Chapter 3 • From Components to Models

The fugacity coefficient of pure liquid is calculated with a Curl-Pitzer [345] corresponding states correlation:

\[
\log \phi_i^{L*} = \log \phi_i^{(0)} + \omega_i \log \phi_i^{(1)}
\]

where \( \log \phi_i^{(0)} \) and \( \log \phi_i^{(1)} \) are a function of the reduced temperature and pressure and constants that may depend on the nature of the component.

A general expression (3.263) calculates the fugacity coefficient of the “pure” components in the liquid phase \( \phi_i^{L*} \). If \( i \) refers to a gas, this method is in fact a Henry constant method:

\[
\phi_i^{L*} = \frac{f_i^{L*}}{P} = \frac{H_i}{P \gamma_i^P}
\]

If \( i \) refers to a liquid component (case “others” in the original paper), as described above, this method in fact calculates a non-dimensional vapour pressure \( \phi_i^{L*} \approx \frac{P \sigma_i}{P} \).

The activity coefficient is calculated using the Scatchard-Hildebrandt theory for regular solutions (see section 3.4.2.2.B, p. 175) while the fugacity coefficient in the vapour phase is obtained using the Redlich Kwong [255] EoS.

3.5 WHAT ARE THE KEY COMPONENTS CONCENTRATION RANGE?

We know that fluid mixtures in the chemical and petrochemical industries generally contain a large number of components. So far, we have stressed the fact that each individual component should be characterised, and all binary parameters should be given suitable values before any calculation can be initiated. The number of binary sub-systems, however, may be very large in a \( N \)-component system:

\[
N_{ij} = \binom{N}{2} = \frac{N!}{(N-2)!2!} = \frac{1 \cdot 2 \cdot 3 \ldots (N-2) \cdot (N-1) \cdot N}{1 \cdot 2 \cdot 3 \ldots (N-2) \cdot 1 \cdot 2} = \frac{(N-1) \cdot N}{2}
\]

The question we want to investigate here is whether all of these subsystems are equally important. We may not be able to answer the question precisely in a general fashion, as it will be highly dependent on the design constraints of the process to be modelled. The process engineer is often in a better position than the thermodynamic specialist to provide a suitable answer. Thermodynamics may nevertheless provide an insight into the sensitivity of a given parameter to the final result.

The above question will be dealt with by using the concept of “key component(s)”, a method of indicating that not all components have the same importance in the final result. It is the responsibility of the process engineer to distinguish between majority components (which make up the main part of the feed), and key components, which may or may not be majority components. The following component characteristics may be of help for this purpose:

- amount of component (often, the majority component may be considered key),
- reactivity (some components may react, and as result change the fluid properties),
• corrosivity (it may be essential to know the fate of components which may damage the equipment),
• catalyst poison (even in small concentrations, the presence of some components may deactivate catalysts),
• potential to freeze under process conditions (upon freezing, some components may deposit on the equipment walls, thus eventually blocking the flow: an example of this is discussed further in the case studies),
• unknown properties at design stage assumptions,
• etc.

For most single-phase property calculations (volume, enthalpy, viscosity, thermal conductivity, etc.) the mixture composition is somehow “averaged out” using mixing rules or other methods, so that the effect of each individual component is essentially proportional to its concentration. The binary interaction parameters are of less importance. The discussion will therefore be focused on the different types of phase equilibrium calculation.

### 3.5.1 Phase appearance or phase envelope calculations

When the limit of appearance of a new phase is required (condensation, vapourisation or crystallisation), the calculation is the same as for a phase envelope calculation: a phase diagram (or phase envelope) provides the boundaries between single-phase and two-phase regions, between two- and three-phase regions, etc.

A general observation is that the key component in these types of calculations is the component that will have most influence on the incipient phase properties (i.e. the phase whose possible appearance is investigated).

#### 3.5.1.1 Vapour-Liquid Equilibrium (VLE) calculations

For VLE calculations, two possibilities are encountered: either a bubble point or a dew point has to be calculated.

At the **bubble point**, the incipient phase is a vapour phase. The vapour is rich in light components. Hence, the bubble conditions will be very sensitive to the concentration, but also to the parameterisation of the gases dissolved in the liquid.

For example, the effect of the parameter $k_{ij}$ between methane (lightest component) and phenanthrene (heaviest component) is shown in figure 3.42. It is worth noting that the phenanthrene concentration in this mixture is very small. Here, the effect on the bubble pressure is obvious.

When calculating a **dew point**, the incipient phase is a liquid, which essentially contains heavy components. Sportisse [347] has shown that, even in very low concentrations, a heavy component has a very large effect on the dew curve. This is also illustrated in figure 3.43: the very small concentration in C$_{11}$ has a tremendous effect on the dew curve depending on whether it is described as $n$-C$_{11}$, $n$-C$_{16}$ or $n$-C$_{20}$ linear paraffins.
Figure 3.42
Effect of the binary interaction parameter ($k_{1,7}$) between the heaviest and the lightest component for the calculation of the VLE phase diagram of a synthetic hydrocarbon mixture [346] using the PR EOS.

Figure 3.43
Effect of the description of the heavy end of a gas condensate on the phase envelope. The three curves are calculated in identical conditions, except that the $C_{11}^+$ pseudo-component is taken as $n-C_{11}$, $n-C_{16}$ or $n-C_{20}$, using the PR EoS.
When calculating the phase boundary of vapour-liquid equilibrium, the most sensitive interaction parameters are between the lightest and the heaviest components in terms of volatility.

### 3.5.1.2 Liquid-Liquid Equilibrium (LLE) calculations

Volatility has no effect at all on liquid-liquid phase equilibrium. Only chemical affinity is at stake: molecules that interact strongly with themselves (as in auto-association: water, alcohols, or strongly polar molecules) will tend to phase split with molecules that do not have the same type of strong interactions (hydrocarbons, and in particular alkanes, are at the other end of that spectrum).

In section 3.3.1 of this chapter (p. 148), it has been shown how a slight change in the behaviour of the activity coefficient can dramatically change the phase behaviour. It is essential to investigate the interactions between the two components that are most unlike each other, but the presence of a co-solvent (molecule that is soluble in both of the other two components) can affect the phase equilibrium significantly. It is therefore recommended not only to rely on binary data, but to further investigate ternary equilibria. In figure 3.44, an example is shown for the glycerol + methanol + methyl-oleate (ester) mixture, important in the trans-esterification process where the purity of the ester and the glycerol phases are essential for the treatment of the products.

![Figure 3.44](image_url)

**Figure 3.44**

Ternary LLE diagram of the glycerol + methanol + methyl ester system.
In multicomponent mixtures, it may be useful to represent this ternary diagram, either by selecting a representative molecule for each group “solvent”, “anti-solvent” and “co-solvent”, or by grouping in one of the three sides the groups of components that behave similarly.

The difficulties related to the simultaneous description of LLE and VLE is further discussed by Cha and Prausnitz [348], who also concludes that the use of ternary data may be a great asset.

### 3.5.1.3 Liquid-Solid Equilibrium (LSE) calculations

When a solid phase can crystallise from a fluid system, it is essential to know what the solid composition should be. The factors that determine which component crystallises first are:

- the crystallisation temperature (discussed in section 3.1 of this chapter, p. 102), and
- the concentration of each component.

An example of such a case is discussed in the Liquefin application [349].

A good knowledge of the interactions between the crystallising component and the bulk fluid mixture is essential to develop a good model. As a first approximation, the bulk fluid composition will be reduced to its majority component, but it may also be worthwhile investigating the interactions with the other fluid components.

### 3.5.2 Distribution coefficients calculation

Distribution coefficients are used for all processes that use phase equilibrium for separation. In the case of stripping or extraction, the key component is generally well identified: always keep in mind that its properties strongly depend on its interactions with the bulk phase composition.

In case of distillation, components are separated based on their relative volatilities (see section 2.2.3.2, p. 81). Analysis and design of recent models used in distillation can be found in the recent book of Doherty and Malone [350]. Most distillation columns have two products: a heavy product (residue) and a light product (distillate). The purpose is often to split the feed at a boiling point range that is as narrow as possible (as shown in figure 3.45). This situation is called simple distillation. More complex situations may occur however, such as distillation of an azeotropic mixture or distillation with strict purity specifications. These cases are discussed below.

### 3.5.2.1 Simple distillation

When the purpose of the process is to split a feed according to a specific cut-point, the interactions between the components on either side of the cut-point will be vitally important when setting up the thermodynamic model.

Figure 3.45 illustrates how in fact the “cut point” is more generally a “cut zone”. The feed is here considered as a continuum in terms of volatility (expressed using the vapour pressure $P^\sigma$). If the column had an infinite reflux ratio, or an infinite number of theoretical
stages, it would be possible to attain a sharp, horizontal split between the two products. In reality, there will always be some of the lightest part of the heavy end that will end up in the distillate, and some of the heavy part of the light end that will be found in the residue. This “cut point zone” is where the attention should be focused for a good thermodynamic model: a good definition of their mutual interaction is essential.

Yet, it must be kept in mind, as always, that the components found in the cut point zone are in fact diluted in either the heavy end or the light end. As a result, following interactions should be taken into consideration:

• cut-point components among each other,
• cut-point components with the majority component(s) of the light end,
• cut-point components with the majority component(s) of the heavy end.

Examples of this situation are de-ethanisers, de-propanisers, etc. where the interactions between ethane and propane, or between propane and butane, respectively, are the most important to evaluate.

The importance of an accurate calculation of the relative volatility is highest when the volatility of the two keys are close, as shown in figure 3.46 ($\alpha$ is close to one). The error that may result on the number of trays to achieve a given separation can become very large.

3.5.2.2 Azeotropic distillation

The fact that in a mixture, the volatility of a given component may change significantly has been discussed extensively in section 3.4.1 of this chapter (p. 160). The result is that the
components can no longer be listed according to their pure volatility, as in figure 3.45. Instead, they should be listed according to the product of their vapour pressure and their activity coefficient: the product $\gamma_i \sigma P_i$. This is not possible as such, since the activity coefficient depends on the liquid composition, which itself varies along the distillation column.

Figure 3.47 attempts to help understanding how this change in volatility may affect the distillation. We only consider here positive deviations from ideality. Interactions between two components may be such that their relative volatilities are inverted within a certain concentration range (this is what happens in case they form an azeotrope). The figure shows the location of the binary azeotrope on the same scale as the volatility scale of the feed (see figure 3.47).

Two situations can occur: either the azeotrope lies entirely within the distillate or residue region (as shown in figure 3.47 a) or it will lie within the cut-point region (as shown in figure 3.47 b). In the former case, investigating the azeotropic binary will not improve the thermodynamic model; in the latter, it is essential for a good representation of the distillation column.

When the azeotropic pressure of a mixture lies above the cut-point, while the individual component volatilities lie in the residue region, a thorough thermodynamic investigation of the mixture is required: it indicates that in the mixture, the volatilities of these components are much higher than expressed by their vapour pressure, and that they will therefore most probably end up in the distillate.
3.5.2.3 Impurities

Knowing the fate of impurities in the process may be essential for various reasons, for example environmental, catalyst poisoning, or other possible risks. However, as already mentioned above and discussed in some detail in section 3.4.1 (p. 160), a component behaves very differently when in a mixture and when pure. The activity coefficient is used to express this deviation. It is often observed that the activity coefficient from the middle-composition is very different from the one at very high dilution (infinite dilution).

In order to illustrate this fact, figure 3.48 shows the methanol + n-hexane binary mixture with activity coefficient calculated from experimental data. It is clear that the NRTL model, used here to calculate the activity coefficient, although very good for medium concentrations, does not capture at all the infinite dilution activity coefficients. Therefore, if the high dilution region is of interest, a specific model must be used, or otherwise specific parameters must be fitted.
In conclusion, fitting a thermodynamic model on binary VLE data may not be sufficient to calculate infinite dilution or Henry constant values. Specific data at infinite dilution should be used. Predictive models (as UNIFAC) are often unable to describe infinite dilution behaviour. This is why a close analysis of the process problem is essential.

**REFERENCE LIST**


