

## UTILIZATION OF MANUAL COMPUTATION TECHNIQUES

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### 13.1 INTRODUCTION

The purpose of this chapter is threefold:

- It provides an overview of the algorithm used by computers to do calculations such as flash and fractionation calculations.
- It includes techniques for doing these calculations by hand, as well as some shortcut approaches.
- It includes comments on the potential problems of computer solutions.

The modern-day widespread availability of desktop and laptop computers, along with process engineering programs, allows the chemical engineer or others to quickly simulate fractionation or flash calculations. In addition, the widespread availability of component data bases and equations of state/equilibrium algorithms enhance the ability of the computers to do such calculations. Because of the expansion of the technology, it may seem that manual calculations are now obsolete. However, there is still a place for manual calculations. While the computer simulation programs are very precise, they also depend on accurate input data and good convergence routines. In addition, they are generally best suited for design rather than problem solving.

The use of any computer program also creates the risk of “user ignorance.” That is, the user of the program simply will provide input data without

understanding the algorithms used to perform the simulation. When using process engineering simulations, the program user must have a good understanding of the computer program to be used. This understanding has to be more than an understanding of how to fill in the blanks provided in the program. The user must understand how the algorithm works. Understanding of how to do the manual calculations will help provide the user's ability to comprehend the simulation programs.

The manual calculations discussed in this chapter include both of the following:

- Calculation techniques which were once well known and taught in the academic world, but have been forgotten due to lack of use.
- New techniques with which the problem solver may not be familiar.

The problems at the end of the chapter are given to illustrate these calculation techniques and are not in the format used in this book for example problems illustrating the five-step problem-solving approach.

Manual calculations are often of value as a "ball park" check on the computer simulation. Using the techniques discussed in this chapter will provide the means to perform checks on computer simulations. While manual calculations can never be as accurate as computer simulations, they provide a potential method to confirm that computer simulations are reasonably accurate. While the computer will not make calculation mistakes, it is subject to three sources of error as follows:

1. Programming errors. The simulation programmer may have made either a blatant or subtle error in the simulation. The blatant errors are almost always discovered and corrected prior to widespread use of the program. The subtle errors are often not detected until after months or years of use. An example of a subtle error is the simulation that uses numerical integration with a limited number of numerical increments. The simulation may work for years and give exact answers. However, it then fails to give the correct answer for a very specialized case that requires a greater number of increments than are used in the simulation. While this subtle error may be easily modified, the design and construction of the facilities based on the erroneous simulation may have already been completed.
2. The user of the simulation may have made a mistake in the input data. While this can also occur when doing manual calculations, the act of doing manual calculations will often allow discovery of simple input errors.
3. In his hurry to complete a computer simulation, the problem solver may compromise the validity of the solution by selecting inappropriate vapor-liquid equilibrium techniques, simulating a component not available in a data base with an inappropriate substitute, or accepting a less-than-acceptable convergence.

Unfortunately, once a computer simulation has been finished and presented, it has a great deal of credibility whether it is correct or not.

Manual calculations for binary systems can often be done quicker than computer simulations' calculations. This is especially true for the problem solver who often finds himself in a process plant control center without full computer simulation capabilities. This situation might also occur if the problem solver is in a country other than his own where he does not have access to a computer either due to security or language limitations. In these situations, and others where the process problem solver has available to him vapor pressure curves for the components under consideration, very good simulations of binary systems can be made by manual calculations. This area is discussed below in Sections 13.2 through 13.7.

Manual calculations can often provide good approximations of complicated equilibrium systems such those involving a polymer and a solvent. Many times the equilibrium between a polymer and a solvent is simulated by assuming that the polymer acts as the heaviest hydrocarbon available in the component data base. This assumption may be valid for high concentrations of solvent in the polymer. However, at low concentrations (almost always important when dealing with a solvent dissolved in a polymer) this is rarely true. This concept is discussed in section 13.8.

## 13.2 BINARY SYSTEMS

A binary system is one that consists of only two components. As indicated earlier, manual calculations for a binary system can be very accurate if vapor pressure curves or equilibrium constants are available for the components under consideration. Some areas where manual computation techniques can be done quickly and are of great value in binary systems are as follows:

- Estimating quickly the vapor and liquid compositions of a binary mixture.
- Estimating quickly the equilibrium of water that is dissolved in a hydrocarbon.
- Estimating quickly the vapor phase concentration when two liquid phases are present. The two liquid phases could be water and a hydrocarbon.
- Estimating quickly the condensation temperature of a gaseous mixture that contains both water and hydrocarbons.

The following paragraphs present examples of each area.

### 13.3 ESTIMATING THE VAPOR-LIQUID EQUILIBRIUM OF A TWO-PHASE BINARY MIXTURE

The phase rule given earlier and reproduced here can be used to understand how the composition of each phase of a binary system can be determined.

$$F = C - P + 2 \tag{11-1}$$

where

$F$  = degrees of freedom (temperature, pressure and composition)

$C$  = number of components in the mixture

$P$  = number of phases present

Thus for a binary ( $C = 2$ ) vapor-liquid mixture ( $P = 2$ ), fixing the temperature and pressure reduces the degrees of freedom to 0. Thus both liquid and vapor phase compositions are fixed.

For example, if a two-phase mixture of propane and isopentane exists at 150°F and 18 atmospheres, the composition of each phase can be calculated as follows:

1. Determine the equilibrium constant for each component. These can be determined either from charts of equilibrium constants as a function of temperature and pressure, or by using the relationship shown below:

$$K = VP/\pi \tag{13-1}$$

where

$K$  = equilibrium concentration of the desired component

$VP$  = vapor pressure of the component at 150°F

$\pi$  = total pressure

2. Assign the following values:

$X$  = composition of  $C_3$  in the liquid phase, mol fraction

$1 - X$  = composition of  $I-C_5$  in the liquid phase, mol fraction

$Y$  = composition of  $C_3$  in the vapor phase, mol fraction

$1 - Y$  = composition of  $I-C_5$  in the vapor phase, mol fraction

3. Solve for  $X$ ,  $1 - X$ ,  $Y$ , and  $1 - Y$  using the following equations. The results are shown in Table 13-1:

$$Y_i = K \times X_i \tag{13-2}$$

$$\sum Y_i = 1.0 \tag{13-3}$$

Component	Liquid, mf	K	Vapor, mf
$C_3$	$X$	1.28	$1.28 \times X$
$I-C_5$	$1 - X$	0.171	$0.171 \times (1 - X)$
Total	1.0		1.0

**Table 13-1 Results of calculations**

Component	Liquid, mf	Vapor, mf
$C_3$	0.748	0.957
$I-C_5$	0.252	0.043

thus

$$1.28 \times X + 0.171 \times (1 - X) = 1.0 \quad (13-4)$$

Solving for  $X$  gives

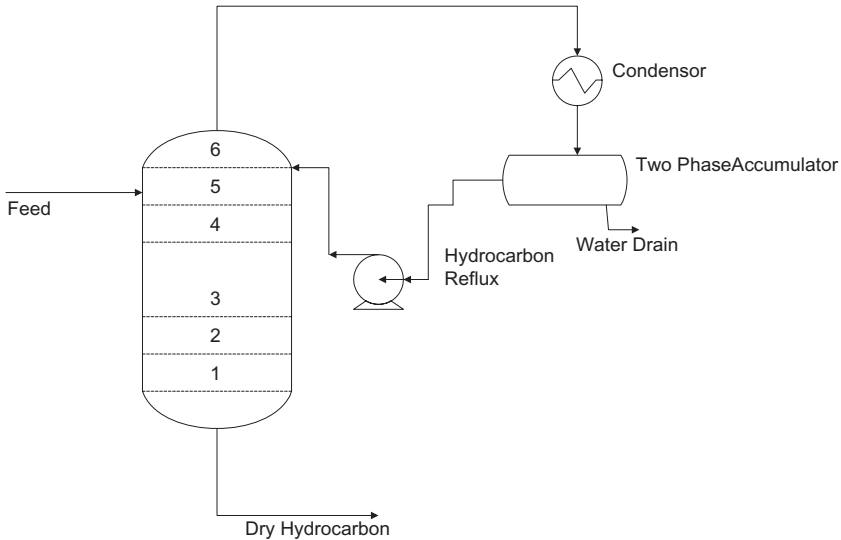
$$\begin{aligned} 1.28X - 0.171X &= 1 - 0.171 \\ X &= 0.748 \end{aligned} \quad (13-5)$$

### 13.4 ESTIMATING THE EQUILIBRIUM CONSTANT OF WATER THAT IS DISSOLVED IN A HYDROCARBON

Estimating the volatility of water relative to the hydrocarbon in which it is dissolved is often required in process engineering calculations. The volatility is the ratio of the equilibrium constant of water to the equilibrium constant of the hydrocarbon. While it may seem apparent that water with a boiling point of 212°F is less volatile than lower molecular weight hydrocarbons such as propane and butane, this is not true if the water is dissolved in the hydrocarbon. Water is a unique molecule. Based on the atomic structure and molecular weight, it should be a gas under atmospheric conditions. The reason that water (molecular weight = 18) exists as a liquid rather than a gas is due to hydrogen bonding between the water molecules. The hydrogen atoms present in water ( $H_2O$ ) associate with each other. This hydrogen bonding causes water to behave like a material of a much higher molecular weight and boil at a higher temperature. When water and hydrocarbons exist together, the water can exist either dissolved in the hydrocarbon or as a separate phase. The volatility of water associated with a hydrocarbon depends on whether the water is dissolved in the hydrocarbon or exists as a separate phase.

The volatility of water that is completely dissolved in hydrocarbon is greatly enhanced due to the breakdown of the hydrogen bonding. This breakdown results in water being more volatile than even low molecular weight hydrocarbons (e.g., propane). The enhanced volatility of water created by the breakdown of hydrogen bonding allows water to be removed from hydrocarbons, in some processes, by taking water as an overhead product. Such a drying by fractionation process is shown in Figure 13-1.

Often it is desirable to estimate the equilibrium constant and, hence, volatility of water dissolved in a hydrocarbon to allow design of a distillation column such as that shown in Figure 13-1. Some simulation programs can correctly handle water that exists as a second phase or dissolved in the hydrocarbon.



**Figure 13-1** Drying by fractionation.

The volatility of water can also be estimated by manual calculations. This can be done knowing that the activity of a component in all phases is equal and assuming that the hydrocarbon is essentially saturated with water. Activity is a property of any chemical component. It is a function of temperature and composition.

This can be expressed mathematically, as follows:

$$A_w = A_v \tag{13-6}$$

$$VP = PP = Y \times \pi \tag{13-7}$$

$$Y = K \times X \tag{13-8}$$

by substitution

$$K = VP / (X \times \pi) \tag{13-9}$$

where

$A_w$  = activity of water in the hydrocarbon phase if it is dissolved in the hydrocarbon

$A_v$  = activity of water in the vapor phase

$K$  = equilibrium constant of water dissolved in any hydrocarbon

$VP$  = vapor pressure of pure water at the chosen temperature

$\pi$  = total pressure which will be approximately the vapor pressure of the hydrocarbon

$PP$  = partial pressure of water vapor

$Y$  = concentration of water in the vapor phase, mol fraction

$X$  = saturation concentration of water in hydrocarbon at the chosen temperature, mol fraction

Equation (13-9) indicates that the equilibrium constant for water in any hydrocarbon at saturation can be estimated knowing only the saturation concentration and the vapor pressure of water and the hydrocarbon. This approach is based on the following assumptions:

- Since the water concentration in the hydrocarbon phase is assumed to be at saturation (that is, a single additional drop will cause formation of a separate water phase), the vapor pressure of water can be assumed to be that of pure water. The vapor pressure should be very close to the activity. These assumptions allow the translation of the left hand side (LHS) of equation 13-6 to the LHS of equation 13-7.
- As equation 13-7 shows, the activity is assumed to be equal to the partial pressure or the vapor phase concentration multiplied by the total pressure.

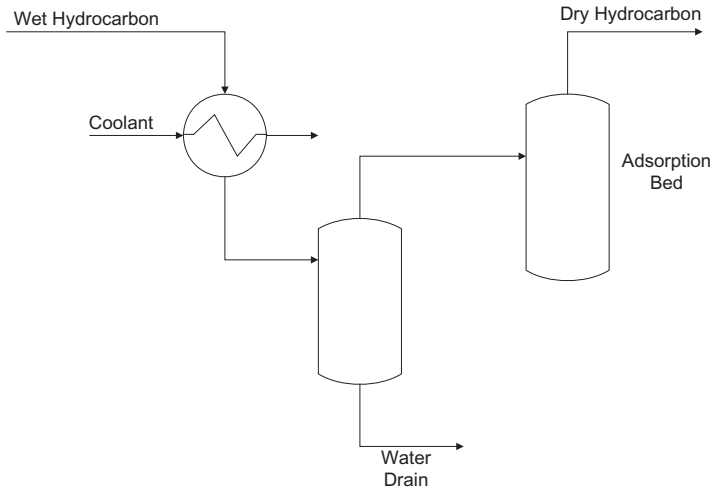
While the expert in thermodynamics may consider the approach described above less than desirable, it is more than acceptable for plant problem solving.

As indicated above, this approach is applicable for estimating the equilibrium constant of water dissolved in a hydrocarbon when the hydrocarbon is saturated with water. If the concentration is below the saturation level, the equilibrium constant for water will likely be even higher. This is expected because as the concentration of a component in a nonideal system decreases, the deviation from ideal increases.

### 13.5 ESTIMATING THE VAPOR PHASE CONCENTRATION WHEN TWO LIQUID PHASES ARE PRESENT

Two immiscible liquid phases are often present within hydrocarbon and water mixtures. It is often desirable to estimate the vapor phase composition in equilibrium with the two liquid phases. An example of this might be a knock-out drum that contains both water and a hydrocarbon. If the vapor phase from the drum is to be dried in an adsorption bed, it will be necessary to know the water content of the vapor leaving the knockout drum. Such a process is shown in Figure 13-2.

The vapor phase composition can be estimated by the simple rule that each liquid phase exerts its own vapor pressure. That is, since the liquid phases are



**Figure 13-2** Drying with condensation and adsorption.

immiscible, they act independently and the vapor pressure of either depends only on the temperature.

Thus

$$\Pi = VP_W + VP_{HC} \quad (13-10)$$

here

$\Pi$  = total pressure of the two liquid phases or the total pressure of the system

$VP_W$  = vapor pressure of the water phase

$VP_{HC}$  = vapor pressure of the hydrocarbon phase

For any given system, if the total pressure ( $\pi$ ) and vapor pressures of the hydrocarbon and water are known, then the vapor phase composition in mol fraction can be calculated as follows:

$$Y_W = VP_W/\pi \quad (13-11)$$

$$Y_{HC} = VP_{HC}/\pi \quad (13-12)$$

here

$Y_W$  = mol fraction water in the vapor phase

$Y_{HC}$  = mol fraction hydrocarbon in the vapor phase



### 13.6 CONDENSATION INTO TWO LIQUID PHASES

A converse of Section 13.5 is the case where a vapor phase containing both a hydrocarbon and water is condensed. In this situation, the temperature of the vapor is reduced until condensation of the vapor begins. Both the initial condensation temperature and which phase condenses first (water or hydrocarbon) depend on the initial composition of the vapor phase. Determination of which phase will condense first, the initial condensation temperature, and the subsequent temperature at which formation of a second liquid phase occurs can be determined by the single process engineering concept as follows:

*The partial pressure of a component in the vapor phase can never exceed the vapor pressure of the component at the given temperature. If the partial pressure exceeds the vapor pressure, condensation must occur.*

Thus one of the components (water or hydrocarbon) will begin to condense at a temperature of  $T_1$  when the partial pressure exceeds the vapor pressure. This can be expressed mathematically as follows:

$$\Pi \times Y_i \leq VP_i \quad (13-13)$$

here

$Y_i$  = vapor phase composition of the first component to condense

$VP_i$  = vapor pressure of the first component to condense

The initial component will continue to condense by itself until the temperature of the vapor is reduced to the point ( $T_2$ ) where the sum of the vapor pressures is equal to the system pressure. At this point, equation (13-10) is satisfied and condensation of the second component will begin. The temperature ( $T_2$ ) will stay constant until the entire second component is condensed. At this point, there will be no vapor left to condense. Additional heat removal will serve to cool the liquid. The vapor phase composition of component "i" (the first component to condense) between  $T_1$  and  $T_2$  can be estimated knowing the temperature as follows:

$$Y_i = VP_i/\pi \quad (13-14)$$

An example problem is provided later to enhance the understanding of this concept.

It should be noted that the concept described above, that the partial pressure of a component in the vapor phase can never exceed the vapor pressure of the component at the given temperature, can also be used to evaluate the validity of plant laboratory or instrument data. For example, vapor phase analytical data must satisfy equation (13-13). The term  $\Pi \times Y_i$  cannot exceed  $VP_i$ . If it does exceed  $VP_i$ , it is likely that composition is wrong.

### 13.7 SHORTCUT FRACTIONATION CALCULATIONS

Computer fractionation simulation programs can be used to both design new distillation towers and to solve problems with existing towers. Most of the simulation programs are intended for design calculations. They can be used for problem solving, but to operate in this mode often requires iterative procedures. For example, the design of a distillation column requires an input of feed and product compositions, rates, tray efficiency, and a criterion for setting the reflux ratio. The reflux ratio is generally set at a multiple of the minimum reflux ratio which is calculated by the computer simulation program. The simulation program can then size the tower. If problem solving is being done on the same tower, the reflux ratio and the number of actual trays are fixed. The tray efficiency must be adjusted to obtain a match between calculated and actual product compositions.

Even though the computer simulation programs are used for the fractionation calculations, there are some advantages to knowing shortcut fractionation techniques. Knowing these techniques will aid in understanding the results of the simulation as well as being able to check the simulation results. Being familiar with shortcut calculation techniques will also be of value on occasions when a quick answer is required to an immediate problem. As indicated earlier, the computer will not make computational errors, however, it will only do what it is told to do. There are three types of errors that might occur in any simulation. These were described in Section 13.1.

Shortcut fractionation calculations can be used to confirm that computer simulations are giving “directionally correct” answers. In addition, these shortcut calculations can often be used to analyze poor performance in an operating tower in a more expeditious fashion than is possible with a full computer simulation program. These shortcut calculations can be set up on a spreadsheet with a minimal amount of effort, as opposed to computer simulations which are quick to run, but take time to set up and develop input data in the correct format.

One of the most valuable parts of a computer simulation program is its capability to determine the minimum reflux ratio for a multicomponent system. Since, in a plant operating column, the reflux ratio is already known, determining the minimum reflux ratio may not be required. Prior to launching a rigorous simulation of an existing fractionation column, a shortcut calculation procedure should be considered. The possible reasons for considering a manual shortcut calculation approach are as follows:

- The shortcut calculation approach is much less complicated.
- The reflux ratio in an existing column is already known and the minimum reflux ratio generally does not need to be determined.
- A plant tower is often a binary fractionation (it has only two components) or can be simulated as one.
- A plant problem often involves only part of the tower (rectification or stripping sections); a complete simulation is not required.

- For ideal systems (such as systems involving only hydrocarbon), a heat balance around each tray is not required since “equal molal overflow” is a good assumption. The assumption of equal molal overflow means that the internal liquid and vapor rates expressed in mols/hour will be equal throughout the tower if there is no addition or withdrawal of material or heat.
- The simplified vapor-liquid equilibrium constants that are used for the shortcut calculations are often much easier to develop than the more complex ones often required for the computer simulations.

Even if a rigorous simulation program is used to predict plant performance or to design a new tower, it will be of value to perform a shortcut calculation to confirm the validity of the simulation. As an example of a shortcut calculation, the rectification section of a tower is shown in Table 13-2. The calculation bases are given in steps 1 and 2 (equations (13-15) and (13-16)). This shortcut procedure assumes that the vapor-liquid equilibrium is constant in the tower and that equal molal overflow is a good assumption. A spreadsheet was developed and the results are shown in Table 13-3.

*Note that if the calculated composition does not equal the assumed composition, a new assumption must be made and the calculations repeated.*

The calculations can be performed in a stepwise fashion using the two equations shown below. These are:

1. An equilibrium relationship between vapor and liquid on any tray

$$Y_N = \alpha \times X_N / (1 + (\alpha - 1) \times X_N) \quad (13-15)$$

2. A material balance relationship between vapor and liquid and overhead distillate product,

**Table 13-2 Shortcut calculations to simulate rectification section**

Given:

- Number of theoretical rectification trays = 15. These are the number of theoretical trays from the feed tray or lowest tray in the section to the overhead product.
- Relative volatility (light key to heavy key) = 1.2. This value is simply the ratio of the equilibrium constant of the more volatile component (light key) to the less volatile component (heavy key).
- Internal liquid to vapor ratio, mol/mol = 0.9. This is the number of mols of liquid flowing down the tower divided by the number of mols of vapor flowing up the tower.
- Liquid concentration of light key on lowest tray, mol % = 70.
- Assumed concentration of light key in distillate, mol % = 93.

**Table 13-3 Results of shortcut calculation**

Tray Number	Compositions of Light Key in Mol Fraction	
	Liquid on Tray	Vapor leaving Tray
1 (starting tray)	0.7	0.737
2	0.715	0.751
3	0.731	0.765
4	0.747	0.78
5	0.763	0.795
6	0.78	0.809
7	0.796	0.824
8	0.812	0.839
9	0.828	0.853
10	0.844	0.867
11	0.86	0.88
12	0.875	0.893
13	0.889	0.906
14	0.903	0.918
15 (top tray)	0.917	0.93

$$X_{N+1} = Y_N/R - X_D \times ((1/R) - 1) \quad (13-16)$$

where

$X_D$  = distillate composition of light key. For simple fractionation towers, it is the same composition as the vapor leaving the tower since all of this is condensed and becomes the distillate product and tower reflux.

$Y_N$  = vapor phase composition of light key on tray N, mol fraction.

$X_N$  = liquid phase composition of light key on tray N, mol fraction.

$X_{N+1}$  = liquid phase composition of light key on tray above tray N, mol fraction.

$\alpha$  = relative volatility, light key to heavy key.

$R$  = internal liquid to vapor mol flow rate ratio.

Light key refers to the component that is the most volatile; heavy key refers to the component that is the least volatile.

The actual procedure for doing these calculations, whether by hand or in the computer, is as follows:

1. Using equation (13-15) and the given relative volatility ( $\alpha = 1.2$ ), calculate the vapor phase composition leaving the lowest tray based on the given composition of 70 mol % for  $X_N$ .

2. Using  $Y_N$  calculated in Step 1, the internal liquid to vapor ratio ( $R$ ), the light key composition in the distillate ( $X_D$ ), and equation (13-16), calculate the liquid phase composition leaving the tray immediately above ( $X_{N+1}$ ).
3. Repeat this calculation approach for each of the theoretical trays. If the vapor leaving the 15th tray does not equal the assumed distillate composition (93 mol % in this case), it will be necessary to assume a new distillate composition and redo the calculations.

Table 13-3 summarizes the results of the spread sheet calculations.

Since the vapor leaving tray 15 is condensed and is the distillate, the calculated composition equals the assumed composition.

These calculations can be simplified even further for a binary tower at constant temperature where *small quantities of a heavy key (lower volatility material) are being fractionated to low levels in the overhead product*. In this case, it can be shown that:

$$X_{n+1} = (X_n \times V \times k) / L \quad (13-17)$$

where

$X_{n+1}$  and  $X_n$  = tray compositions of the heavy key in mol fraction, where tray  $n+1$  is above tray  $n$

$V$  = internal vapor rate in mol/hr

$L$  = internal liquid rate in mol/hr

$k$  = volatility of the heavy key relative to the light key. Note that this will always be less than 1.

Equation (13-17) can be transformed into the equation below, which can be used to make a quick estimate of the low volatility material in the distillate product.

$$X_D = X_T \times (V \times k / L)^N \quad (13-18)$$

where

$X_D$  = composition of the heavy key in mol fraction in the overhead distillate product

$X_T$  = composition of the heavy key in mol fraction at the start of the rectification section

$N$  = number of theoretical trays in the rectification section

## 13.8 POLYMER-SOLVENT EQUILIBRIUM

The problem solver will often not have available to him simulations that allow predictions of polymer-solvent equilibrium. Faced with this dilemma, he often

will select the heaviest component in the computer data base to simulate a polymer. This may be adequate for solvent-polymer systems that contain solvent concentrations greater than 10 to 20 volume percent. However, below this level, the polymer begins to reduce the volatility of the solvent, and the vapor phase composition of the solvent will be less than anticipated when the polymer is simulated using the heaviest component in the data base. The converse will also be true. That is, at solvent concentrations below 10 to 20 volume percent, the amount of solvent in the polymer will be greater than that calculated based on the vapor phase composition of the solvent and simulating polymer as the heaviest component in the data base.

There are techniques for dealing with this nonideality. Perhaps the best known relationship dealing with the equilibrium between a polymer and solvent is the Flory-Huggins relationship. The use and limitations of this relationship are described in *Seymour/Carraher's Polymer Chemistry*.

The Flory-Huggins relationship predicts the equilibrium of a solvent in the noncrystalline polymer phase. Polymers exist in either the crystalline or noncrystalline (also referred to as amorphous) phase. The crystalline phase can be visualized as a piece of metal. Since all the molecules are aligned in the available, specific places, there is no location available for solvent molecules. Hence the solvent molecules cannot be present in the crystalline region. This is not true for the noncrystalline or amorphous phase. Thus any solvent present in a polymer is assumed to be present in the amorphous phase of the polymer. Typical polyolefins, for example, have a crystalline phase that is equal to 70–90% of the polymer.

Equation (13-19) below shows the original Flory-Huggins relationship. The modification developed by the author is shown in equation (13-20).

The original Flory-Huggins relationship:

$$\ln(P P / V P) = \ln V_1 + (1 - M_1 / M_2) \times V_2 + U \times V_2^2 \quad (13-19)$$

where

$P P$  = solvent partial pressure; this is equal to the vapor phase composition multiplied by the total system pressure

$V P$  = vapor pressure of solvent

$V_1$  = volume fraction of solvent in polymer

$V_2$  = volume fraction of polymer

$M_1$  = molar volume of solvent, cc/g-mol

$M_2$  = molar volume of polymer, cc/g-mol

$U$  = interaction parameter between the solvent and the polymer

Manipulation and assumptions ( $V_2 = 1$  and  $M_1 / M_2 = 0$ ) by the author of this book yield

$$\ln(PP/VP) = \ln(D_2 \times X_1 / (D_1 \times 1,000,000)) + 1 + U \quad (13-20)$$

where

$D_1$  = density of the solvent

$D_2$  = density of the polymer

$X_1$  = weight of the solvent in the polymer, ppm

The interaction parameter can be evaluated knowing the solubility parameters.

$$U = M_1 \times (S_1 - S_2)^2 / (R \times T) + Z \quad (13-21)$$

where

$S_1$  = solvent solubility parameter,  $(\text{cal}/\text{cm}^3)^{0.5}$

$S_2$  = polymer solubility parameter,  $(\text{cal}/\text{cm}^3)^{0.5}$

$Z$  = lattice constant. In theory =  $0.35 \pm 0.1$

The values of solubility parameters are given in various handbooks. It should be emphasized that the assumed concentrations of solvent in the polymer are the concentrations of solvent which exists in the noncrystalline or amorphous region. That is, the standard assumption is that there is no solvent in the crystalline region.

While this book cannot delve into all aspects of polymer-solvent equilibrium, the approach described above is meant to show that there are techniques available to estimate the equilibrium as opposed to simulating a polymer as the heaviest component in the data base. While there are computer simulations that allow prediction of a polymer-solvent equilibrium, the above analysis will be of value in understanding the basis for these simulations or in doing the simulation by manual calculation.

### 13.9 EXAMPLE PROBLEMS

The following example problems illustrate the application of these concepts. These are shown to illustrate the calculation approach. As such, they are not formatted in the style of the standard problem-solving technique proposed in this book.

#### EXAMPLE PROBLEM 13-1

A two-phase liquid mixture consisting of hexane and water is present in a process vessel at a pressure of 5 psig. The mixture enters the vessel at the

**Table 13-4 Vapor pressure data**

Component	Temperature, °F					
	100	120	140	160	180	200
	Vapor Pressure, psia					
Water	0.95	1.69	2.89	4.74	7.51	11.53
Hexane	5	7.79	11.02	15.4	22	28.7

**Table 13-5 Boiling point estimate**

	Temperature, °F			
	100	120	140	160
VP of water, psia	0.95	1.69	2.89	4.74
VP of hexane, psia	5	7.79	11.02	15.4
Total ( $\pi$ ), <sup>a</sup> psia	5.95	9.48	13.91	20.14
Mols water/mol hexane	0.19	0.22	0.26	0.308

<sup>a</sup> By interpolation,  $\pi$  will equal 19.7 (5 psig + 14.7) when the temperature of the mixture is equal to 159°F. This is, by definition, the boiling point.

boiling point. What is the boiling point of this mixture? The vapor from this drum must be dried to remove water. How could the amount of water present in the vapor phase be reduced below 0.26 mols per mol of hexane? The vapor pressure data in psia is given in Table 13-4.

Since there are two liquid phases present and the mixture is at the boiling point, equation (13-10) shown below provides the basis for the solution.

$$\Pi = VP_W + VP_{HC} \quad (13-10)$$

where

$\Pi$  = total pressure of the two liquid phases

$VP_W$  = vapor pressure of the water phase

$VP_{HC}$  = vapor pressure of the hexane phase

Using the vapor pressures given earlier, the boiling point of the mixture can be determined as shown in Table 13-5.

The vapor phase compositions expressed as mols of water/mol of hexane in Table 13-5 were developed remembering that:

- The partial pressure of a component is equal to the vapor pressure multiplied by the mol fraction of the component in the liquid. Since the hexane and water exist as separate phases, each has a mol fraction in the liquid of 1. Thus, in this case, the partial pressure is equal to the vapor pressure of each component.



- The ratio of the mols of each component is then simply the vapor pressure ratio.

From an examination of Table 13-5, if the vessel were operated at a slight vacuum (<13.9 psia), the amount of water in the vapor would be below 0.26 mols of water/mol of hexane.

### EXAMPLE PROBLEM 13-2

A vapor phase mixture at 200°F and 20 psia, containing 50 mol percent water and 50 mol percent hexane, flows into a cooler. Determine the following using the vapor pressures given in the previous problem:

- The temperature of the initial condensation and which component condenses first.
- The temperature at which the remaining component begins to condense.

The solution of this problem depends on utilizing the concepts discussed earlier. That is, *the partial pressure of a component can never exceed the vapor pressure of the component at the given temperature.*

Mathematically, this was expressed as:

$$\Pi \times Y_i \leq VP_i \quad (13-13)$$

The partial pressure of both hexane and water is 10 psia, since the vapor phase contains 50 mol percent of each component. As noted in equation (13-13), the vapor pressure must always be equal to or greater than the partial pressure. Since the mixture is being condensed, the vapor pressure and partial pressures will be equal. Interpolating the vapor pressures given earlier, it can be shown that a vapor pressure of 10 psia occurs at the temperatures shown in Table 13-6.

Since as the temperature is decreased, the condensation point of water occurs first, it will form the initial liquid phase and it will begin to condense at 192°F. It is important to recognize that the calculation shown above is valid only for finding the component which condenses first and its condensation point.

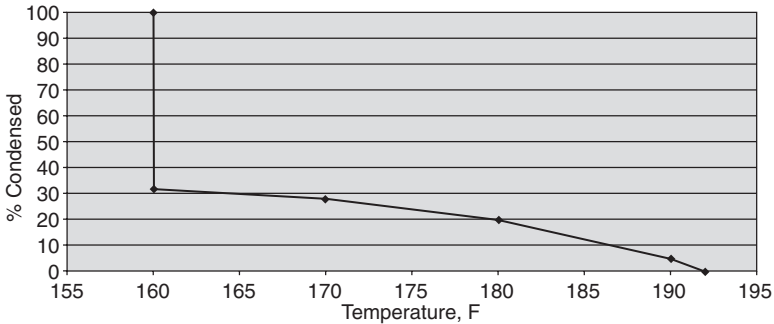
Hexane will not begin to condense until the total vapor pressure of the two liquid phases equals the total pressure (20 psia). This can be estimated as shown in Table 13-7.

**Table 13-6 Estimation of condensation point**

Component	Temperature, °F for $VP = 10$ psia
Water	192
Hexane	134

**Table 13-7 Estimation of condensation point of second phase**

Component	Temperature, °F		
	120	140	160
Water, psia	1.69	2.89	4.74
Hexane, psia	7.79	11.02	15.4
Total, psia	9.48	13.91	20.14



**Figure 13-3** Percentage condensation vs. temperature.

Thus at a temperature  $\approx 160^\circ\text{F}$ , sufficient hexane will condense to form a second phase. At this point ( $160^\circ\text{F}$ ), the vapor phase composition can be estimated from the vapor pressures by dividing the water vapor pressure by the hexane vapor pressure, which gives a composition of 0.308 mol of water per mol of hexane.

If a heat exchanger to do this condensation job were being designed, it would be split into different zones. From  $200^\circ\text{F}$  to  $192^\circ\text{F}$ , there will be no condensation. This is a vapor cooling zone only. From  $192^\circ\text{F}$  to  $160^\circ\text{F}$ , only water will condense. There will be trace amounts of hexane that condense as necessary to saturate the water phase with hexane. The vapor phase composition in this range can be estimated based on equation (13-22) as follows:

$$Y_w = VP_w/\pi \tag{13-22}$$

where

$Y_w$  = mol fraction of water in the vapor phase

$VP_w$  = vapor pressure of water at the temperature of interest, psia

$\Pi$  = total pressure, psia

When a temperature of  $160^\circ\text{F}$  is reached, hexane will begin to condense. The temperature will remain at  $160^\circ\text{F}$  until all hexane and water are condensed. A condensation curve for this system is shown in Figure 13-3.

**EXAMPLE PROBLEM 13-3**

Find the approximate relative volatility for water dissolved in propane at 70°F.  
Given:

- Vapor pressures at 70°F:

Water	0.363 psia
Propane	118 psia

- Solubility of water in propane at 70°F = 0.016 lb/100 lb propane

Calculations:

Converting the solubility to mol fraction gives 0.00039 mol water/mol propane

Since essentially all of the pressure on the system is due to propane

$$\Pi = 118 \text{ psia}$$

Substituting in (13-9) gives the following results:

$$K = VP/(X \times \pi) \quad (13-9)$$

$$K = 0.363/(0.00039 \times 118) \quad (13-23)$$

$$K = 7.88 \quad (13-24)$$

Since the equilibrium constant for propane is 1 (vapor pressure/total pressure), the relative volatility of water to propane is approximately 8. Thus water would be more volatile than propane.

**NOMENCLATURE**

$A_v$	Activity of water in the vapor phase
$A_w$	Activity of water in the hydrocarbon phase if it is dissolved in the hydrocarbon
$C$	Number of components in the mixture
$D_1$	Density of the solvent
$D_2$	Density of the polymer
$F$	Degrees of freedom (temperature, pressure, and composition)
$K$	Equilibrium concentration of the desired component. In this chapter it is used in reference to a hydrocarbon or water dissolved in a hydrocarbon.
$k$	Volatility of the heavy key relative to the light key. Note this will always be less than 1.
$L$	The internal liquid rate in a fractionation tower, mol/hr

$M_1$	Molar volume of solvent, cc/g-mol
$M_2$	Molar volume of polymer, cc/g-mol
$N$	Number of theoretical trays in the rectification section
$P$	Number of phases present
$PP$	Partial pressure of the component under study
$R$	Internal liquid to vapor mol flow rate ratio in a fractionation tower
$S_1$	Solvent solubility parameter, $(\text{cal}/\text{cm}^3)^{0.5}$
$S_2$	Polymer solubility parameter, $(\text{cal}/\text{cm}^3)^{0.5}$
$U$	Interaction parameter between the solvent and the polymer
$V$	Internal vapor rate in a fractionation tower, mol/hr
$V_1$	Volume fraction of solvent in polymer
$V_2$	Volume fraction of polymer
$VP$	Vapor pressure of the component under study. In this chapter, it could be the vapor pressure of the hydrocarbon phase ( $VP_{\text{HC}}$ ), the vapor pressure of the water phase ( $VP_{\text{w}}$ ), the vapor pressure of the first component to condense ( $VP_i$ ) or the vapor pressure of a solvent dissolved in a hydrocarbon ( $VP$ ).
$X$	Concentration of a component in the liquid phase, mol fraction. As used in this chapter it could be either the saturation concentration of water in hydrocarbon at the chosen temperature or the hydrocarbon concentration in a mixture.
$X_D$	Composition of the heavy key in mol fraction in the overhead distillate product
$X_N$	Liquid phase composition of light key or heavy key on tray $N$ , mol fraction
$X_{N+1}$	Liquid phase composition of light key or heavy key on tray above tray $N$ , mol fraction
$X_T$	Composition of the heavy key in mol fraction at the start of the rectification section
$X_1$	Weight of the solvent in the polymer, ppm
$Y$	Concentration of a component in the vapor phase, mol fraction. It could be water ( $Y_{\text{w}}$ ), hydrocarbon ( $Y_{\text{HC}}$ ), or the composition of the first component in a hydrocarbon-water mixture to condense ( $Y_i$ ).
$Y_N$	Vapor phase composition of light key or heavy key on tray $N$ , mol fraction
$Z$	Lattice constant. In theory = $0.35 \pm 0.1$ .
$\alpha$	Relative volatility, light key to heavy key
$\Pi$	Total pressure
<i>Note</i>	Light key refers to the component that is the most volatile. Heavy key refers to the component that is the least volatile.