

In this chapter, which is an introduction to the case studies, a first section summarizes the proposed procedure for a thermodynamic analysis, and a second section lists some of the major processes found in the chemical and petroleum industry, along with some key questions that can help the process engineer in his/her analysis.

## 5.1 PROBLEM SOLVING PROCEDURE

Once the problem has been correctly identified as discussed in the chapters 2 to 4 of this book, the solution procedure can start. A three-step procedure is proposed:

- evaluate **the best model**, including the adequate simplifying assumptions, based on the problem analysis discussed above,
- determine **the data** that exist or that are needed in order to either fit or validate the model,
- **regress and evaluate** the result in order to decide which is the best model/parameter combination.

### 5.1.1 Evaluation of the most appropriate model(s)

In this first step, the observations that have been made in the problem analysis are used in order to justify possible simplifying assumptions that will guide the choice.

There is generally no single choice for a thermodynamic model [2]. Hence, it may be good at this stage to retain several options, which will be evaluated at the end of the problem-solving procedure.

#### 5.1.1.1 Properties required

Concerning the **properties required**: which have the most impact on the final results? What simplifications can be afforded? The properties can be subdivided in two main families: single phase or equilibrium.

##### A. Single phase properties

Is there a need for a calculation method for single phase properties (volume, enthalpy, entropy...)? Simplifying assumptions may be either low pressure (gas properties are ideal gas; liquid properties can be taken at the vapour pressure) or ideal mixture (no mixing properties), as discussed in section 2.2.2 (p. 52) or in section 4.1.4 (p. 259).

It is important to mention that some equilibrium calculations may require single phase properties. Examples are *PH* calculations (as in a distillation column), where an enthalpy calculation is needed in addition to the distribution coefficients.

## B. Equilibrium properties

Both for chemical and phase equilibrium calculations, a model must be provided for calculating fugacities (or chemical potentials) of each component in each phase.

In case phase equilibrium is considered, these fugacities are often transformed into distribution coefficients (section 2.2.3.1.B, p. 70):

$$K_i = \frac{x_i^\alpha}{x_i^\beta} = \frac{\phi_i^\beta}{\phi_i^\alpha} \quad (5.1)$$

where  $\alpha$  and  $\beta$  are the phase labels and  $\phi_i$  is the fugacity coefficient. For **vapour-liquid equilibrium**, following simplifying approximations can be envisaged:

- Distribution coefficients independent of composition: this is the case for ideal mixtures. Whether or not a mixture is ideal is discussed in section 3.4.2.1 (p. 173).
- Low or moderate pressure (below 1.5 MPa), in addition to ideal mixture, in which case the distribution coefficient is written as:

$$\ln(K_i P) = \alpha_i(T) + \beta_i(T) P \quad (5.2)$$

as discussed in the example 4.2 page 277 (expressions for  $\alpha_i(T)$  and  $\beta_i(T)$  are provided). At pressures below 0.5 MPa, equation (5.2) can be further simplified to yield Raoult's law:

$$K_i P = P_i^\sigma(T) \quad (5.3)$$

In case the mixture is not ideal, but low pressure conditions are validated, the use of the activity coefficient may be convenient, as it can help understand phase behaviour as discussed in section 3.4.1 (p. 160):

$$K_i = \frac{P_i^\sigma(T)}{P} \gamma_i(T, x) \quad (5.4)$$

In some cases, when a high dilution problem or a supercritical component is involved, it may be useful to write equation (5.4) using the asymmetric convention, presented in section 2.2.3.1.B (p. 68), using the Henry constant for the solute, keeping (5.3) or (5.4) for the solvents:

$$K_i = \frac{H_i(T)}{P} \quad (5.5)$$

When **liquid-liquid equilibrium** is expected, the mixture is per definition not ideal. The assumption that is often made is that pressure has no effect on this type of equilibrium. Only activity coefficients are in principle enough for calculating these type of equilibria (see discussion section 3.4.1.3, p. 166).

When **equilibrium with a solid phase** is to be calculated, the freezing or crystallisation properties must also be known, as shown in section 3.4.4.1 (p. 222) or example 4.6 (p. 282).

If a **chemical equilibrium** is to be calculated, the discussion in section 2.2.4 (p. 86) and example 2.11 (p. 92), shows the importance of the accuracy of the formation properties.

Phase equilibrium may be required for different purposes, as discussed in section 2.2.3.2 (p. 81) (component separation according to volatility, component separation according to affinity, component separation using crystallization; phase boundary calculation or calculation of

the relative amount of each phase): it is important that the process engineer know what his/her true problem is in order to further identify the key components in his/her mixture (see below).

### 5.1.1.2 Fluid composition

Concerning the **fluid composition**, the process engineer should be able to distinguish the type of mixture as well as the key components in his/her mixture. Chapter 3 is designed to help him/her in this search.

The type of mixture is needed both for identifying the adequate physical model as for identifying the best method for parameter identification:

- Three types of pure components have been identified (section 3.1.2, p. 121): database components, complex molecular components and pseudo-components. Each of these require a different approach for parameter identification.
- It is stressed, in section 3.4.1 (p. 160) that a component in a mixture may behave very differently from the same component as it is pure. This is probably the reason why so many different methods and mixing rules have been developed. All section 3.4 (p. 160) is devoted to the discussion of the main models that are available today.

Since the parameters are often determined by fitting on experimental data, section 3.3, (p. 148) discusses the methodology of parameter regression.

Yet, in view of the specific process problem that is addressed, all mixture components may not have the same importance. As an example, it can be understood that if the condition of water condensation from a natural gas must be calculated, the exact ratio of methane and ethane is probably of little importance. Instead, the water concentration must be known with high accuracy. This is why in section 3.5 (p. 225) the question of the “key components” is raised. Obviously, the answer to that question very much depends on the process problem. This question refers back, therefore, to the true property that must be investigated:

- **Phase boundary:** here, it is the composition of the nascent phase that will provide the answer. The fugacity or chemical potential of the majority (or perhaps only) component of this phase must be known with great precision within the bulk phase. This is often a challenge because the key component may in reality be a minority component in the bulk phase, and as a result behave in a strongly non-ideal manner.
- **Component separation:** in this case, the distribution coefficient of some components should be regarded as more important than others. Again, it can happen that one of the component to be separated from the others is a minority component (e.g. in case of severe specifications).

As a conclusion of this analysis, the process engineer must be able to identify the nature of the components, both taken individually and in a mixture. He or she must then evaluate whether key component(s) should be identified, either as individual component, or as binary, ternary, etc.

### 5.1.1.3 Representative phases

The fourth chapter of this book describes in detail the type of phases than can be encountered for a number of industrially relevant systems. Throughout the chapter, model recommendations

are provided depending on the type of mixture and of problem considered. The conclusion (section 4.3, p. 325) of this chapter provides some general guidelines.

The applicability of a model may be restricted to some particular phase:

- **Vapour phases** require an equation of state (which can be very simple – the ideal gas – if only low pressure conditions are considered). The use of these type of equations is summarised in section 2.2.2.1 (p. 52) and a list of the most common such equations is found in section 3.4.3 (p. 189).
- **Liquid phases** can be described by either an equation of state or an activity coefficient model. The use of this latter type of models is summarised in section 2.2.2.2 (p. 60) and a list of the most common such models is found in section 3.4.2 (p. 171). The choice will be guided by the degree of non-ideality of the mixture, as explained in section 3.4.2.1 (p. 173).
- **Critical conditions** are found when two phases become identical. Obviously, if this is the region of interest, it is essential that the same model be used in the two phases: vapour-liquid critical points can only be computed by equations of state. Yet, the true properties close to such a critical point may require a specific approach, as the asymptotic behaviour close to this point can not be described by any analytic equation.
- **Solid, crystalline phases** necessitate a specific model, as shown in section 2.2.3.1.A (p. 67); section 3.4.4.1 (p. 222) and illustrated in section 4.2.2.3 (p. 282). They are calculated from pure component fusion properties (section 3.1.1.1.F, p. 105 and 3.1.1.2.B and C, p. 113), and possibly with an activity coefficient model.

## 5.1.2 Search for the most significant physical data

Once a list of models capable of describing the requested phenomena have been identified, a set of experimental data needs to be found for:

- adjusting the model parameters (discussed in section 3.3, p. 148),
- evaluating the quality of the model(s).

As is stressed over and over again, the experimental data will be the final referee on whether a model is good or not. However, it is important to select the correct type of data, and to make the right decisions if new data must be gathered. In case no data exist, it is important to be able to still provide some reasonable guidelines as to the trends that can be expected. This is why different types of data can be identified. They are listed here in decreasing order of pertinence:

1. Obviously, of most value are the **data that originate from a recognised laboratory** and that correspond to the actual physical property that must be calculated, in the process pressure and temperature range. If possible, these data should come with an evaluation of their experimental uncertainty. It is important to make sure that the data are obtained in true equilibrium conditions, are sampled correctly and analysed according to well-accepted methods. Each of these steps requires a good knowledge of the phenomena. This is not so much a question of date or equipment (very ancient data may be quite accurate), than of expertise of the researchers. From this point of view, data originating from a pilot plant

should be considered with great caution, as many phenomena may occur simultaneously (reaction, mechanical entrainment, non-equilibrium sampling) that are unrelated to the equilibrium properties that we are interested in. Evaluation of the quality of experimental data has been discussed in section 3.1.3 (p. 139) for pure components, and section 3.2 (p. 142) for mixtures.

2. When no direct experimental data exist in the process conditions, **unrelated data can be extrapolated**. This can be done, but should require a good knowledge of the physical trends. Examples are extrapolation of vapour pressures or solubilities according to well-known equations (for example using the corresponding states principle introduced in section 2.2.2.1.C, p. 57). It is also possible to consider data for other components of the same family, and to consider that their behaviour will be similarly. Finally, the use of thermodynamic relationships for calculating data of a different type (e.g. enthalpy of vapourisation using a vapour pressure curve) is also acceptable. All of these options have been further discussed in sections 3.1 (p. 102) and 3.2 (p. 142), where some methods for evaluating the quality of the data are proposed.

3. So-called “**pseudo-experimental**” data can be produced using predictive calculation methods. They have the advantage of offering the possibility to calculate data in conditions that are experimentally difficult to realise (unstable components, toxic components, extreme pressure or temperature conditions...). Yet, the quality of these data obviously greatly depends on the complexity of the predictive calculation tool:

- Probably the most promising approach for this purpose is the use of **molecular simulation** [3-5]. The panoply of potential models available in both Monte-Carlo (for equilibrium properties) as dynamic simulation (for both equilibrium and transport properties) is rapidly increasing and commercial tools<sup>1</sup> are becoming now increasingly user-friendly for non-expert use. Quantum-mechanical tools can also be used, as for example COSMO-RS<sup>2</sup> [6]. Their results should first be compared to true experimental data for validation, but they allow completing the databases in a reasonable amount of time for mixtures or molecules that are not too complex.
- In a more classical mode, **group contribution methods** may provide pseudo-experimental data that are of rather good quality as long as they are used for applications that have been validated previously. Today, many such tools exist, of which the most well-known is probably PSRK [7], but others have been developed for equation of state type calculations (for cubic equations: [8, 9], or for SAFT-type equations [10-13]) or for pure component properties [14-18]. They are further discussed in chapter 3.

---

1. From companies as Materials Design; Accelrys; Scienomics.

2. Available from COSMO-Logic.

### 5.1.3 Evaluation of the result

The data that have been identified should be separated in two sets. One will be used for parameter regression, the other for model validation. Sometimes (for predictive models, or when parameters are provided through a database), no regression is needed. In that case, all data can be used for validation. In any case, it is preferable to keep in the second category data that are close to the process conditions, and somewhat in extrapolation with respect to the data used for regression. This way, it will be possible to discriminate between the approaches that have been selected in step 1 here above (section 5.1.1, p. 350).

**Data regression** is an issue that can be discussed in great detail, but others have done this with much more authority [19], and we therefore refer to them directly. A short section is devoted to this topic in section 3.3 (p. 148) of this book. Let us simply stress at this stage the importance of a good match between the choice of objective function and parameters to regress. As an example, it seems pointless to regress parameters of a component that is highly diluted on bulk properties (a density, for example).

Once the different model/parameter sets have been developed, they can be **tested on the validation** set, in order to select the most appropriate combination for use in the process simulator. Most probably, the process engineer will select the set that yields the lowest overall deviation on the validation. However, probably more importantly, he/she should look at the trends of these deviations with respect to the process conditions. If a wrong trend exists in a domain where the process may run, the model should be abandoned, as its true behaviour cannot be ascertained. On the opposite, if no real trend exists, he/she can use the values of the deviations as an estimate of the uncertainty of the model, which he/she should incorporate in his/her design plan.

## 5.2 REVIEW OF MAJOR PROCESS PROBLEMS

It is impossible to provide an exhaustive review of all possible problems that may be encountered in the process industry. Yet, in order to provide some general guidelines, we discuss here a number of issues to be kept in mind for a list of process operations.