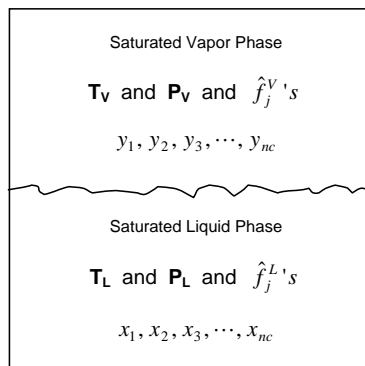


Introduction

This chapter on phase equilibrium has three major objectives. First, vapor-liquid equilibrium, environmental equilibrium, and solubility are examined using the first principle of the distribution coefficient discussed in Chapter 2. You should review this material in Chapter 2 before continuing to read here. Second, several key concepts are described in the form of [graphic organizers](#). Third, example phase equilibrium problems are provided, whose solutions were generated using the problem solving strategy described in Chapter 4. Most of these examples are worked-out problems found in various editions of the Felder and Rousseau textbook [2005] entitled “*Elementary Principles of Chemical Processes*.” Once you understand the solution to an example in this *CinChE* chapter, you should compare it to its counterpart in the appropriate edition of the Felder and Rousseau textbook (including the 4th Ed.) and analyze the differences. The information on vapor-liquid equilibrium, environmental equilibrium, and solubility, as well as the graphic organizers, will help you to understand the example problems.

Vapor-Liquid Equilibrium

Based on the presentation in Chapter 2, the criteria for phase equilibrium are that the temperature in all phases is the same, the pressure in all phases is the same, and the fugacity for each chemical component in all phases is the same. When the fugacity of each component in each phase is the same, the composition in each phase has its own set of fixed values. For example, consider the following isolated system for vapor-liquid equilibrium:



where “ nc ” is the number of chemical components in the system, and the temperature, pressure, and composition of each phase are measurable properties. An isolated system is a hypothetical construct that has neither material nor energy crossing the system boundary. Each of the chemical components (j -th = 1, 2, 3, ..., nc) is distributed in both phases and no chemical reactions are occurring. The vapor mole fractions ($y_1, y_2, y_3, \dots, y_{nc}$) have fixed values, while the liquid mole fractions ($x_1, x_2, x_3, \dots, x_{nc}$) have fixed but different values. If the temperature or pressure in the above diagram were to increase (or decrease) slightly, the compositions in the vapor and liquid phases would adjust to a new state of equilibrium, so that the fugacity of each j -th component (\hat{f}_j) becomes the same in both phases. In this hypothetical system, its boundary is flexible and, thus, allows for expansion or contraction of its volume, in order to account for changes in temperature or pressure.

As was defined in Chapter 2, the first principle for phase equilibrium is called the distribution coefficient, or sometimes it is also known as the partitioning coefficient or the equilibrium vaporization ratio. This first principle is expressed as follows for the j -th component in the equilibrium system:

$$K_j = \frac{\text{composition of component } j \text{ in one phase}}{\text{composition of component } j \text{ in another phase}}$$

where K_j is the dimensionless distribution coefficient for the j -th chemical component, and the two composition quantities can be expressed as either the mass fraction, mole fraction, or concentration of component j in each phase. The concentration is either mass or moles of j per volume of the phase or per amount of the solvent in that phase. In general, this relationship for the distribution coefficient can be written for each chemical component in the equilibrium system. The distribution coefficient for each j -th chemical component (K_j) is a function of the temperature, pressure, and compositions of the equilibrium system. For example, as temperature increases, its value will increase. Conversely, as temperature decreases, its value will decrease.

For multicomponent systems, the following **rigorous thermodynamic criteria** apply for vapor-liquid equilibrium (VLE), where no simplifying assumptions are made about the isolated system:

VLE Criteria		Rigorous VLE Model	
$T_V = T_L$	<i>thermal equilibrium</i>	$K_j = \frac{y_j}{x_j} \quad \text{and} \quad K_j = \frac{\hat{\phi}_j^L}{\hat{\phi}_j^V} \quad \text{for each } j\text{-th component}$ $\hat{\phi}_j^V = \text{phiV}[T_V, P_V, \bar{y}] \quad \text{for each } j\text{-th component}$ $\hat{\phi}_j^L = \text{phiL}[T_L, P_L, \bar{x}] \quad \text{for each } j\text{-th component}$	
$P_V = P_L$	<i>mechanical equilibrium</i>		
$\hat{f}_j^V = \hat{f}_j^L$	<i>chemical equilibrium</i>		
$\hat{\phi}_j^V y_j P = \hat{\phi}_j^L x_j P$	<i>for each } j\text{-th component}</i>		

In the “VLE Criteria” column, the fourth equation is another way to write the chemical equilibrium of the fugacities (\hat{f}_j) in terms of fugacity coefficients ($\hat{\phi}_j$). Note that $\hat{f}_j^V = \hat{\phi}_j^V y_j P$ and $\hat{f}_j^L = \hat{\phi}_j^L x_j P$. The “Rigorous VLE Model” column defines the equilibrium distribution coefficient for each j -th component (K_j) in terms of the vapor and liquid mole fractions (y_j and x_j). The second equation for K_j represents how to calculate its value. This equation is obtained by rearranging the fourth equation in the “VLE Criteria” column. Finally, the fugacity coefficient of the j -th component in each phase is a function of the temperature, pressure, and mole fractions (\bar{y} or \bar{x}) of that phase. In the above **Rigorous VLE Model**, the four equations are to be written for each chemical compound that distributes itself into both the vapor and liquid phases. For a four-component system, we would thus write sixteen equations, four for each of the four chemical components.

Fugacity (\hat{f}_j) can be thought of as a “corrected pressure” that accounts for the attractive and repulsive forces between molecules within a phase. It is an abstract concept that defines the tendency for a chemical compound to escape from a specific phase. It has units of pressure, and it is not a measurable property. However, it can be related using thermodynamics to the temperature, pressure, and composition of a phase through the fugacity coefficient using function **phiV** or **phiL** in the above rigorous VLE model. Note that a fugacity coefficient function can be represented by a graph, table, equations, or computer software tool like the Aspen HYSYS[®] simulator or [ThermoSolver](#).

The fugacity coefficient ($\hat{\phi}_j$) is a dimensionless quantity that describes the relative balance between attractive and repulsive forces for molecules within a phase. A fugacity coefficient of one means the two forces are in balance. A value less than one means attractive forces between molecules dominate, and the molecules want to stay more in the liquid phase. A value greater than one means repulsive forces between molecules dominate, and the molecules want to stay more in the vapor phase. For the case of an ideal gas, a gas molecule has no effect on its neighboring molecules because no attractive and repulsive forces exist. For the case of an ideal liquid solution, a liquid molecule sees its neighboring molecules being similar to it and thus the attractive and repulsive forces are in balance.

How are the functions ϕ_i^V and ϕ_i^L modeled? The fugacity coefficient of the j -th component in the saturated vapor phase is represented using an equation of state like Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), or Peng-Robinson Stryjek-Vera (PRSV). The $\hat{\phi}_j^V$ equation based on the PR equation is shown in Chapter 3 of this *CinChE* manual (p. 3-25). If the saturated vapor phase behaves like an ideal gas, then $\hat{\phi}_j^V = 1$. Two methods exist to represent the fugacity coefficient of the j -th component in the saturated liquid phase. First, a cubic equation of state can be used if it can predict both the vapor and liquid phases like SRK, PR, and PRSV. To account for the mixture of chemical compounds, mixing rules are used to predict the coefficients in an equation of state. Example mixing rules are shown for the Peng-Robinson equation in Chapter 3. Second, a liquid activity coefficient model such as Wilson, NRTL, and UNIQUAC can be used to predict the non-ideal behavior of the liquid phase. These types of models have binary interaction parameters that must be fitted to experimental data. For this method, $\hat{\phi}_j^L = \gamma_j f_j^\circ / P$, where γ_j is the activity coefficient and f_j° is the standard state fugacity for the pure chemical compound j .

The activity coefficient models are beyond the scope of this introductory course, but you will have an opportunity to examine them in a later course on chemical engineering thermodynamics. Note that these models tend to be more reliable than the equation-of-state method, because they are based on experimental data. For this introductory course, our focus will be to use simplified models for $\hat{\phi}_j^V$ and $\hat{\phi}_j^L$, or to use equations of state for both of them. For the latter, we use computer software like Aspen HYSYS® and *ThermoSolver* to do the complex calculations associated with an equation of state.

Rigorous VLE Mathematical Model

<p style="text-align: center;">Multicomponent Vapor-Liquid Equilibrium</p> <div style="border: 1px dashed red; padding: 10px; margin: 10px auto; width: 80%;"> <p style="text-align: center;">Saturated Vapor Phase</p> <p style="text-align: center;">T_V and P_V and \hat{f}_j^V</p> <p style="text-align: center;">$y_1, y_2, y_3, \dots, y_{nc}$</p> <hr style="border: 1px solid black;"/> <p style="text-align: center;">Saturated Liquid Phase</p> <p style="text-align: center;">T_L and P_L and \hat{f}_j^L</p> <p style="text-align: center;">$x_1, x_2, x_3, \dots, x_{nc}$</p> </div> <p style="text-align: right;">n_V</p> <p style="text-align: right;">n_L</p>	<p style="text-align: center;">TXY Diagram for a Binary Mixture</p>
<p style="text-align: center;">Mathematical Model</p> $1.0 = V_f + L_f$ $z_j = V_f y_j + L_f x_j \quad \text{for } j=1, 2, \dots, nc$ $y_j = K_j x_j \quad \text{for } j=1, 2, \dots, nc$ $K_j = \hat{\phi}_j^L / \hat{\phi}_j^V \quad \text{for } j=1, 2, \dots, nc$ $\hat{\phi}_j^L = \text{phiL}[T, P, \bar{x}] \quad \text{for } j=1, 2, \dots, nc$ $\hat{\phi}_j^V = \text{phiV}[T, P, \bar{y}] \quad \text{for } j=1, 2, \dots, nc$ $\sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j = 0$	<p>\bar{x} is vector elements x_1, x_2, \dots, x_{nc}</p> <p>\bar{y} is vector elements y_1, y_2, \dots, y_{nc}</p> <p>\bar{z} is vector elements z_1, z_2, \dots, z_{nc}</p> <p>\bar{K} is vector elements K_1, K_2, \dots, K_{nc}</p> <p style="text-align: center;">Degrees-of-Freedom Analysis:</p> $\# \text{ vars} = 6 \cdot nc + 4$ $\# \text{ eqns} = 5 \cdot nc + 2$ $\text{dof} = 1 \cdot nc + 2$

Gibbs Phase Rule Model

$y_j = K_j x_j \quad \text{for } j=1, 2, \dots, nc$ $K_j = \hat{\phi}_j^L / \hat{\phi}_j^V \quad \text{for } j=1, 2, \dots, nc$ $\hat{\phi}_j^L = \text{phiL}[T, P, \bar{x}] \quad \text{for } j=1, 2, \dots, nc$ $\hat{\phi}_j^V = \text{phiV}[T, P, \bar{y}] \quad \text{for } j=1, 2, \dots, nc$ $\sum_{j=1}^{nc} x_j = 1 \quad \text{and} \quad \sum_{j=1}^{nc} y_j = 1$ $\# \text{ vars} = 5 \cdot nc + 2$ $\# \text{ eqns} = 4 \cdot nc + 2$ $\text{dof} = 1 \cdot nc$	
<p style="text-align: center;">Gibbs Phase Rule: $\text{dof} = 2 + nc - \pi$</p>	<p>The Gibbs model is a partial subset of the VLE model, and it represents the solid red line from Points L to V in the above TXY diagram. The VLE model depicts not only the solid red line but also the vertical dotted blue line from Points "b" to "c" in its TXY diagram above.</p>

Rigorous Mathematical Algorithm VLET

Page 2 of 3

$[T, \bar{x}, \bar{y}] = vlet[P, V_f, \bar{z}]$ <ol style="list-style-type: none"> 1. $L_f \leftarrow 1.0 - V_f$ 2. ITERATE T in ITERATE \bar{K} in $x_j \leftarrow z_j / (V_f K_j + L_f) \quad \text{for } j = 1, 2, \dots, nc$ $y_j \leftarrow K_j x_j \quad \text{for } j = 1, 2, \dots, nc$ $\hat{\phi}_j^L \leftarrow phiL[T, P, \bar{x}] \quad \text{for } j = 1, 2, \dots, nc$ $\hat{\phi}_j^V \leftarrow phiV[T, P, \bar{y}] \quad \text{for } j = 1, 2, \dots, nc$ $K'_j \leftarrow \hat{\phi}_j^L / \hat{\phi}_j^V \quad \text{for } j = 1, 2, \dots, nc$ UNTIL $\bar{K} = \bar{K}'$ $f(T) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$ UNTIL $f(T) = 0$ 	<p>The “Development of a Mathematical Algorithm” in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.</p> <p>Algorithm VLET has an outer iteration loop on temperature (T, a scalar quantity) and an inner iteration loop on the distribution coefficients (\bar{K}, a vector quantity).</p> <p>An initial estimate for T can be found with:</p> $T = \sum_{j=1}^{nc} z_j T_j^{sat} \quad \text{where } T_j^{sat} = tsat[P, pure j]$ <p>The $tsat$ function is the Antoine equation.</p> <p>An initial estimate for \bar{K} can be found with:</p> $K_j = P_j^* / P \quad \text{where } P_j^* = psat[T, pure j]$ <p>The $psat$ function is the Antoine equation.</p>
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Rigorous Mathematical Algorithm VLEVF

$[V_f, \bar{x}, \bar{y}] = vlevf[T, P, \bar{z}]$ <ol style="list-style-type: none"> 1. ITERATE V_f in $L_f \leftarrow 1.0 - V_f$ ITERATE \bar{K} in $x_j \leftarrow z_j / (V_f K_j + L_f) \quad \text{for } j = 1, 2, \dots, nc$ $y_j \leftarrow K_j x_j \quad \text{for } j = 1, 2, \dots, nc$ $\hat{\phi}_j^L \leftarrow phiL[T, P, \bar{x}] \quad \text{for } j = 1, 2, \dots, nc$ $\hat{\phi}_j^V \leftarrow phiV[T, P, \bar{y}] \quad \text{for } j = 1, 2, \dots, nc$ $K'_j \leftarrow \hat{\phi}_j^L / \hat{\phi}_j^V \quad \text{for } j = 1, 2, \dots, nc$ UNTIL $\bar{K} = \bar{K}'$ $f(V_f) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$ UNTIL $f(V_f) = 0$ 	<p>The “Development of a Mathematical Algorithm” in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.</p> <p>Algorithm VLEVF has an outer iteration loop on vapor fraction (V_f, a scalar quantity) and an inner iteration loop on the distribution coefficients (\bar{K}, a vector quantity).</p> <p>An initial estimate for V_f is bounded by</p> $0 \leq V_f \leq 1$ <p>Start with a value of 0.5.</p> <p>An initial estimate for \bar{K} can be found with:</p> $K_j = P_j^* / P \quad \text{where } P_j^* = psat[T, pure j]$ <p>The $psat$ function is the Antoine equation</p>
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Rigorous Mathematical Algorithm VLEP



Page 3 of 3

$[P, \bar{x}, \bar{y}] = vlet[T, V_f, \bar{z}]$ <ol style="list-style-type: none"> 1. $L_f \leftarrow 1.0 - V_f$ 2. ITERATE P in ITERATE \bar{K} in $x_j \leftarrow z_j / (V_f K_j + L_f)$ for $j=1, 2, \dots, nc$ $y_j \leftarrow K_j x_j$ for $j=1, 2, \dots, nc$ $\hat{\phi}_j^L \leftarrow phiL[T, P, \bar{x}]$ for $j=1, 2, \dots, nc$ $\hat{\phi}_j^V \leftarrow phiV[T, P, \bar{y}]$ for $j=1, 2, \dots, nc$ $K'_j \leftarrow \hat{\phi}_j^L / \hat{\phi}_j^V$ for $j=1, 2, \dots, nc$ UNTIL $\bar{K} = \bar{K}'$ $f(P) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$ UNTIL $f(P) = 0$ 	<p>The “Development of a Mathematical Algorithm” in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.</p> <p>Algorithm VLEP has an outer iteration loop on pressure (P, a scalar quantity) and an inner iteration loop on the distribution coefficients (\bar{K}, a vector quantity).</p> <p>An initial estimate for P can be found with:</p> $P = \sum_{j=1}^{nc} z_j P_j^{sat} \quad \text{where} \quad P_j^{sat} = psat[T, pure\ j]$ <p>The $psat$ function is the Antoine equation.</p> <p>An initial estimate for \bar{K} can be found with:</p> $K_j = P_j^* / P \quad \text{where} \quad P_j^* = psat[T, pure\ j]$ <p>The $psat$ function is the Antoine equation</p>
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The above **rigorous** mathematical model for vapor-liquid equilibrium of a multicomponent system has three mathematical algorithms as given above and summarized below.

$$[T, \bar{x}, \bar{y}] = vlet[P, V_f, \bar{z}]$$



$$[V_f, \bar{x}, \bar{y}] = vlevf[T, P, \bar{z}]$$



$$[P, \bar{x}, \bar{y}] = vlep[T, V_f, \bar{z}]$$

Because the above mathematical algorithms use fugacity coefficient functions ($phiV$ and $phiL$) that are rigorously represented by equations of state and activity coefficient models, a software tool like the Aspen HYSYS[®] simulator and ThermoSolver are needed to automate their solution. Manually solving the rigorous versions of these algorithms is a complex and often error prone task, and it is rarely done.

The three functional equations highlighted above for $vlet$, $vlevf$, and $vlep$ are the first principles that we will write in the mathematical models of problems that involve vapor-liquid equilibrium.

However, we will assume that Raoult’s law is applicable for all chemical components in most equilibrium problems. This assumption simplifies the three rigorous mathematical algorithms by eliminating the inner iteration loop on the distribution coefficients. The K_j ’s are not dependent upon the vapor and liquid mole fractions under Raoult’s law, as they are for the rigorous mathematical algorithms above.

The mathematical model and its three mathematical algorithms for multicomponent vapor-liquid equilibrium (VLE) based on Raoult’s law are presented on the next three pages. Whenever you need to solve one of these mathematical algorithms, you would process the VLE mathematical model with “**EZ Setup**” for a **binary** system and have the Excel **Solver** tool do the iterative calculations. Alternately, you will use Aspen **HYSYS**[®] or ThermoSolver for system with greater than two chemical components. You will need to provide the Excel “**EZ Setup**”/Solver, HYSYS, or ThermoSolver printouts as part of your solution documentation.

