
5

FUNDAMENTALS OF CHEMICAL ENGINEERING FOR PROCESS OPERATORS

5.1 INTRODUCTION

In order to solve chronic process-operating problems, some basic understanding of chemical engineering is required. This chapter summarizes some of the basic chemical engineering skills necessary to develop solutions to chronic process problems. Mastery of this chapter will aid in the formulation of theoretically correct working hypotheses. A failure to master the concepts will cause one to propose working hypotheses that are fundamentally impossible. While the rapid development of working hypotheses may seem to be the most expedient approach, the emphasis on speed will almost always delay the development of a theoretically correct working hypothesis.

The concepts are presented in a format designed to be understood by a reader with a basic understanding of algebra and chemistry. A quick review of the different means by which to measure flow rates around a process vessel will be helpful. These different measurements are as follows:

- *Mass Rate*: This is the most helpful measurement when working with material balances as will be described later. It is simply the mass rate of material leaving or entering a vessel expressed in units such as lb/hr.
- *Volume Rate*: This is a similar measurement, expressed in volumetric units such as gallons/minute.
- *Mol Rate*: The mol rate is an empirical value that is determined by dividing the mass rate by the molecular weight of the material. It has limited

value in discussions involving material or heat balances or fluid flow, but has great value in discussions of equilibrium or reaction rates.

The concepts in this chapter deal with the basic aspects of chemical engineering. They do not touch on process technology. As indicated in an earlier chapter, the specific details of the process technologies are normally presented in operating manuals or licensing packages. The basic concepts discussed in this chapter are as follows:

- *Material Balances:* Around any process vessel at steady state, the material leaving (expressed in mass per unit time, e.g., lb/hr) must equal the material entering the vessel. “Steady state” means that there is no change in the vessel inventory. If there is change in the vessel inventory, the steady state assumption will not apply because material is being accumulated or deaccumulated. It is important that the material balance be expressed in mass units rather than mol or volume units. Often, if a reaction is occurring, there will not be full closure unless mass units are used. That is because reaction often changes the density or number of mols. The same concerns are present if there is a great temperature difference between the inlet and outlet flow of a vessel. In this case, the mass balance will still be valid, but because of the change in density associated with the temperature change, a volume balance will show more or less material leaving than entering.
- *Heat Balances:* When a system is at steady state, any heat added to or removed from the process must be from either the heat of a reaction or heat added/removed by way of direct or indirect heating or cooling. An example of this is an exothermic reaction, which adds heat to the process. In this case, the heat of reaction must be removed by way of direct or indirect cooling for the system to remain at a constant temperature.
- *Fluid Flow:* The flow of fluids (gas or liquids) results in a frictional pressure drop. It is of value to know how to calculate the pressure loss.
- *Equilibrium:* All chemical engineering operations have an equilibrium limit. A reaction that has reached equilibrium will not proceed further, regardless how much time is provided.
- *Kinetics:* Kinetics deal with the speed of a chemical engineering process. They can be associated with heat transfer, reaction, solvent removal, or other unit operations.
- *Equipment Design:* This section is certainly not an exhaustive discussion of equipment design. However, since equipment design is a key factor in determining the speed of a chemical engineering process, it is important to have some knowledge of equipment design factors that influence this parameter.

Each of these concepts is discussed in the following sections.

5.2 CONSISTENCY OF UNITS AND DIMENSIONAL ANALYSIS

There is a well-worn cliché used in elementary algebra which states, “You cannot add apples and oranges.” If you do add apples and oranges, you cannot call them by either specific name and have to resort to calling them “pieces of fruit.” Likewise, any chemical engineering analysis requires that consistent units be utilized. In the simplest examples of this concept, lb/hr cannot be added to gal/min. The values must be converted to the same set of units. The conversion of gal/min to lb/hr is very simple; it can be done by multiplying the value in gals/min by the density in lb/gal and the number of minutes in an hour. While this appears very simple, there is often a question of whether a factor should be used as a multiplier or a divisor. Often, even highly skilled people will multiply when they should be dividing. Dimensional analysis provides a means to confirm the validity of the mathematical operation that is being used. For example, to convert a flow of gal/min to lb/hr, the dimensional check is as shown in equation (5-1) below:

$$\text{lb/hr} = \frac{\text{gal}}{\text{min}} \times \text{lb/gal} \times 60 \frac{\text{min}}{\text{hr}} = \text{lb/hr} \quad (5-1)$$

The gallon terms in the numerator and denominator cancel each other out, as does the minute term, leaving only the lb/hr term. This can become more difficult when more complicated relationships are involved. However, the principle of dimensional analysis is still valid. While this is a simple concept, it is unfortunately often overlooked in calculations and in stating the results of a calculation. The key ideas to remember are to state the dimensions of the calculations, to be consistent with units, and to make sure that all conversions of units are done correctly.

5.3 ABSOLUTE UNITS

While absolute units of temperature and pressure are covered in all high school chemistry courses, they are such an integral part of chemical engineering that they are reviewed in this section. The actual pressure in a vessel is that which is measured plus atmospheric pressure. This can be easily visualized by considering the measurement of the pressure in an automobile tire. The stem on the pressure gage being used is displaced by a distance that is proportional to the difference between the pressure inside the tire and the pressure outside the tire (atmospheric pressure). Thus the pressure inside the tire is actually the atmospheric pressure plus the measured pressure. This is referred to as “absolute pounds per square inch” (psia). It is this factor that is important in all calculations involving material characteristics that depend on pressure, for example, density. It is also important in determining compression ratio and in almost any calculation in chemical engineering.

In a similar fashion, absolute temperature must be used in the evaluation of such items as material density, radiant heat transfer, compressor compression ratios, and head calculations, as well as other terms. While, thermodynamically, absolute zero is defined as the temperature at which all molecular motion ceases, this does not have much pragmatic meaning. When you are using the English units of temperature, Fahrenheit or °F, the absolute temperature in Rankine units, or °R, is obtained by adding 460 to the temperature in °F.

5.4 MATERIAL BALANCES

The key concept in understanding material balances is that matter can neither be created nor destroyed. This concept is valid for every process except those dealing with atomic fusion or fission. This means that if the amount of material entering a given process or unit operation is known, the amount of material leaving is also known—it is equal to the amount of material entering. However, this concept is valid for mass units *only* at steady state. In the process industry, the quantity of material can be measured by mass units (pounds or kilograms), volume units (gallons or liters), or in mols. When dealing with material balances, only mass units should be used. A process that is operating at steady state is one in which there is no component accumulation or deaccumulation. For example, if an accumulator drum is included in the process, the level must be constant for the process to be considered to be at steady state.

Figure 5-1 shows a simple storage drum. If the fluid entering the drum is close to the ambient temperature, there will be no temperature change in the

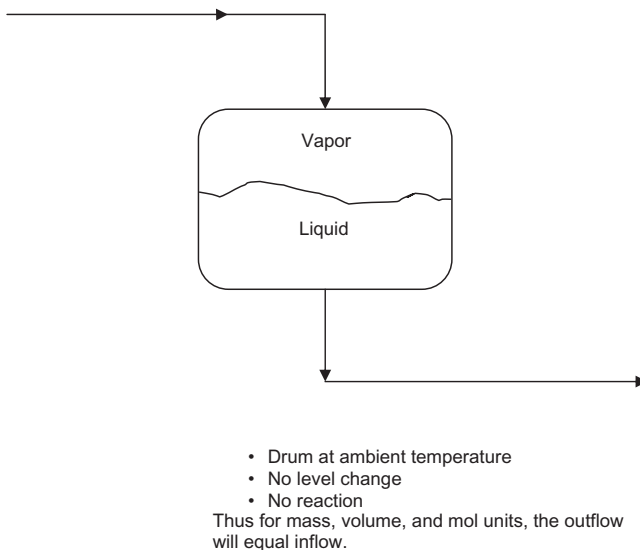


Figure 5-1 Material balance for simple drum.

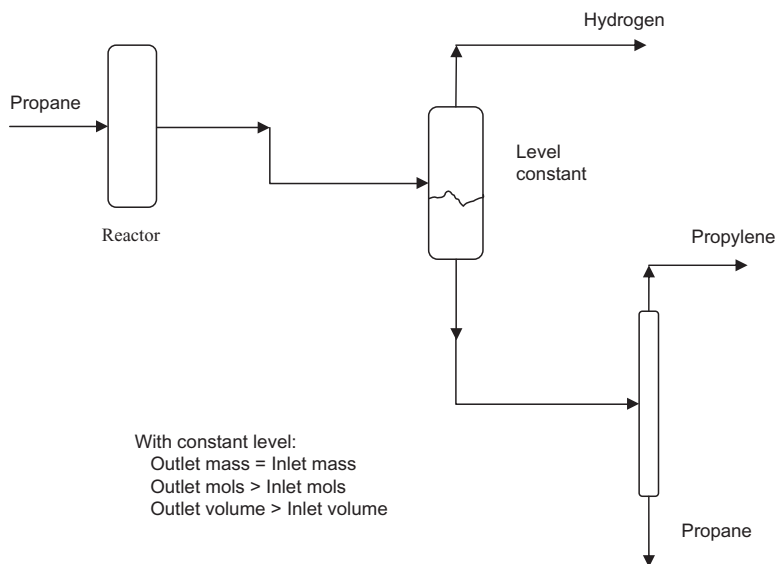


Figure 5-2 Simple process with reaction.

drum. In addition, there is no reaction occurring in the simple drum. Thus in this isolated case, the mass balance, volume balance, and mol balance will show no change. That is, the units (mass, volume, or mol) entering will equal those leaving, as long as there is no change in level.

As an example of a more complicated system, consider the reactor system shown in Figure 5-2. The reaction being conducted in the reactor is the dehydrogenation of propane to produce propylene and hydrogen. The chemistry of the process is shown below:



By material balance if there are 100lb/hr of propane in the reactor feed, there must be 100lb/hr of propylene and hydrogen leaving the reactor. If the flow meters on the feed and products validate this concept, the process is said to be “in material balance.” In addition, the material balance concept can be used to confirm flow meter accuracy or determine the flow of an unmeasured stream. An inspection of equation (5-2) indicates that there are more mols leaving the reactor than entering the reactor. That is because 1 mol of propane generates 1 mol of propylene plus 1 mol of hydrogen. Thus the material balance concept is not applicable for a mol balance. In a similar fashion, it can be shown that the material balance does not apply to a volume balance. In some industries such as refining that utilize volume units consistently, some processes will have either a volume gain or loss. Therefore, mass balances are the only valid use of material balances.

In addition to only using mass units for material balances, the process being considered must be at steady state. In Figure 5-2, if the level in the gas separator is constant, the process will be in material balance if the flow meters are correct. However, if the level is not constant, it is not operating at steady state and it will appear to be “out of material balance.” Ensuring that a process is at steady state is imperative in any utilization of material balance concepts.

The simplified sketch shown in Figure 5-2 makes it relatively easy to understand the material balance concept. In actual practice, the process flows are always more complicated. The utilization of a technique to make sure that the input and output streams, as well as the components, are adequately accounted for is often required. One technique for this is shown in Figure 5-3. In this figure, the same process (propane dehydrogenation) is shown. A possible internal recycle stream is added. To ensure that all streams are adequately accounted for, the technique of encircling the process is shown. Using this technique, any stream that is “cut” by the encircling line must be included in the material balance. Conversely, any stream that is not “cut” is not included in the material balance. Therefore the recycle stream would not be included in the material balance.

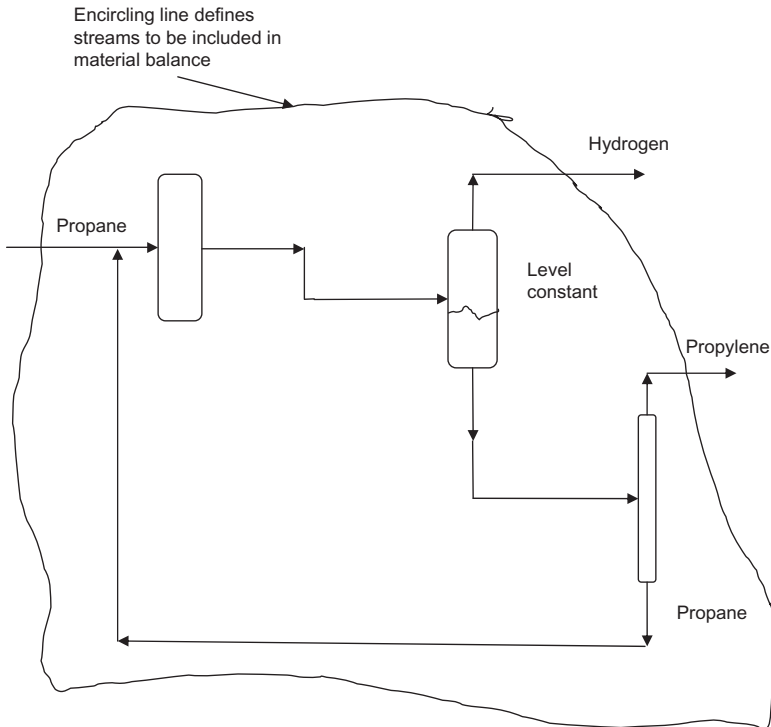


Figure 5-3 Material balance with encircling line.

The material balance concept can also be used as a technique to measure the rate of accumulation or deaccumulation in a process or process vessel. For example, if the measured flow going into and out of a process accumulator, such as the one shown in Figure 5-1, were known, the difference would represent the rate of accumulation in the vessel. For example, if the inlet flow meter to a process vessel showed 15,000 lb/hr and the outlet flow meter showed 10,000 lb/hr, the liquid would be accumulating at a rate of 5000 lb/hr or, if the liquid was water with a density of 62.4 lb/ft³, the accumulation rate would be 80 ft³/hr. As will be discussed in later chapters, this is a means of confirming the accuracy of a level instrument. However, it is also a possible source of error. If the accumulation or deaccumulation is determined as a small difference between two large numbers, a small error in either number can create a significant error in the difference.

5.5 VOLUME/MOL/MASS CONVERSIONS

As indicated, to fully utilize the concept of material balance, the rates should be given in mass units (lb/hr, kg/min, etc.). The process for converting from volume or mol units to mass units is fairly simple. If the flow rates are given in volume units (gallons, liters, etc.), they can be converted to mass units through multiplication by the appropriate density. If the rates are given in mols, they can be converted to mass units through multiplication by the molecular weight. Molecular weights and liquid densities can be found in reference books or internet sources.

However, gas densities require some elaboration. Gas densities in English units (lb/ft³) can be calculated with the equation shown below:

$$\rho = MW \times P \times 520 / (379 \times T \times 14.7 \times Z) \quad (5-3)$$

where

ρ = gas density in lb/ft³

MW = average molecular weight of the gas

P = pressure of the gas in psia

T = absolute temperature in °R (460+°F)

Z = compressibility factor (will be equal to 1 for low pressures)

The basis for equation (5-3) is that 1 mole of any gas at atmospheric pressure (14.7 psia) and 520°R occupies a volume of 379 ft³. Then, by definition, 1 mole contains a mass equivalent to the molecular weight of the gas. As the gas pressure is increased or the gas temperature is decreased, the gas becomes denser, as more molecules can now fit into the same space. At moderate and high pressures, the simple ratios between temperature and pressure are not completely adequate to calculate the gas density. The compressibility factor is

necessary at the higher pressures, to account for the fact that more gas can be compressed into the given volume than is explained simply by the pressure and temperature relationship.

EXAMPLE PROBLEM 5-1

Assume that you need to find the density of a mixture of propane and butane gas at the following conditions:

- The gas is 50 mol% of each compound.
- The pressure is 25 psig.
- The temperature is 90°F.
- The molecular weight of propane is 44 and the molecular weight of butane is 58.
- Since the gas is at low pressure, the compressibility is equal to 1.

When dealing with gases, a key concept to understand is that the composition given in mol % is equal to the composition in volume %. Using this concept, there are actually two different approaches to calculating the density of the gas mixture.

Approach 1: Using Mol %.

Step 1: Determine the average molecular weight of the gas. This can be accomplished with the following equation:

$$MW = (44 \times 50 + 58 \times 50) / 100 = 51 \quad (5-4)$$

Step 2: Determine the density, using equation (5-3).

$$\begin{aligned} \rho &= 51 \times (25 + 14.7) \times 520 / (379 \times (460 + 90) \times 14.7 \times 1) \\ &= 0.34 \text{ lb/ft}^3 \end{aligned} \quad (5-5)$$

Approach 2: Using volume % and individual gas densities.

Step 1: Determine the density of each gas using equation (5-3).

For propane

$$\begin{aligned} \rho &= 44 \times (25 + 14.7) \times 520 / (379 \times (460 + 90) \times 14.7 \times 1) \\ &= 0.30 \text{ lb/ft}^3 \end{aligned} \quad (5-6)$$

For butane

$$\begin{aligned} \rho &= 58 \times (25 + 14.7) \times 520 / (379 \times (460 + 90) \times 14.7 \times 1) \\ &= 0.39 \text{ lb/ft}^3 \end{aligned} \quad (5-7)$$

Step 2: Determine the average density. Remember that volume% and mol% are equal. Thus, the average gas density is:

$$\rho = (0.30 \times 50 + 0.39 \times 50) / 100 = 0.34 \text{ lb/ft}^3 \quad (5-8)$$

Either technique gives the same value for the average gas density.

One detail to be especially careful of when converting from one type of composition to another (e.g., volume% to weight%) is the method of using the given composition. The best method is to convert the old measurements to the new ones and to then make the calculations of average density or average molecular weight or composition. For example, the average density of two liquids cannot be determined by multiplication of the densities by weight% of each component, but must be determined as shown below:

$$\rho = 100 / (w_1 / \rho_1 + w_2 / \rho_2) \quad (5-9)$$

where

ρ = the average density or densities of liquids 1 and 2

w = the weight% of liquid 1 and 2

Note that this approach gives units that are equivalent to density units (mass/volume). The apparently easier method of just multiplying densities by the weight% of each liquid and dividing by 100 will give incorrect answers. While the results yielded by the easier method are sometimes close to the correct values, the difference will often be significant. In summary, when converting from one composition base to another, first of all convert the units (mass, volume or mols) to the new unit of measurement and then determine the composition.

5.6 HEAT BALANCES

When considering heat balances around parts of a process, three of the concepts discussed earlier are valid. They are as follows:

- The concept of “heat in must equal heat out” can be substituted for the similar material balance concept that “mass in must equal mass out.” However, it should also include the idea that the heat removed by a stream must be equal to the amount of heat gained by another stream. An example of this is a fractionation tower where heat is rejected to a water-cooled condenser. The heat removed by the condenser must be equal to the heat gained by the cooling water stream. This heat gained by the cooling water stream will be rejected to the atmosphere as the cooling water is routed to a cooling tower and cooled by contact with air.

- The need to have a steady state condition in order to achieve a satisfactory heat balance is similar to the need to have steady state conditions in order to achieve a satisfactory material balance. The potential for accumulation or deaccumulation of heat is also present. An example of this is an exothermic (heat generated) reaction that is occurring inside a process vessel with no means to remove the heat generated. The vessel and its contents will increase in temperature, creating an unsteady-state accumulation of heat.
- The concept of the encircling line is valid for heat balances as well as for material balances. If a stream such as that described in Figure 5-3 is cut by an encircling line, the line must be included in the heat balance. If, as in the case of the recycle stream in Figure 5-3, it is not cut by the encircling line, it should not be included in the heat balance.

A general equation that represents a heat balance around a process vessel where an exothermic reaction is taking place is as follows:

$$Q_{AC} = Q_I + Q_G - Q_O - Q_R \quad (5-10)$$

where

Q_{AC} = heat being accumulated in the process vessel (at steady state, this will be equal to zero)

Q_I = heat content of the incoming fluids

Q_G = heat generated by the reaction

Q_O = heat content of the fluids leaving the vessel

Q_R = heat removed by the cooling system

When equation (5-10) is applied, if the temperature in the process vessel is constant, there will be no heat accumulation in the vessel and Q_{AC} will be equal to zero. In that case, equation (5-10) can be rearranged as shown in equation (5-11) below:

$$Q_R = Q_I + Q_G - Q_O \quad (5-11)$$

Equation (5-11) indicates that at steady state (the process vessel is at a constant temperature), the amount of heat that must be removed by the cooling system is equal to the amount of heat added by the incoming fluids plus the heat generated by the reaction, less the heat removed by the fluids leaving the vessel. Equation (5-11) can be used for two different types of calculations. It can be used to determine how much heat must be removed by the cooling system, and it can be used to determine how much reaction is occurring, if the heat being removed by the cooling system is known.

Since a high percentage of the reactions in the process industry are exothermic, the focus of this book is on this type of reaction. However, a very

similar equation to equation (5-11) can be developed for endothermic reactions. These are reactions that require that heat be added in order to maintain the process vessel at a constant temperature.

While equations (5-10) and (5-11) appear to be conceptually relatively simple, there are obviously some questions regarding how the terms in the equations are developed. The following paragraphs are provided to describe how these terms are developed.

The heat content terms designated by the letter Q consist of a flow rate in mass/time units (e.g., lb/hr) and an enthalpy term in heat units per mass (e.g., BTU/lb). These two terms are multiplied together to give heat units/unit time (e.g., BTU/hr). Enthalpy is a thermodynamic term that is a measure of how much heat a unit mass (lb) of material contains. The English unit of enthalpy is the British thermal unit, or BTU. It is defined as the amount of energy required to raise the temperature of 1 lb of water 1 degree Fahrenheit. Enthalpy is a function of both specific heat and actual temperature. It can be found in handbooks, computer programs, or determined by calculations. The calculation technique helps to understand the meaning of the variable. It is usually calculated as follows:

$$H = C_p \times (t_A - t_R) \quad (5-12)$$

where

H = enthalpy, BTU/lb

C_p = specific heat, BTU/lb-°F

t_A = actual temperature, °F

t_R = reference temperature, °F

Specific heat, in technical terms, is the amount of heat required to raise 1 lb of a material 1°F. It can be viewed as the sensitivity of the material to heat input. Water has a specific heat of approximately 1 BTU/lb-°F. Hydrocarbon liquids have a specific heat of 0.4 to 0.6 BTU/lb-°F. Nitrogen gas, on the other hand, has a very low specific heat, about 0.14 BTU/lb-°F. The reference temperature is an arbitrary value. It can be -200°F, 0°F or any other value. *The only key is that it must stay the same for any single heat balance.*

The enthalpy term that has been considered so far has only dealt with what is known as sensible heat. Sensible heat is the heat that is removed from or added to a system in which there is no change of state, that is, in which there is no vaporization, condensation, melting, or solidification. Examples that require only consideration of sensible heat include a home water heater, process cooler, or process heater. When there is a change of state, such as condensation of vapors or vaporization, there is a change in the enthalpy, which is referred to as latent heat. Thus condensation of a vapor such as propane might occur with no temperature change, but with a significant change in enthalpy, as the vapor changes state to a liquid. Similarly, the heat of

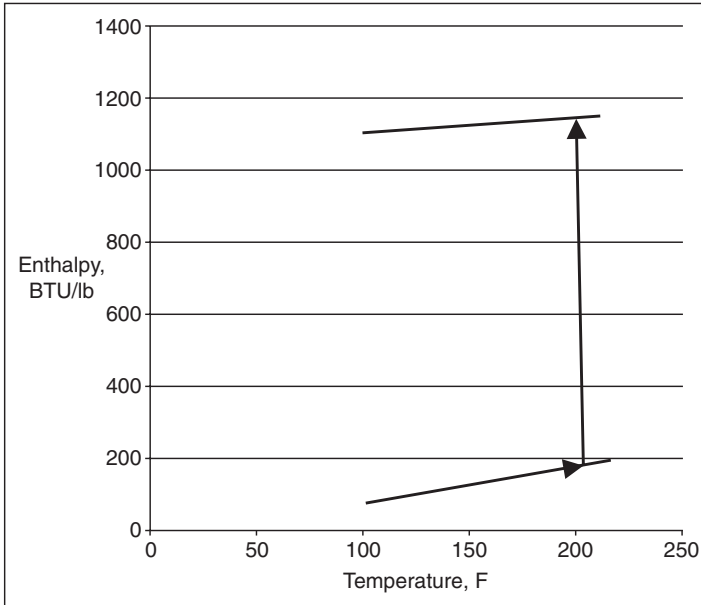


Figure 5-4 Enthalpy path to heat and vaporize water.

reaction is the heat generated when a single pound of material changes composition, and possibly state, from one component and/or state to another. Again, there may be no temperature change, but there will be a significant change in enthalpy.

These concepts are illustrated in Figure 5-4. In this figure, the enthalpy of water or steam is shown on the vertical axis and temperature is shown on the horizontal axis. The lower curve represents the enthalpy of water at its boiling point. The upper curve represents the enthalpy of steam at the boiling point of water. The actual pressure will also be a function of temperature. For example, at 212°F, we know that the pressure is atmospheric, or, 14.7 psia. At this temperature, the enthalpy of water is 180 BTU/lb and the enthalpy of the vapor (steam) is 1150 BTU/lb. By taking their difference, the latent heat of vaporization can be calculated to be 970 BTU/lb. Thus it will take 970 BTU to vaporize 1 lb of water if the water is at its boiling point. If the water is only at 100°F, sensible heat must be added to raise the temperature to 212°F. The amount of sensible heat required can be calculated using equation (5-12). In using equation (5-12), the enthalpy must be determined at the two temperatures (100° and 212°). Assuming a specific heat of water is 1 BTU/lb-°F and a reference temperature of 0°F, equations (5-13) and (5-14) show these calculations.

$$H_{100} = 1 \times (100 - 0) = 100 \text{ BTU/lb-}^\circ\text{F} \quad (5-13)$$

$$H_{212} = 1 \times (212 - 0) = 212 \text{ BTU/lb-}^\circ\text{F} \quad (5-14)$$

Thus the sensible heat required to heat the water to the boiling point is 112 BTU/lb and the total heat required to heat and vaporize a pound of water is 1082 BTU/lb (970+112). The overall path of this process is shown as a heavy line in Figure 5-4.

The purpose of this book is not to provide a source of all of the possible values of specific heat, latent heat of vaporization, or heat of reaction, but to illustrate how these values are used once they are obtained from other sources. It is likely that the procedure for determining the appropriate heat content of a process is an area in which a process operator may require assistance from a process engineer or a specialist in data resources.

EXAMPLE PROBLEM 5-2

The production process of polypropylene provides excellent examples of heat removal. The reaction is highly exothermic, which requires that heat be removed to ensure that the reactors are kept at a constant temperature. The feed streams are fed to the reactors at a temperature lower than the reaction temperature. Therefore, some of the heat of reaction is removed by the process of heating the feed streams to the temperature of the reactors. The reactor heat, though normally rejected to the atmosphere in a cooling tower, is rejected to cooling water. In this example, the following are given:

- Bulk polymerization (the only feed is propylene and a catalyst). The reactor is operated at a high enough pressure that propylene is in its liquid phase.
- Propylene is fed to the reactor at 100°F and a feed rate of 40,000 lb/hr.
- The specific heat of propylene is 0.60 BTU/lb-°F.
- The specific heat for polypropylene is 0.45 BTU/lb-°F.
- The heat of polymerization is 970 BTU/lb.
- The polymerization rate is 20,000 lb/hr, at a reactor temperature of 160°F.
- Heat is rejected to cooling water, which enters the exchangers at 90°F and exits the exchangers at 110°F.

Determine the total heat of polymerization, the amount of heat rejected to the cooling water, and the cooling water rate.

Step 1: Determine the total heat of polymerization. This can be done as shown in equation (5-15)

$$Q_G = 20,000 \times 970 = 19,400,000 \text{ BTU/hr} \quad (5-15)$$

Step 2: Determine the heat rejected to the cooling water. This can be done using equation (5-11) and equation (5-12), and assuming a reference temperature of 0°F, as follows:

$$Q_R = Q_I + Q_G - Q_O \quad (5-11)$$

$$Q_I = (100-0) \times 0.6 \times 40,000 = 2,400,000 \quad (5-16)$$

$$\begin{aligned} Q_O &= (160-0) \times 0.6 \times 20,000 + (160-0) \times 0.45 \times 20,000 \\ &= 3,360,000 \end{aligned} \quad (5-17)$$

$$\begin{aligned} Q_R &= 2,400,000 + 19,400,000 - 3,360,000 \\ &= 18,440,000 \text{ BTU/hr} \end{aligned} \quad (5-18)$$

Step 3: Determine the cooling water rate. Knowing that the heat rejected to the cooling water is 18,440,000 BTU/hr, and that the cooling water with a specific heat of 1 BTU/lb-°F enters the exchanger at 90°F and leaves at 110°F, the cooling water rate can be calculated as follows:

$$WC = 18,440,000 / ((110-90) \times 1) = 922,000 \text{ lb/hr} \quad (5-19)$$

Since cooling water rates are traditionally expressed in gallons/minute, this value can be determined as follows:

$$WC_{\text{gpm}} = 922,000 / (60 \times 8.34) = 1840 \text{ gpm} \quad (5-20)$$

Eventually, all of this 18,440,000 BTU/hr that is rejected to the cooling water must be rejected to the atmosphere, either by heating air or by vaporizing the water in the cooling tower that is used to cool the return water to 90°F.

5.7 FLUID FLOW

Any discussion of chemical engineering principles must cover fluid flow. The analyses of pump and compressor problems, as well as that of pipeline networks, all involve consideration of fluid flow. Bernoulli's equation is one of the keys to understanding fluid flow. It is shown below:

$$\Delta P / \rho + \Delta(v^2) / 2g_c + \Delta z = -w - lw \quad (5-21)$$

where, in English units,

ΔP = pressure difference between two points, lb/ft²

ρ = fluid density, lb/ft³

$\Delta(v^2)$ = difference in velocity squared between two points, (ft/sec)²

g_c = gravitational constant, ft/sec²

Δz = difference in elevation between two points, ft

w = amount of work added by the prime mover, ft

lw = frictional loss in the piping system, ft

There are several key points to be learned from an inspection of this equation.

- The units are “feet of head.” For example, when considering the units on the first term, lb/ft^2 divided by lb/ft^3 gives the units of feet. The use of feet units provides an easy means to include changes in elevation and velocity.
- For incompressible fluids (liquids) flowing in a pipe of uniform diameter with no work added and no elevation change:

$$\Delta P/\rho = -lw \quad (5-22)$$

$$\text{or } \Delta P = -lw \times \rho \quad (5-23)$$

Thus, equation (5-23) allows expression of the pressure drop in more conventional units of lb/ft^2 , or, when divided by $144 \text{in}^2/\text{ft}^2$, values of psi are obtained.

- Under certain conditions, the change in elevation will equal the frictional loss in the pipe, there will be no change in pressure head, and the pressure drop will appear to be zero.
- If there is a change in pipe diameter, there will be a direct change in pressure. That is, if the pipe diameter is increased at constant elevation and frictional loss can be ignored, the pressure will increase, since the velocity decreases.
- While Bernoulli’s equation is valid for compressible fluids (gases), the change in density with pressure makes the analysis much more complicated.

The process designer of a new plant will optimize the piping design to allow for a balance of investment and operating cost. The larger the diameter of the pipe that is used, the lower the energy loss and, hence, the lower the operating cost, but the higher the investment. In addition to this investment/operating cost optimization, there may be other factors such as vacuum operation that dictate the size of the pipe. Typical flow velocities in a pipe are 4 to 6 ft/sec for liquids and 60 to 100 ft/sec for gases.

The industrial problem solver is often faced with a situation in which there appears to be an excessive pressure drop in a pipe. Thus, he needs to know if the calculated pressure drop is really lower than the observed pressure drop. The next area to be covered in this section deals with the calculation of frictional losses. Once the calculated pressure drop is known, it can be compared with the actual pressure drop. If the actual pressure drop is higher than the calculated pressure drop, there is a chance that there is a restriction in the line. All of the terms in Bernoulli’s theory, equation (5-21) must be taken into account in the calculation of pressure drop. This is illustrated later in Example Problem 5-3.

Liquids in a pipe can have either turbulent or streamline flow; these names are descriptive of the type of flow. Streamline flow is smooth, with a well-defined flow pattern across the diameter of the pipe. The appearance is much like the flow appearance of the deep part of a river. On the other hand, turbulent flow consists of an undefined pattern, much like that of the rapids in a river. In the process industry, viscosity and flow velocity are the biggest factors in determining whether a liquid is in turbulent flow or streamline flow. Viscosity is a fluid property that measures how flowable a liquid is. For example, lubricating oil has a relatively high viscosity and flows very slowly, compared with gasoline or water. With the exception of high-viscosity liquids, most industrial flow is in the turbulent category. When considering a liquid flowing in a pipe with turbulent flow, frictional pressure losses can be calculated using equation (5-24). While this equation does not appear to be dimensionally consistent, the dimension conversion factors have been included in the constant of 0.323:

$$\Delta P = 0.323 \times f \times S \times U^2 \times L/D \quad (5-24)$$

where

ΔP = pressure drop, psi

f = a friction factor that can be approximated from the equation below:

$$f = -0.001 \times \ln(D \times U \times S/Z) + 0.0086 \quad (5-25)$$

S = specific gravity relative to water (can be obtained either from handbooks or by dividing the density of the fluid by the density of water)

U = velocity in the pipe, ft/sec (can be calculated by dividing the flow rate in ft³/sec by the cross sectional area of the pipe, ft²)

L = pipe equivalent length, ft

D = pipe diameter, in

Z = fluid viscosity, centipoises

$\ln(D \times U \times S/Z)$ = natural logarithm of the term $(D \times U \times S/Z)$

The “equivalent pipe length” is a term that takes into account fittings such as tees and elbows. These short runs of pipe cause much more pressure drop than an equivalent length of straight pipe. An approximation of the equivalent length can be made by doubling the actual linear length.

While equation (5-24) was developed for liquids which are not compressible, it can be used for compressible gases provided that the pressure drop is less than 10% of the initial pressure. If the pressure drop is greater than this, more complicated techniques to determine the pressure drop in gases will be

required. This is an area in which assistance of a graduate engineer will likely be necessary.

In addition to frictional losses in a pipe with uniform cross-sectional area, there are also frictional losses when a process fluid enters or leaves a process vessel. These losses are known as expansion or contraction losses, respectively. They are usually small, relative to the losses encountered in the pipe, although occasionally they do need to be considered. Assuming that the ratio of the pipe area to the vessel area approaches zero, the pressure drop due to expansion (flow entering the vessel) and pressure drop due to contraction (flow leaving the vessel) can be determined by equations (5-26) and (5-27), respectively.

$$\Delta P_C = 0.5 \times U^2 \times S/148.2 \quad (5-26)$$

$$\Delta P_E = U^2 \times S/148.2 \quad (5-27)$$

where

ΔP_C = pressure drop due to friction in contraction, psi

ΔP_E = pressure drop due to friction in expansion, psi

U = velocity in the pipe, ft/sec

These relationships can be used for either liquid or gas flow. The relationships can also be used to calculate the expansion or contraction loss when the pipe diameter changes. They will give elevated values, due to the assumption of the pipe-to-vessel diameter ratio being zero. Generally, the expansion and contraction loss when the pipe diameter is changed can be ignored, except for the case of exceptionally high flow velocities.

The relationships described above are valid as long as the calculated gas velocity does not exceed a value that is referred to as either sonic or acoustic velocity. Sonic velocity has been defined as the velocity of sound in a gas. For example, the velocity of sound in the atmosphere is about 1100 ft/sec. Thus the distance between a location and a lightning strike can be gauged by counting the number of seconds between the observation of the flash and the sound of the thunder and multiplying that time by 1100. In fluid flow, sonic velocity represents the maximum velocity a gas can obtain in a pipe of constant diameter or across an orifice. With a series of converging and diverging nozzles, a velocity greater than the speed of sound can be obtained. This design principle of converging and diverging nozzles is used in steam jets to achieve supersonic velocity. However, it is beyond the scope of this book to cover this area. What is important is to recognize that there is a maximum flow that can be achieved in a pipe or across an orifice. While there are calculation procedures for determining the actual sonic velocity in any fluid, most applications of this concept use the calculated ratio of the downstream and upstream pressures to determine if sonic velocity is being approached. A general rule is that sonic velocity is occurring across an orifice if the ratio of the downstream pressure to upstream pressure is less than 0.52. This is shown mathematically in equation (5-28) below:

$$P_D/P_U > 0.52 \quad (5-28)$$

where

P_D = pressure downstream of the orifice

P_U = pressure immediately upstream of the orifice

If the ratio is less than 0.52, the flow and pressure drop calculation procedures discussed earlier are not applicable.

The most common area in which this concept is applied is in the design of the orifice in safety valves. The orifice is designed to release whatever quantity is necessary to avoid over-pressuring the vessel. Essentially, all safety valves discharge to a low pressure (P_D). The upstream pressure immediately ahead of the orifice (P_U) that is in the safety valve is often much greater by several hundred psia. For example, if the discharge pressure of a safety valve is 20 psia and the upstream pressure is 150 psia, the ratio is as shown in equation (5-29) below:

$$P_D/P_U = 20/150 = 0.13 \quad (5-29)$$

Therefore, since the ratio is below 0.52, sonic velocity will occur across the orifice and a different calculation approach must be used in sizing the orifice. This is also an area in which the assistance of a graduate engineer or someone trained in sonic flow calculations will be required.

EXAMPLE PROBLEM 5-3

Water is flowing through a pipe with diameter of 3 in and length of 200 ft, at a rate of 40,000 lb/hr, at 70°F. What is the total pressure drop in the pipe? What is the “exit pressure drop” as the liquid leaves the storage vessel and enters the pipe? Assume that water has a viscosity of 1 centipoise and a density of 62.4 lb/ft³.

Step 1: Calculate the flow velocity in the pipe:

$$\text{Volumetric flow} = 40,000 / (62.4 \times 3600) = 0.178 \text{ ft}^3/\text{sec} \quad (5-30)$$

$$\text{Area of pipe} = \pi \times 3^2 / (4 \times 144) = 0.0491 \text{ ft}^2 \quad (5-31)$$

$$\text{Flow velocity} = U = 0.178 / 0.0491 = 3.6 \text{ ft/sec} \quad (5-32)$$

Step 2: Calculate the friction factor from equation (5-25):

$$DUS/Z = 3 \times 3.6 \times 1/1 = 10.8 \quad (5-33)$$

Since the density of water was given as 62.4, the specific gravity (S) of water is equal to 1.

$$f = -0.001 \times \ln(D \times U \times S/Z) + .0086 \quad (5-25)$$

$$f = -0.001 \times \ln(10.8) + 0.0086 = 0.00622 \quad (5-34)$$

Step 3: Calculate the pressure drop in the pipe using equation (5-24):

$$\Delta P = 0.323 \times f \times S \times U^2 \times L/D \quad (5-24)$$

$$\Delta P = 0.323 \times 0.00622 \times 1 \times 3.6^2 \times 200 \times 2/3 = 3.47 \text{ psi} \quad (5-35)$$

Note that the factor of 2 is included, to take into account the nonstraight run fittings (valves, elbows and tees).

Step 4: Calculate the pressure drop in the exit of the storage vessel using equation (5-26):

$$\Delta P_c = 0.5 \times U^2 \times S/148.2 \quad (5-26)$$

$$\Delta P_c = 0.5 \times 3.6^2 \times 1/148.2 = 0.043 \text{ psi} \quad (5-36)$$

This would be a fairly typical result. That is, the exit loss is generally small compared to the overall pressure drop. However, there are times when this exit loss is significant in problem solving.

The steps shown above give approximate answers which are generally sufficient for problem solving. However, the inherent errors in the procedures given are as follows:

- The empirical approach of doubling the actual length of pipe to take into account fittings is not always correct. If an accurate calculation is required, it will be necessary to count the number of each type of fitting and use handbook values to obtain the equivalent length of each fitting, and, hence, the exact total equivalent length of the pipe.
- A nominal 3-in pipe has an inside diameter that can be greater or less than 3 in, depending on the type and thickness of the pipe material. There are handbooks that provide the actual inside diameter of various types and pressure ratings of pipe.
- The equation for calculating the friction factor gives an approximate factor for commercial pipe. More accurate tables are available in handbooks that give the factor as a function of pipe roughness.

5.8 EQUILIBRIUM AND RATE

Operations other than fluid flow in the process industry can either be “equilibrium limited or “rate limited.” This is true whether the process being considered is a chemical reaction or a physical operation such as heat exchange, fractionation, adsorption, or drying. It is important to be able to understand and differentiate between the two limitations.

When attempting to understand equilibrium, an example from the day to day world might help. Think about the following questions:

- Is the earth in equilibrium with the sun?
- Is the earth getting continuously closer to or farther away from the sun? Think in terms of distances that can be easily measured on a day to day basis.

If it is believed that the earth is approximately the same distance from the sun as it was at this time last year, then it makes sense to say that the earth and sun are in equilibrium. That is, the forces that would tend to push the earth farther away from the sun or pull it closer to the sun are in balance.

Similar concepts can be applied to the process industry. In the process industry, equilibrium is a state in which there is no further change in properties, regardless of the amount of time provided. Examples of equilibrium from the process industry are:

- *Concentration of a solvent in the vapor space:* In a nitrogen-blanketed tank containing a solvent, the concentration of solvent in the vapor space will not be higher than an equilibrium amount that is a function of the temperature of the solvent.
- *Equilibrium-limited reactions:* Many chemical reactions are equilibrium-limited, meaning that the conversion of one component to another will only go to a certain level regardless of how long the reaction is allowed to continue. Again, this equilibrium can be shifted by temperature and/or the initial concentration of one of the reactants.
- *Removal of solvent from a polymer:* The drying or removal of a solvent from a polymer will sometimes be limited by the equilibrium between the solvent phase in the polymer and the solvent in the vapor. Again, this can be shifted by changes in temperature. It should be recognized that it is rare that an equilibrium concentration can be zero regardless of the temperature.
- *Dissolving of a material in a solvent:* The saturation concentration of a solute in a solvent is the equilibrium concentration at that temperature. A real world example of this principle occurs when sugar is dissolved in tea or coffee. Regardless of how hard one stirs, there is a limit to how much sugar can be dissolved.

The previous comments give a brief summary of the concept of equilibrium. Many of these concepts are discussed in more detail in subsequent chapters.

One area which requires further explanation before the information in the subsequent chapters is encountered is the concept of vapor-liquid equilibrium. The understanding of vapor-liquid equilibrium is fundamental to many key concepts, such as the understanding of the estimation of the concentration of

a solvent in the atmosphere and the understanding of the removal of a solvent from a polymer, as well as fractionation and other operations during which there is an interface between liquid and vapor phases or between polymer and vapor phases. There is some terminology that must be learned to fully understand this form of equilibrium. The key terms are as follows:

- Vapor pressure is one of the key factors in determining how much of a liquid will be in the vapor phase. For example, at the boiling point of a liquid at atmospheric pressure, the vapor pressure is equal to 14.7 psia, or 0 psig. At its boiling point, a liquid will completely vaporize, given sufficient time and heat input. Below the boiling point, the higher the vapor pressure, the higher will be the concentration of liquid in the vapor phase. Water at 100°F has a vapor pressure of 0.949 psia. Thus the mol fraction of water in the vapor immediately above a tank of water at 100°F is 0.0646 (0.949/14.7). Even though the water is more than 100°F below the boiling point, there will be water vapor in the vapor phase. Vapor pressure values can be obtained from handbooks or computer programs.
- Partial pressure is proportional to the amount of a compound in the vapor phase. It is also related to the vapor pressure and the amount of the compound in the liquid phase. Mathematically it can be expressed as follows:

$$PP = Y \times \pi = X \times VP \quad (5-37)$$

where

PP = partial pressure, psia

π = total pressure, psia

VP = vapor pressure, psia

Y = vapor phase concentration, mol fraction

X = liquid phase concentration, mol fraction

- The equilibrium constant (k) is the ratio of the vapor phase composition to the liquid phase composition, using mol fractions. This can be expressed mathematically as follows:

$$k = Y/X \quad (5-38)$$

The value of the constant (k) can often be determined from tables, charts, or computer programs. If the value is not available, it can be approximated as shown in equation (5-39) below:

$$k = VP/\pi \quad (5-39)$$

Once k is determined from tables, charts, computer programs, or from equation (5-39), equation (5-38) can be used to obtain a relationship between the

vapor and liquid phase composition. Similar relationships can be developed for polymer-vapor equilibrium; these relationships will be more complex. They are discussed in detail in Chapter 13.

The discussion of equilibrium between phases discussed above is based on ideal systems. The approach works reasonably well for a pure component or for mixtures that contain only one type of component—hydrocarbons or alcohols, for example. When considering a mixture of different types of compounds there will almost always be some “nonideality.” For example, at a fixed temperature, the k value for small amounts of methanol dissolved in hexane will almost always be higher than the k value for methanol available from charts, tables, computer programs, or calculated using equation (5-39). These mixtures are referred to as “nonideal solutions.” Water with almost any other component will form a nonideal solution.

Once the equilibrium concentration in a process is known, there will always be the question of whether this concentration can be achieved. The speed at which a solution moves from a given concentration to the equilibrium concentration is known as rate. It can be rate of reaction, rate of drying, or rate of mass transfer. As described in Chapter 9, this rate will be a function of a constant that incorporates surface area, mass transfer rates and driving force. The driving force represents the difference between the equilibrium value and actual value, and is often dictated by the process conditions.

On the other hand, the constant can be strongly influenced by equipment design. For example, if a design calls for cooling a process liquid from 120°F to 95°F, using cooling water at 90°F, which then leaves the heat exchange equipment at 110°F, the driving force is fixed. The difference in temperatures through the exchanger is the driving force, and inlet and outlet conditions for both the hot and cold sides are specified by the design. However, the surface area and the physical design of the exchanger can be varied to improve the speed of heat transfer. Therefore, the speed of heat transfer is influenced by the type of equipment to be utilized.

Table 5-1 shows the relationship between some selected variables and their effect on equilibrium, rate, or both. For example, temperature and pressure can influence both equilibrium and rate. However, catalyst and equipment can only influence rate. While rate-limited processes are dealt with extensively in chapters 8 and 9, some examples of how equipment design can influence rates are described in the following paragraphs.

Table 5-1 Variable influences

Variable	Equilibrium	Rate
Temperature	x	x
Pressure	x	x
Catalyst		x
Equipment design		x

Fractionation columns are analyzed with the assumption that there are multiple equilibrium stages in each column. The term “tray efficiency” is used to gauge how close the composition of each tray approaches to its equilibrium. A tower with a tray efficiency of only 50% would require two actual trays to reach equilibrium between the vapor phase and liquid phase. Thus if the tray could be designed to provide a tray efficiency of 100%, the number of actual trays could be reduced by a factor of 2. While it is unlikely that 100% tray efficiency can be achieved, improved design of both the vapor-liquid contacting region of the tray and the vapor-liquid separation region of the tray can improve tray efficiency. This is an example of how fractionation equipment design can impact the rate at which equilibrium is achieved.

The rate at which heat is transferred into a cooler can be gauged by the approach of the hotter fluid-outlet side temperature to the cooler fluid-inlet side temperature. This is because the only equilibrium limit in heat exchange is that the hot side outlet temperature cannot be cooler than the cold side inlet temperature. Plate and frame heat exchangers, by nature of their mechanical design, allow for a very close approach compared to that of more conventional shell and tube heat exchangers.

In certain rate-limited reactions, the speed of the reaction can be enhanced by changing the size of the catalyst particle in fixed-bed reactors. As the catalyst particle size is decreased, the catalyst particle surface area increases. As more surface area is available, there are more catalyst sites accessible to the reactants.

These are three examples of reaction rate being enhanced by equipment design without any changes in temperature or pressure.

EXAMPLE PROBLEM 5-4

Assume that hexane liquid at 85°F is in a vessel with a nitrogen atmosphere in the vapor phase. The total pressure on the drum is 5 psig. Determine the equilibrium constant value of hexane at 85°F, and the concentration of hexane in the vapor phase. Vapor pressure data indicates that the vapor pressure of hexane at 85°F is 3.7 psia.

Step 1: Determine the equilibrium value using equation (5-39).

$$k = VP/\pi \quad (5-39)$$

$$k = 3.7/(5 + 14.7) = 0.19 \quad (5-40)$$

Step 2: Use the calculated equilibrium constant (k) to calculate the vapor phase composition with the modified equation (5-38) below. This approach assumes that there is essentially no nitrogen dissolved in the hexane. Thus the liquid phase has a mol fraction of hexane of 1.

$$Y = k \times X \quad (5-41)$$

$$Y = 0.19 \times 1.0 = 0.19 \text{ mol fraction of hexane in the vapor} \quad (5-42)$$

As indicated in this section, a process does not always achieve equilibrium. However, when considering vapor-liquid equilibrium of low viscosity liquids, it is almost always correct to assume that equilibrium is reached in a process vessel with good vapor-liquid disengaging characteristics.