the feed solution.

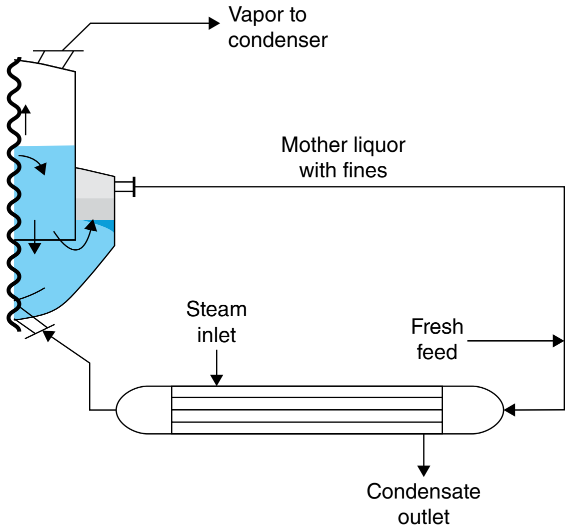

Figure 12.7 Batch vacuum crystallizer. Source: Chemical Engineering Progress, 10/08, pp. 33–39c. Reproduced with permission of American Institute of Chemical Engineers.

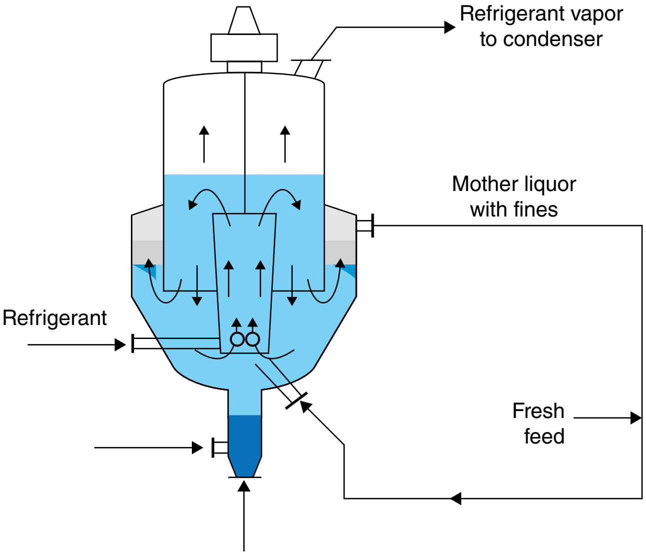

Figure 12.8 Forced circulation with indirect cooling. Source: Chemical Engineering Progress, 10/08, pp. 33–39c. Reproduced with permission of American Institute of Chemical Engineers.

2) Forced Circulation with Indirect Cooling. This process can be continuous, and it is critical to ensure that the temperature drop across the heat exchanger is small to minimize the potential for solids to cake and plug up the heat exchanger (Figure 12.8).

In addition to the particle size and entrained mother liquor in the crystals, there are a number of other product characteristics affected by the design and operation of a crystallizer:

1) Agglomeration and Caking. The nature of the particle size and distribution will have an effect on the material's cohesive bonding and strength, which will in turn affect to what degree a solid agglomerates and cakes in downstream storage in silos, bins, and hoppers as well as in shipping containers.
2) Surface area, which will impact the items mentioned in (1), can also impact the interaction of the crystalline product with other materials, especially if it is used in a catalyst formulation.
3) Morphology. This refers to the shape and structure of the crystal. Anyone who has shopped for a diamond understands that the shape and structure of the same carat weight diamond, and how it refracts light, can have a significant impact on its perceived value and price. The same can be true for specialty chemicals.
4) Bulk Density. The particle size and particle size distribution can greatly affect how much volume a given amount of weight of material occupies. This will affect packaging size and the design of bulk storage equipment.

5) Bioavailability. If the crystalline product is used in a pharmaceutical or drug application, the rate of dissolution in the stomach and/or blood stream can be critical issues. Let's assume that we have a distribution of particle size in a drug that looks like that in Figure 12.9.

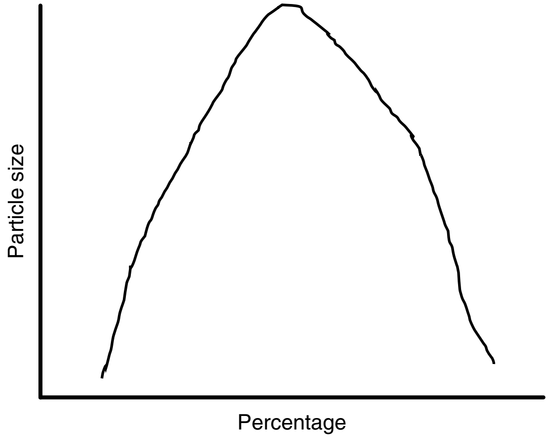

Figure 12.9 Particle size distribution.

If small particle size dissolves faster than a large particle size, then this crystal will most of its material dissolved after being taken or absorbed, with a small fraction dissolving quickly and another small fraction dissolving quickly at the end. If we wanted to have the crystalline drug dissolve all at once, very quickly, we would design the crystallization process to produce a narrow range of very small particles, which when compared with the previous particle size distribution, would look like that shown in Figure 12.10.

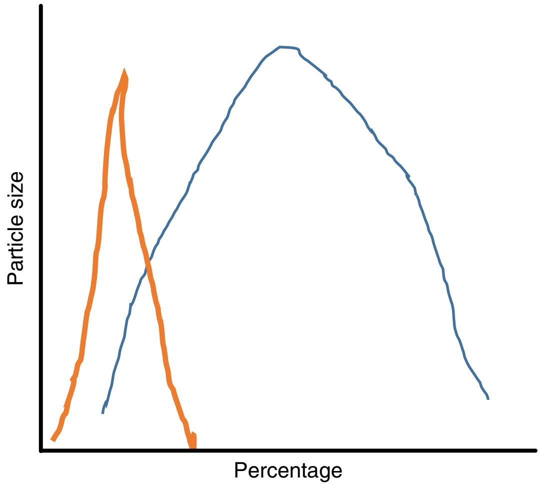

Figure 12.10 Changing particle size distribution.

This type of particle size distribution is the basis for such products as rapidly dissolving aspirin to deal with heart attacks.

It is also worth noting that whatever is done to create a certain particle size, shape, and distribution will have a major effect on downstream processing including drying, conveying and transport, and storage. We will discuss these unit operations in Chapters 13 and 14.

Crystal Phase Diagrams

Most of the time when we think about salts being soluble or insoluble, we tend to think in terms of "in solution" or "out of solution." In many cases, especially in the inorganic salt world, things are a bit more complicated. Many inorganic salts can form *hydrates* with water. For example, calcium chloride ($CaCl_2$) can exist in its normal anhydrous (without water) form or it can exist as a hydrated crystal, that is, $CaCl_2 \cdot 2H_2O$. This material, if we go back to the periodic table and calculate the weights of the various molecules, is approximately 111/147 or 75.5% $CaCl_2$. Though this material is approximately 25% water, it looks like a white solid. Calcium chloride also forms hydrates with 1 and 6 moles of waters of hydration. Sodium chloride (NaCl) on the other hand has no hydrates and is either in solution or not. A crystalline phase diagram shows where and which hydrates form at various temperatures and concentrations. This information is critically important to have when operating an evaporator or crystallizer as it clearly defines what kinds of materials it is possible to have at any condition.

One of the most interesting and complex examples of such an inorganic salt phase diagram is that for magnesium sulfate ($MgSO_4$). This salt forms hydrates with 0.5, 1, 2, 4, 6, and 7 moles of hydration. The compound with 7 moles of water, $MgSO_4 \cdot 7H_2O$, is the product sold in grocery and drug stores as "Epsom salts." Again, if we calculate the percentage of $MgSO_4$ in the product, it is approximately 120/120 + 126 or 49% $MgSO_4$. But if we pour it out of its container, it appears to be a normal anhydrous solid. Figure 12.11 shows the phase diagram for this compound and its waters of hydration.

There are some very important points that we know about this system by simply looking at the phase diagram:

1) A *liquid* solution of $MgSO_4$ can only exist at conditions indicated on the left side of the phase diagram (approximately 0–40%) $MgSO_4$ over the temperature range of 25–200°F.
2) At each weight fraction and temperature, the phase diagram tells us which species will exist; a mass balance calculation will tell us how much of each we have. For example, between 120 and 150°F and a concentration

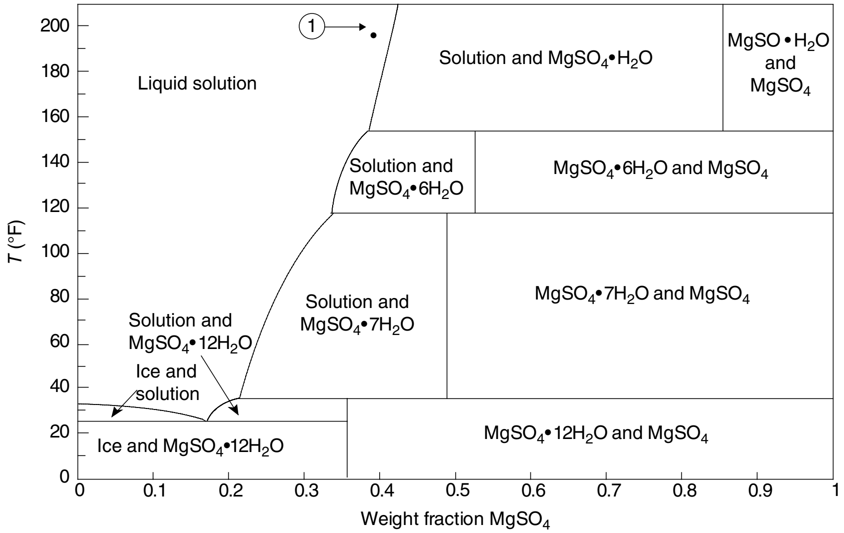

Figure 12.11 Phase diagram for magnesium sulfate ($MgSO_4$). Source: Reproduced with permission of NASA.

(weight fraction) of 53–100% $MgSO_4$, we will have a mixture of two solids, $MgSO_4{\cdot}6H_2O$ and $MgSO_4$ (anhydrous). We do not get to choose what we have within this part of the diagram. That is why it is so important to know whether a salt being crystallized has such a diagram and what it looks like.

3) The consequence of not understanding such a diagram (if it exists) is obtaining an undesired product and, from a practical and operating perspective, plugged lines and vessels when solids are present or when liquids were assumed to be present.

Supersaturation

This is a process technique occasionally used to produce very fine particle size. All of us have heard the tale about the frog sitting in a pan of hot water, and the temperature being raised so slowly that the frog never realizes what is happening and gets scalded to death before it realizes how hot the water is. The reverse of this is true for crystallizers. It is possible to cool a saturated salt solution extremely slowly so that, in effect, the solution forgets that it is supposed to precipitate out the salt it contains. At some point though, the phase diagram takes over and a large amount of very fine crystals is generated very rapidly.

Crystal Purity and Particle Size Control

As the crystals are precipitating from the mother liquor, there will be some entrapment of the solvent (from which they are precipitating from) inside the crystals. This will be affected by the rate of crystallization, the particle size distribution, particle morphology, and surface tension effects. Depending upon the quality requirements for the final product, it may be necessary to redissolve the product from the first crystallization and recrystallize (possibly in a slightly different manner) to produce the product quality needed.

Particle size control will be affected by all the process variables we have discussed, and again there may need to be second or third crystallization to obtain the crystal purity and particle size distribution required. It is critical to understand the customer and business requirements as crystallizers are designed and operated.

Summary

The unit operations of evaporation and crystallization are used to concentrate liquid solutions, with dissolved solids, or to precipitate and recover materials dissolved in solution as products. Optimization of these processes depends upon a thorough understanding of the physical chemistry of the solutions (including phase diagrams and liquid properties such as density, surface tension, and viscosity), the particle size and particle size distribution requirement of the final products, and how the wet solids will be further processed. These downstream processes, which we will discuss in Chapters 13–15, include filtration, drying, and solids handling and storage.

Evaporation in Coffee Brewing

As the coffee from a drip coffeemaker drops into a carafe that sits on a hot plate, evaporation starts, and the rate is determined by the basic equations discussed in this unit. The higher the temperature of the hot plate, the higher the rate of evaporation, significantly increasing the evaporation of water and the concentration of the remaining coffee. As discussed earlier, this will also increase the kinetic rate constant of the coffee degradation chemistry. There are coffee carafes that have no hot plates and are some form of a vacuum bottle. Since there is no way for water vapor to escape, evaporation does not occur but flavor and taste (chemical) degradation still continue, but at a lower rate.

If a traditional coffee carafe on a hot plate is left long enough, solids will begin to precipitate out of solution, just as in a crystallizer.

Discussion Questions

1 If your processes use evaporation, what is the desired concentration? How is it controlled? How is its operation affected by changes in steam pressure or temperature of the heat source?

2 How is the level in the evaporator controlled? Is it ensured that all of the steam tube area is used?

3 If a salt solution is being evaporated, is it known whether there is a phase diagram? If so, what is the impact of operating changes?

4 What can affect the heat transfer coefficient inside the evaporator?

5 To what degree is fouling an issue?

6 If crystallization is being used, is the phase diagram understood (if applicable)?

7 How do changes in operating conditions (agitation speeds, rate of temperature decrease, etc.) affect particle size and particle size distribution? What is the effect on any changes on product use and quality?

Review Questions (Answers in Appendix with Explanations)

1 Evaporation involves concentrating:
A __A liquid in a solid
B __A solid in a liquid
C __A gas in a liquid
D __A liquid in a gas

2 The primary design equation for an evaporator considers:
A __Boiling point of the liquid
B __Pressure in the evaporator
C __Temperature difference between the heat source and the boiling point of the solution
D __All of the above

3 The boiling point of a solution to be evaporated with steam is affected by all but:
A __Pressure
B __Steam price
C __Concentration of dissolved salts
D __Temperature differential between heat source and boiling point of the solution

4 The boiling point of a salt solution will ____ with increased concentration of the dissolved salt:
A __Decrease
B __Need more information to answer
C __Increase
D __Rise by the square root of concentration change

5 If the steam pressure feeding an evaporator slowly decreases with time, the salt concentration leaving the evaporator will _____over the same time period:
A __Increase
B __Decrease
C __Stay the same
D __Depends (on what?) _____

6 Salt solution carry over into the vapor phase of an evaporator can be minimized through the use of:
A __Prayer
B __Filters
C __Cyclones
D __Demisters

7 Multi-effect evaporators function by:
A __Using the vapor from one stage to vaporize another stage
B __Using the "super-effect" of steam
C __Condensing the first stage vapor and then boiling it a second time
D __Taking advantage of off-peak power prices

8 Film evaporators are used primarily for:
A __Temperature-sensitive and high viscosity materials
B __Emotionally sensitive materials
C __Hold your temper materials
D __All of the above

9 The basic difference between evaporation and crystallization is that the solution is concentrated by:

A __Use of diamonds
B __Cooling
C __Any type of heat sources that is available except steam
D __Suction

10 The types of crystals produced in a crystallizer are affected by:

A __Phase diagram
B __Rate of cooling
C __Amount of agitation
D __All of the above

11 A phase diagram for a salt and solvent will determine all but:

A __The types of crystals that will be formed
B __Where various hydrates will form as a function of temperature and concentration
C __Cost incurred to operate at a particular point within the phase diagram
D __How to produce certain types of salt hydrates

Additional Resources

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