Substance	$p =$ vapor pressure, mmHg	$m = \frac{p}{760}$	z_F	$\frac{W}{D} = 3.0$ $\frac{z_F(W/D + 1)}{1 + W/D_m} = y_D^*$	$\frac{W}{D} = 2.08$ y_D^*	$x_W = \frac{Fz_F - Dy_D^*}{W} = \frac{y_D^*}{m}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
A	1370	1.803	0.50	$\frac{0.5(3 + 1)}{1 + 3/1.803} = 0.750$	0.715	0.397
B	550	0.724	0.25	0.1940	0.1983	0.274
C	200	0.263	0.25	0.0805	0.0865	0.329
				$\Sigma = 1.0245$	0.9998	1.000

Successive flash vaporizations can be made on the residual liquids in a series of single-stage operations, whereupon the separation will be better than that obtained if the same amount of vapor were formed in a single operation. As the amount of vapor formed in each stage becomes smaller and the total number of vaporizations larger, the operation approaches differential distillation in the limit.

DIFFERENTIAL, OR SIMPLE, DISTILLATION

If during an infinite number of successive flash vaporizations of a liquid only an infinitesimal portion of the liquid were flashed each time, the net result would be equivalent to a differential, or simple, distillation.

In practice this can only be approximated. A batch of liquid is charged to a kettle or still fitted with some sort of heating device such as a steam jacket, as in Fig. 9.16. The charge is boiled slowly, and the vapors are withdrawn as rapidly as they form to a condenser, where they are liquefied, and the condensate (distillate) is collected in the receiver. The apparatus is essentially a large-scale replica of the ordinary laboratory distillation flask and condenser. The first portion of the distillate will be the richest in the more volatile substance, and as distillation proceeds, the vaporized product becomes leaner. The distillate can therefore be collected in several separate batches, called *cuts*, to give a series of distilled products of various purities. Thus, for example, if a ternary mixture contained a small amount of a very volatile substance A, a majority of substance B of intermediate volatility, and a small amount of C of low volatility, the first cut, which would be small, would contain the majority of A. A large second cut would contain the majority of B reasonably pure but nevertheless contaminated with A and C, and the residue left in the kettle would be largely C. While all three cuts would contain all three substances, nevertheless some separation would have been obtained.

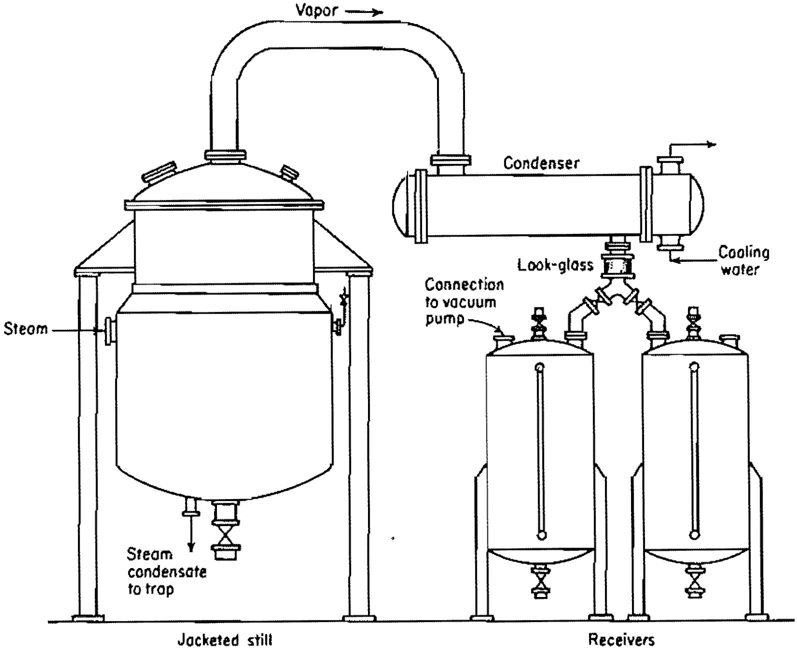

Figure 9.16 Batch still.

For such an operation to approach even approximately the theoretical characteristics of a differential distillation, it would have to proceed infinitely slowly so that the vapor issuing from the liquid would at all times be in equilibrium with the liquid. All entrainment would have to be eliminated, and there could be no cooling and condensation of the vapor before it entered the condenser. Despite the fact that these conditions are substantially impossible to attain, it is nevertheless useful to study the limiting results which a differential distillation could produce as a standard for comparison.

Binary Mixtures

The vapor issuing from a true differential distillation is at any time in equilibrium with the liquid from which it rises but changes continuously in composition. The mathematical approach must therefore be differential. Assume that at any time during the course of the distillation there are L mol of liquid in the still of composition x mole fraction A and that an amount dD mol of distillate is vaporized, of mole fraction y^* in equilibrium with the liquid. Then we have the following material balances:

	Total material	Component A
Moles in	0	0
Moles out	dD	y^*dD
Moles accumulated	dL	$d(Lx) = Ldx + xdL$
In—out = accumulation	$0 - dD = dL$	$0 - y^*dD = Ldx + xdL$

The last two equations become

$$y^*dL = Ldx + xdL \tag{9.41}$$

$$\int_W^F \frac{dL}{L} = \ln\frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{y^* - x} \tag{9.42}$$

where F is the moles of charge of composition x_F and W the moles of residual liquid of composition x_W. This is known as the *Rayleigh equation*, after Lord Rayleigh, who first derived it. It can be used to determine F, W, x_F, or x_W when three of these are known. Integration of the right-hand side of Eq. (9.42), unless an algebraic equilibrium relationship between y^* and x is available, is done graphically by plotting $1/(y^* - x)$ as ordinate against x as abscissa and determining the area under the curve between the indicated limits. The data for this are taken from the vapor-liquid equilibrium relationship. The *composited* distillate composition $y_{D,\text{av}}$ can be determined by a simple material balance,

$$Fx_F = Dy_{D,\text{av}} + Wx_W \tag{9.43}$$

Differential Condensation

This is a similar operation where a vapor feed is slowly condensed under equilibrium conditions and the condensate withdrawn as rapidly as it forms. As in distillation, the results can only be approximated in practice. A derivation similar to that above leads to

$$\ln\frac{F}{D} = \int_{y_F}^{y_D} \frac{dy}{y - x^*} \tag{9.44}$$

where F is the moles of feed vapor of composition y_F and D the vaporous residue of composition y_D.

Constant Relative Volatility

If Eq. (9.2) can describe the equilibrium relation at constant pressure by use of some average relative volatility α over the concentration range involved, this can be substituted in Eq. (9.42) to yield

$$\ln\frac{F}{W} = \frac{1}{\alpha - 1}\ln\frac{x_F(1 - x_W)}{x_W(1 - x_F)} + \ln\frac{1 - x_W}{1 - x_F} \tag{9.45}$$

and graphical integration can be avoided. This can be rearranged to another useful form

$$\log\frac{Fx_F}{Wx_W} = \alpha \log\frac{F(1-x_F)}{W(1-x_W)} \tag{9.46}$$

which relates the number of moles of A remaining in the residue, Wx_W, to that of B remaining, $W(1 - x_W)$. These expressions are most likely to be valid for ideal mixtures, for which α is most nearly constant.

Illustration 9.6 Suppose the liquid of Illustration 9.4 [50 mol % *n*-heptane (A), 50 mol % *n*-octane (B)] were subjected to a differential distillation at atmospheric pressure, with 60 mol % of the liquid distilled. Compute the composition of the composited distillate and the residue.

SOLUTION *Basis*: $F = 100$ mol. $x_F = 0.50$, $D = 60$ mol, $W = 40$ mol. Eq. (9.42):

$$\ln\frac{100}{40} = 0.916 = \int_{x_W}^{0.50}\frac{dx}{y^* - x}$$

The equilibrium data are given in Illustrations 9.1 and 9.4. From these, the following are calculated:

x	0.50	0.46	0.42	0.38	0.34	0.32
y^*	0.689	0.648	0.608	0.567	0.523	0.497
$1/(y^* - x)$	5.29	5.32	5.32	5.35	5.50	5.65

x as abscissa is plotted against $1/(y^* - x)$ as ordinate, and the area under the curve obtained beginning at $x_F = 0.50$. When the area equals 0.916, integration is stopped; this occurs at $x_W = 0.33$ mole fraction heptane in the residue. The composited distillate composition is obtained through Eq. (9.43),

$$100(0.50) = 60y_{D,\text{av}} + 40(0.33)$$

$$y_{D,\text{av}} = 0.614 \text{ mole fraction heptane}$$

Note that, for the same percentage vaporization, the separation in this case is better than that obtained by flash vaporization; i.e., each product is purer in its majority component.

Alternatively, since for this system the average $\alpha = 2.16$ at 1 atm (Illustration 9.1), Eq. (9.46):

$$\log\frac{100(0.5)}{40x_W} = 2.16 \log\frac{100(1-0.5)}{40(1-x_W)}$$

from which by trial and error $x_W = 0.33$.

Multicomponent Systems—Ideal Solutions

For multicomponent systems forming ideal liquid solutions, Eq. (9.46) can be written for any two components. Ordinarily one component is chosen on which to base the relative volatilities, whereupon Eq. (9.46) is written once for each of the others. For example, for substance J, with relative volatility based on substance B,

$$\log\frac{Fx_{J,F}}{Wx_{J,W}} = \alpha_{JB} \log\frac{Fx_{B,F}}{Wx_{B,W}} \tag{9.47}$$