

last previous trial. When the K_j are affected more strongly by composition, it may be necessary to converge the K_j as an inner loop for each assumed value of T or to converge all composition variables simultaneously in a full multivariate Newton solution (Appendix A).

When two immiscible liquid phases are in equilibrium with a vapor phase, the computation becomes more complex. Henley and Rosen (1969) suggest methods for approaching that problem.

CHECKING PHASE CONDITIONS FOR A MIXTURE

By extending the reasoning involved in dew- and bubble-point calculations it can be seen that a mixture for which $\sum K_i x_i < 1$ will be a subcooled liquid, whereas if $\sum K_i x_i > 1$, the mixture must contain at least some vapor. Similarly, if $\sum (x_i/K_i) < 1$, a mixture will be a superheated vapor, and if $\sum (x_i/K_i) > 1$, the mixture must contain at least some liquid. Thus we can set up the following criteria to ascertain the phase condition of a mixture which potentially contains both vapor and liquid:

$\sum K_i x_i$	$\sum (x_i/K_i)$	Phase condition
< 1	> 1	Subcooled liquid
$= 1$	> 1	Saturated liquid
> 1	> 1	Mixed vapor and liquid
> 1	$= 1$	Saturated vapor
> 1	< 1	Superheated vapor

Similar criteria can be set up for mixtures that are potentially combinations of two immiscible phases, mixtures of a vapor and two liquids, etc.

ANALYSIS OF SIMPLE EQUILIBRIUM SEPARATION PROCESSES

The analysis of equilibrium or ideal separation processes is important for two reasons: (1) It is frequently possible to provide a close approach to product equilibrium in real separation devices. Such is true, for example, for most vapor-liquid separators and for mixer-settler contactors for immiscible liquids. (2) A common practice is to correct for a lack of product equilibrium or ideality by introducing an *efficiency* factor into the calculation procedures used for equilibrium or ideal separations.

In analyzing the performance of a simple separation device one might typically want to calculate the flow rates, compositions, thermal condition, etc., of the products, given the properties and flow rates of the feed and such additional imposed conditions as are necessary to define the separation fully, e.g., the quantity of separating

agent employed and the temperature of operation. The quantities to be calculated will vary from situation to situation. For example, one might want to compute the amount of separating agent necessary to give a certain product recovery or the amount of product which can be recovered in a given purity. In any event, the solution will involve:

1. Specifying the requisite number of process variables
2. Developing enthalpy and mass-balance relationships
3. Relating the product compositions through the separation factor or through equilibrium or ideal rate data with corrections for any departure from equilibrium or ideality
4. Solving the resulting equations to obtain values for unknown quantities

Process Specification: The Description Rule

To solve a set of simultaneous equations one must specify the values of a sufficient number of variables for the number of remaining unknowns to be exactly equal to the number of independent equations. If there are five independent equations, there may be no more than five unknown variables for there to be a unique solution. The same reasoning applies to any separation process. If the behavior of the process is to be fully known or is to be uniquely established, there must be a sufficient number of specifications concerning flow rates, temperatures, equipment sizings, etc. The *number* of variables which must be set will depend on the process; on the other hand, the *particular* variables which are set will depend on the problems posed, the answers sought, and the methods of analysis available for calculation. If the problem is overdefined, no answer is possible; if it is underdefined, an infinite number of solutions may exist.

A separation process (or for that matter any process) can always be described by simply writing down all the independent equations which apply to it. Inevitably, the number of unknowns in these equations will be greater than the number of equations. Thus the equations cannot be solved until a sufficient number of the unknowns have had values assigned to them to reduce the remaining number of unknowns to the number of equations. The unknowns to which we assign values are the independent variables of the particular problem under consideration, and the remaining unknowns are the dependent variables.

The procedure of itemizing and counting equations is tedious, however, and is open to error if one misses an equation or counts two equations which are not independent. As we have seen, the phase rule also can be of assistance in determining the number of variables which can be independently specified, but it becomes difficult to apply the phase rule in a helpful way as processes become more complex. A more direct approach is afforded by the *description rule*, originally developed by Hanson et al. (1962), which relies upon one's physical understanding of a process.

Put in its simplest form, the description rule states that *in order to describe a separation process uniquely, the number of independent variables which must be specified is equal to the number which can be set by construction or controlled during*

operation by independent external means. In other words, if we build the equipment, turn on all feeds, and set enough valves, etc., to bring the operation to steady state, we have set just enough variables to describe the operation uniquely. In any particular problem where we wish to specify values of any variables which are not set in construction or by external manipulation, we must leave an equal number of construction and external-manipulation variables unspecified. We can replace specified variables on a one-for-one basis.

The description rule is useful for determining the *number* of variables which can be specified. The *particular* variables which are specified will vary considerably from one type of problem to another. If the problem at hand deals with the *operation* of an already existing separation process, the list of specified variables may coincide very nearly or exactly with the list of variables set by construction and controlled during operation. If the problem deals with the *design* of a new piece of equipment, the list of specified variables may be quite different. Typically, variables relating to equipment size will be replaced by variables giving the quality of separation desired.

Often there are upper and lower limits placed upon the values which can be specified for independent variables. For example, amounts of feed must be positive, mole fractions must lie between 0 and 1, etc. For simple equilibration processes identifying these limits is often trivial, but for many more complex processes it is not.

For a new student use of the description rule can be confusing at first because it requires a physical feel for the cause-and-effect relationships occurring. However, it is certainly desirable for an engineer to develop this physical feel, and using the description rule to help specify problems is a direct way of developing it. Furthermore, physical consideration of the degrees of freedom is basic to the selection and understanding of control schemes for separation processes. For that reason control systems are included in diagrams and process descriptions for examples in this book. The number of variables left to be specified after construction of the equipment is the number to be controlled somehow.

A continuous steady-state flash process with preheating of the feed is shown in Fig. 2-6. A liquid mixture (feed) receives heat (separating agent) from a steam heater and then passes through a pressure-reduction, or expansion, valve into a drum in which the phases are separated. Vapor and liquid products are withdrawn from the drum and are close to equilibrium with each other. It is possible to eliminate either the heater or the pressure-reduction valve from the process. In the scheme shown in Fig. 2-6 the drum temperature is held constant by control of the steam rate, the drum pressure controls the vapor-product drawoff, and the liquid product is on level control. Several other control schemes are possible.

Design and construction ensure simple equilibrium between the gas and liquid products, since we assume that there is adequate mixing in the feed line and adequate phase disengagement in the drum. We can apply the description rule further and let the control schemes set the pressure and temperature of the equilibrium. The level control system holds the liquid level in the drum constant, thereby making steady-state operation and satisfactory phase disengagement possible. The process will then be fully specified if the feed composition and flow rate are established before the feed comes to the process. Notice that the temperature and pressure of the feed to the

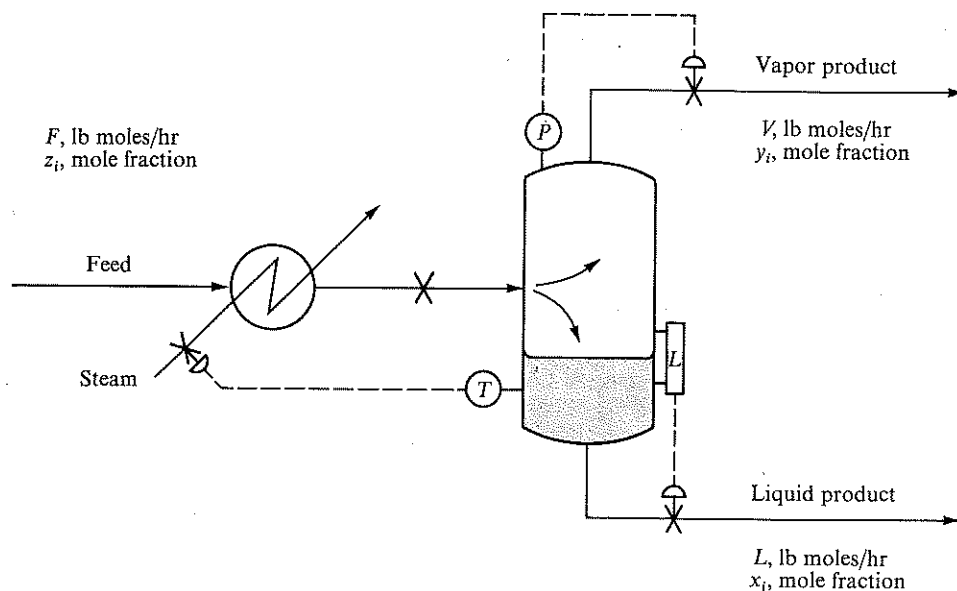


Figure 2-6 Continuous equilibrium flash vaporization.

process do not affect the separation since they are both changed to the temperature and pressure desired for the equilibrium.

For the problems to be considered in this chapter, we shall take the feed composition and flow rate to be specified in all cases, postulate simple equilibrium in all cases, and keep the level control loop to hold steady-state operation. Two more variables must be specified in order to define the process. In Fig. 2-6 these are the pressure and temperature of the equilibrium, but in general these variables may be any two of the group:

T = temperature

P = pressure

V/F = fraction vaporization

v_i/f_i = fraction vaporization for component i

H = total product enthalpy (as in adiabatic flash where heater is absent)

We shall consider problems where various pairs of these variables are specified.

Algebraic Approaches

An algebraic approach to the complete analysis of a separation generally involves the use of K 's or α 's to relate product compositions. We shall develop the appropriate equations and discuss solution procedures in terms of an equilibrium vaporization or flash process; however, the equations will be general to all simple continuous-flow equilibrium separations for which K 's and α 's can be determined.