

# Extended abstract

## 1.1 Summary

This thesis was devoted to the development and parameterization of cubic and SAFT-type equations of state (EoS) and has intended to provide an insight about the aspects that impacts EoS's accuracy and performance. One of the main contributions of this thesis to the field of chemical engineering thermodynamics consists in the definition of a strategy to parameterize SAFT-type and cubic EoS. In particular, the type of experimental data absolutely required for the regression of a given EoS's parameters in order to get accurate and reliable results has been established. Moreover, component-dependent parameters for SAFT-type and cubic EoS were determined and published for 1800 pure fluids. Another key innovation in the field was the development of the most accurate cubic EoS ever published after the assessment of the influence of the  $\alpha$ -function, the volume-translation parameter, and the universal constants  $u$  and  $w$  included in the volumetric function. In order to safely extend EoS to mixtures addressing the question of mixing rules is capital. The research work of this thesis introduced a brand-new type of advanced mixing rules ( $EoS/a_{res}^{E,\gamma}$ ) derived by equating the residual part of the excess Helmholtz energy from a cubic EoS and from an explicit activity-coefficient model. Concerning the issue of assessing in a reliable way the accuracy of a thermodynamic model or to cross-compare two models, the doctoral work was focused on the development of pure-compound and mixtures reference databases. The first one contains more than 300,000 experimental data and aims to identify the strengths and weaknesses of a given thermodynamic model for pure fluids. The second one contains fluid phase equilibria and caloric data for 200 binary systems and is used to determine how well a thermodynamic model predicts the behavior of binary mixtures according to the associating character of their components. In the end, thanks to the accuracy on the prediction of saturation and caloric properties, one of the developed EoS in this thesis was included in a methodology for the selection of promising working fluids for Combined Cooling, Heating and Power (CCHP) applications.

## 1.2 Problem addressed

In the last two centuries, equations of state (EoS) have become a key tool for the correlation and prediction of thermodynamic properties of fluids. They can be applied not only to pure substances as well as to mixtures but they also constitute the heart of commercially available computer-aided-process-design software. The quest for highly accurate EoS is a huge driving force for research in chemical engineering thermodynamics. In order to have a better understanding of the aspects that impacts EoS's accuracy and performance, the objective of this thesis was to work on the development, parameterization of [cubic equations of state](#) and [equations based on the statistical association fluid theory \(SAFT\)](#), and their validation against high-quality databases and through industrial energy conversion applications.

It is worth noting that independently of the modifications, a key point that defines the capabilities of any EoS is the parameterization, i.e., the attribution of numerical values to component-dependent parameters. For this reason, the research work of this thesis got started by evaluating the impact of the parameterization method on the performances of CEoS and SAFT-type EoS.

The next stage of the doctoral work dealt with the fact that in chemical engineering thermodynamics is capital to assess the accuracy of a thermodynamic model or to cross-compare two models, and particularly, it is necessary to confront model predictions with experimental data. In this context, the importance of reliable free-to-access benchmark databases is pivotal and becomes absolutely necessary. In consequence, the doctoral work continued with the development of pure-compound and mixtures reference databases.

Finally, one of the developed EoS in this thesis was integrated into the framework of working fluid selection of an innovative combined cooling, heating and power (CCHP) system. The objective was to ensure the calculation of vapor pressure, density, enthalpy and entropy, which are included in the mass, energy and exergy balances necessary for the calculation of thermodynamic cycles' performances.

### 1.3 Key innovations and results

#### Impact of the parameterization method on the performances of CEoS and SAFT-type EoS

Equations of state for pure fluids contain two types of parameters: those fixed by the theoretical foundations and those that are component-dependent. Typically, the pure-component parameters are either evaluated by regression on vapor-pressure and saturated liquid density data or are determined from critical coordinates and acentric factor data. The parameterization method consists in attributing numerical values to component-dependent parameters.

Usually, the *parameterization method* is implicitly associated with the model itself. In the case of CEoS, the covolume ( $b$ ) and the critical value of the attractive parameter ( $a_c$ ) for pure compounds are conventionally determined from the knowledge of the experimental critical temperature and pressure in order the model exactly reproduces such values. The acentric factor is usually added as a third parameter in order to improve the correlation of vapor pressures. In the case of non-associating SAFT-type EoS, they are typically parameterized by fitting the component-dependent parameters to vapor pressure and liquid density data whereas other procedures are scarcely applied.

The impact of the parameterization method on the performances of CEoS and SAFT-type EoS is discussed in [Publication \[1\]](#). Two parameterization methods were tested:

- Parameterization method 1 (P1): the three input parameters are constrained to exactly reproduce  $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$  and a second point of the vapor-pressure curve by means of the acentric factor (i.e., the vapor pressure at a reduced temperature equal to 0.7).
- Parameterization method 2 (P2): the three input parameters are fit to  $P^{\text{sat}}$ ,  $\Delta_{\text{vap}}H$ ,  $c_{P,\text{liq}}^{\text{sat}}$  and  $v_{\text{liq}}^{\text{sat}}$  data so that the model is not constrained to pass through the experimental critical coordinates ( $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$ ).

In [Publication \[1\]](#), it is shown that vapor pressures, enthalpies of vaporization and saturated-liquid heat capacities are not impacted by the change of parameterization method. Nevertheless, it is impossible to obtain simultaneously accurate prediction of the critical coordinates (especially critical pressure) and liquid densities with a CEoS or a SAFT-type EoS. In particular, it is possible to highlight the antagonism between the reproduction of the critical pressure and liquid densities. Therefore, this duality imposes a choice. One option is to have an accurate reproduction of liquid densities by using the parameterization method P2 and try to correct the calculation of critical pressures. The other option is to exactly reproduce the critical point by using the parameterization method P1 and try to correct liquid densities.

#### How a sound parameterization allows to get a highly accurate cubic equation of state

In a general form, a cubic equation of state can be written as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2} \quad (1)$$

where the constants  $u$  and  $w$  are either universal constants (the same values apply to all compounds) or substance-dependent quantities. The temperature-dependent  $a(T)$  parameter is classically written as:

$$a(T) = a_c \cdot \alpha(T) \quad (2)$$

It is the product of the value of the attractive parameter at the critical temperature ( $a_c$ ) multiplied by a so-called  $\alpha$ -function, which is dimensionless. Such an  $\alpha$ -function has a great influence on the calculated vapor-liquid equilibrium properties like vapor pressure, enthalpy of vaporization and saturated-liquid heat capacity. On the other hand, the volume function of the attractive term ( $v^2 + ubv + wb^2$ ) and, in particular, the numerical values assigned to  $u$  and  $w$ , govern essentially the accuracy of the predicted volumetric properties.

Throughout this thesis, it has been shown that two major concepts are necessary for the development of accurate CEoS: the *consistency* and *volume-translation* concepts. First, the consistency concept relies on the requirements that are absolutely necessary to get physically meaningful behaviors in both the subcritical and supercritical domains. The consistency test imposes that  $\alpha$ -functions must:

- I. Be of class  $C^2$ , i.e., their first ( $d\alpha/dT$ ) and second ( $d^2\alpha/dT^2$ ) derivatives must exist and must be continuous at any temperature.
- II. Be positive at any temperature ( $\alpha(T) \geq 0$ ).
- III. Be monotonically decreasing for any temperature value ( $d\alpha/dT \leq 0$ ).
- IV. Be convex for any temperature value ( $d^2\alpha/dT^2 \geq 0$ ).
- V. Verify  $d^3\alpha/dT^3 \leq 0$  at any temperature.

In turn, the volume-translation concept consists in a substance-dependent volume-translation parameter,  $c$ , that is determined, component by component, in order the translated EoS exactly reproduces the experimental saturated liquid volume at a reduced temperature of 0.8, [ $v_{liq,exp}^{sat}(T_r = 0.8)$ ], that is:

$$c = v_{liq}^{sat,u-CEoS}(T_r = 0.8) - v_{liq,exp}^{sat}(T_r = 0.8) \quad (4)$$

where  $v_{liq}^{sat,u-CEoS}(T_r = 0.8)$  is the molar volume calculated with the original (*untranslated*) CEoS at  $T_r = 0.8$ .

The coupling of these concepts allows the definition of very accurate CEoS such as the *translated-consistent* Peng-Robinson EoS (*tc-PR*) [2]:

$$P(T, v) = \frac{RT}{v + c - b} - \frac{a_c \cdot \alpha(T_r)}{(v + c)(v + c + b) + b(v + c - b)} \quad (5)$$

with:  $\alpha(T_r) = T_r^{N(M-1)} \exp[L(1 - T_r^{MN})]$

The remaining question is on which experimental data the 3 parameters L, M, N of the Twu 91 function should be regressed in order to obtain the best possible results. For this reason, [Publication \[3\]](#) dealt with the analysis of the combinations of property data among vapor pressure, enthalpy of vaporization and saturated-liquid heat capacity that are suitable for a safe estimation of consistent Twu  $\alpha$ -function parameters. Depending on the availability of these 3 properties, it is possible to arbitrarily define seven types of pure compounds.

The methodology used in [Publication \[3\]](#) was to work with fluids for which  $P^{sat}$ ,  $\Delta_{vap}H$  and  $c_{P,liq}^{sat}$  experimental data were simultaneously available. The interest of choosing these pure compounds was that if it was decided to fit the (L, M, N) parameters using not three but one or two of the selected properties, it became possible to predict the remaining ones and to compare them with experimental values. It was thus possible to determine whether taking specific combinations of 1 or 2 properties into account for parameter fitting could lead to unreliable sets of (L, M, N) parameters. The conclusion of the study is that reliable parameters are obtained on the condition that they are – at least – fitted to vapor-pressure data and that it is strongly advised to not exclusively fit  $\alpha$ -function parameters to enthalpy of vaporization and/or saturated-liquid heat capacity data.

In the end, Twu  $\alpha$ -function parameters (L, M, N) suitable for the *tc-PR* and *tc-RK* CEoS were determined for 1800 molecules, for which at least accurate vapor-pressure data are available in the DIPPR database.

Concerning SAFT-type EoS, a similar study was carried out in [Publication \[4\]](#). It was concluded that it is necessary and sufficient to fit PC-SAFT EoS parameters using both vapor-pressure and density data. Moreover, including  $\Delta_{vap}H$  and/or  $c_{P,liq}^{sat}$  data in the regression procedure is not a necessity and only

marginally improves the reproduction of these properties. Finally, a molecular-parameter database for the PC-SAFT EoS was proposed for 1252 non-associating compounds disposing of at least  $P^{sat}$  and  $\rho_{liq}^{sat}$  data. Such a database is the largest available today.

Back to the study of CEoS, the next stage was to assess the difference in their accuracy if a generalized or a component-dependent  $\alpha$ -function such as the Twu91  $\alpha$ -function was implemented. For this purpose, the Soave 1972  $\alpha$ -function was retained for comparison since it has been demonstrated over the years to be a safe, robust and soundly developed function. It is worth noting that Soave came up with the form of the  $\alpha$ -function by using experimental data. However, the  $m$  polynomial was determined by correlating different values of  $\omega$  and the corresponding  $m$  values enabling to exactly reproduce reduced vapor pressures at  $T_r = 0.7$  calculated as:  $P_r^{sat}(T_r = 0.7) = 10^{-\omega-1}$ .

In [Publication \[5\]](#), it was decided to propose an updated version of the Soave  $\alpha$ -function, and specifically of the  $m$  polynomial, suitable for the PR and SRK EoS considering molecules for which at least accurate vapor-pressure data are available in the DIPPR database (which contains a large amount of experimental data that were not available at the time of Soave's proposal). The approach retained in [Publication \[5\]](#) differs from that of Soave in the fact that the  $m$  values were no longer obtained in order to ensure the reproduction of the reduced vapor pressures at  $T_r = 0.7$ , but by minimizing an objective function containing deviations on at least  $P^{sat}$ , and/or  $\Delta_{vap}H$  and/or  $c_{P,liq}^{sat}$ . By updating the Soave  $\alpha$ -function, the comparison between it and the Twu91  $\alpha$ -function would be fairer. With the study, it was possible to conclude that significant improvement on the reproduction of heat capacities was obtained when a component-dependent Twu91  $\alpha$ -functions along with CEoS was used.

After the study of  $\alpha$ -functions parameterization and the advantage of implementing a consistent and component-dependent expression instead of a generalized one for the reproduction of  $P^{sat}$ ,  $\Delta_{vap}H$  and  $c_{P,liq}^{sat}$ , it is time to discuss about the volumetric function and its impact on liquid densities. In [Publication \[6\]](#), it was analyzed through a systematic methodology how parameters  $u$  and  $w$  influence the accuracy of predicted volumetric and vapor-liquid equilibrium properties, both for untranslated and translated cubic equations of state. The methodology consisted of exploring the  $(u - w)$  space, i.e., defining a mesh and testing every point  $(u, w)$  in order to look for such points (or zones) for which the reproduction of  $P^{sat}$ ,  $\Delta_{vap}H$  and  $\rho_{liq}^{sat}$  was the best as possible.

On the light of results obtained in [Publication \[6\]](#), it was concluded that:

- The unique solution to predict accurate volumetric properties is to make  $u$  and  $w$  component-dependent.
- The volume translation technique is probably the best option to make  $u$  and  $w$  component-dependent. Such a technique indeed avoids the development of a correlation between  $(u, w)$  and  $\omega$ . Moreover, its application is straightforward.
- The optimal values of  $u$  and  $w$  for both untranslated and translated CEoS are  $(u_{opt} = 2.16, w_{opt} = -0.86)$ . The choice of Peng and Robinson ( $u = 2; w = -1$ ) was thus a very good one. Moreover, if both pairs of parameters are coupled with the consistent Twu91  $\alpha$ -function, and a volume-translation parameter, the resulting models *tc*-Optim (with  $u_{opt} = 2.16, w_{opt} = -0.86$ ) and *tc*-PR (with  $u = 2; w = -1$ ) are able to correlate vapor pressures with an error of 1% whereas errors on  $\Delta_{vap}H$ ,  $c_{P,liq}^{sat}$  and  $v_{liq}^{sat}$  are close to 2%.

### **Reference database for pure compounds**

An important point had not been analysed yet: the influence of the associating character of the molecules, i.e., their ability to be involved in a hydrogen bond. How a model performs with non-self-associating (NSA) and self-associating (SA) molecules gives a deeper insight of its performance. In particular, for the *tc*-PR model, having such an insight could open the way to further improvement. This is one of the

main motivations of [Publication \[7\]](#), which is devoted to the constitution of a database suitable for the identification of the strengths and weaknesses of a given thermodynamic model for pure compounds. 1800 molecules for which, in addition to the critical coordinates ( $T_c$ ,  $P_c$  and  $v_c$ ), accurate correlations for  $P^{sat}$  and  $\rho_{liq}^{sat}$  are available. Among them, 1536 fluids also possess an accurate correlation for  $\Delta_{vap}H$  and 890 for  $c_{P,liq}^{sat}$ , resulting in a database containing 306 700 high-quality pseudo-experimental data points. The proposed database was used to assess the performance of 4 CEoS: Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), and the *translated-consistent* versions of PR (*tc*-PR) and RK (*tc*-RK). Results obtained over 1800 compounds and more than 306 000 data points highlight:

- The use of the highly flexible, component-dependent Twu91  $\alpha$ -function drastically improves the reproduction of vapor pressures, enthalpies of vaporization and liquid heat capacities.
- The spectacular improvement in the reproduction of liquid molar volumes when a substance-dependent volume-translation parameter is used.
- The impressive accuracy of the *tc*-PR EoS that got an average overall deviation lower than 2% over the 306 700 available experimental data points. Excellent results are obtained for all the properties, except the molar critical volumes.
- The striking fact that not all the non-self-associating molecules are well modeled by the studied CEoS and that almost 2/3 of the self-associating compounds of the database are represented with high accuracy by CEoS. At this step, one might wonder whether the addition of an association term is the right solution to improve the accuracy of EoS.

Finally, in [Publication \[8\]](#), the performance of the PC-SAFT [\[9,10\]](#) and the *I*-PC-SAFT EoS ([Publication \[1\]](#)) without an association term was evaluated over the non-associating and self-associating molecules contained in the database proposed in [Publication \[7\]](#) by determining their capacity at correlating the following properties:  $P^{sat}$ ,  $\rho_{liq}^{sat}$ ,  $\Delta_{vap}H$ ,  $c_{P,liq}^{sat}$ ,  $T_c$ ,  $P_c$  and  $v_c$ . It was found that the PC-SAFT equation is able to reproduce  $P^{sat}$  and  $\rho_{liq}^{sat}$  data with a deviation close to 1% what is really excellent. The price to pay is however a large deviation on the critical pressure. The *I*-PC-SAFT EoS exactly reproduces the critical pressure and temperature but at the expense of a larger liquid density deviation. The key conclusion is that there is no correlation between the strength of association and the accuracy with which the experimental data were correlated. Poor results are obtained for more than 15% of the non-self-associating compounds but 70% of the self-associating compounds are accurately correlated although no association term was included in the considered equations of state.

### **Extension of cubic equations of state to mixtures. Revisited advanced mixing rules**

The second stage of the development of an EoS is its extension to mixtures. For this purpose, Van der Waals proposed the one-fluid theory, which considers that the properties of a fluid mixture are assumed identical to those of a hypothetical pure fluid, at the same temperature and pressure, whose EoS parameters also depend on mole fractions of species. Based on the one-fluid theory, cubic equations of state can be expressed with the following generic formulation:

$$P(T, v, \mathbf{z}) = \frac{RT}{v - b_m} - \frac{a_m}{(v - r_1 b_m)(v - r_2 b_m)} \quad (6)$$

where  $r_1$  and  $r_2$  are two universal constants which just depend on the selected equation of state, and  $a_m$  and  $b_m$  are the energy and covolume parameters of the mixture, related to the composition of the mixture  $\mathbf{z}$ , to the energy ( $a_i(T)$ ) and covolume ( $b_i$ ) parameters of a given number of pure components by means of properly defined functions, the so-called *mixing rules*. A popular choice is the so-called Van der Waals one-fluid (vdW1f) mixing rules, which consider parameters  $a_m$  and  $b_m$  as quadratic functions of the composition:

$$\begin{cases} a_m = \sum_i \sum_j z_i z_j a_{ij} \\ b_m = \sum_i \sum_j z_i z_j b_{ij} \end{cases} \quad \begin{cases} a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \\ b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \end{cases}$$

where  $a_{ij}$  and  $b_{ij}$  are determined from pure-component parameters,  $a_i$  and  $b_i$ , through the application of combining rules. The classically-applied combining rules are the geometric-mean rule for the cross-energy and the arithmetic-mean rule for the cross-co-volume parameter, where  $k_{ij}$  and  $l_{ij}$  are binary interaction parameters, adjustable over experimental data or obtained from suitable correlations.

Cubic EoS with VdW1f mixing rules lead to very accurate results at low and high pressures for simple mixtures (containing components showing little or no polarity, e.g., hydrocarbons, gases etc.). However, such mixing rules cannot be applied with success to polar mixtures. In return, excess Gibbs energy ( $g^E$ ) models (activity coefficient models) are applicable at low pressures and are able to correlate phase equilibrium data for polar mixtures. From this observation arises the idea to combine cubic EoS and activity coefficient models in order to obtain a single model suitable for describing the phase equilibria of polar and non-polar mixtures from low to high pressures. This combination of EoS and  $g^E$  models is possible via the so-called EoS/ $g^E$  approach, which is essentially a set of mixing rules for the energy parameter of cubic EoS [11]. The starting point for deriving EoS/ $g^E$  models is to equal the expressions of the excess Gibbs energy obtained from an EoS [ $g^{E,EoS}(T, P, \mathbf{z})$ ] with that from an explicit activity coefficient model [ $g^{E,\gamma}(T, \mathbf{z})$ ]. By construction, this latter is temperature- and composition-dependent but pressure-independent; however, the  $g^{E,EoS}$  quantity depends on pressure, temperature and composition explaining why a reference pressure, noted  $P_{ref}$ , needs to be selected before equaling the two quantities. The starting equation to derive EoS/ $g^E$  models is thus:

$$g^{E,EoS}(T, P_{ref}, \mathbf{z}) = g^{E,\gamma}(T, \mathbf{z}) \quad (7)$$

The activity coefficient model (ACM) may be chosen among the classical forms of molar excess Gibbs energy functions (such as Redlich-Kister, Margules, Wilson, Van Laar, NRTL, UNIQUAC, UNIFAC and others). Eq. (7) is the cornerstone of the approach pioneered by Huron and Vidal (HV) [12], who assumes infinite reference pressure; and by Michelsen [13–15] who employed the zero-pressure reference and deduced the MHV-1 and MHV-2 mixing rules.

Although HV and MHV mixing rules have been widely used since their initial proposal, over the last decades various studies have shown that:

- in the case of HV mixing rules, researchers could not explain why satisfactory results were obtained with ACM models that contained only a residual (enthalpic) contribution such as the NRTL model. This is supported by the fact that the combinatorial term from the EoS cancels out. In consequence, it would not be pertinent to use a  $g^{E,\gamma}$  model with both a combinatorial and a residual contribution.
- in the case of MHV mixing rules, the presence of two types of combinatorial terms in the MR, i.e., from the  $g^{E,\gamma}$  model and from the EoS, which are of the same type but are not quantitatively equivalent, penalizes the accuracy of the model [16,17]. This phenomenon is referred as the **presence of a double combinatorial term**. To increase the accuracy of their model, the authors of the UMR-PRU [17] and VTPR [18] mixing rules thus decided to arbitrarily cancel the two combinatorial contributions.

Moreover, the consistency of Eq. (7) can be questioned for the following two main observations:

1. In accordance with the way they were derived, low-pressure  $g^{E,\gamma}$  models classically used to calculate activity coefficients should be better regarded as  $a^E$  models (they will be noted  $a^{E,\gamma}$  hereafter to avoid confusion with the same quantity stemming from the EoS);
2. In Eq. (7), the combinatorial part and the residual part of  $g^E$  stemming from the EoS and from the activity coefficient model do not match. Although  $g^{E,EoS} = g^{E,\gamma}$ , we do not get:  $g_{combinatorial}^{E,EoS} = g_{combinatorial}^{E,\gamma}$  and  $g_{residual}^{E,EoS} = g_{residual}^{E,\gamma}$ . We can thus expect poor results when athermal or regular solutions that only require a combinatorial or a residual contribution are modeled. To derive mixing rules, and contrary to Eq. (7), it is believed that a particular attention has to be given separately to the combinatorial and residual contributions. It is advised to equal separately the combinatorial and residual contributions stemming from the EoS and from the  $a^{E,\gamma}$  model in order to ascertain to equal quantities that contain the same information.

For these reasons, in this dissertation it was decided to propose a modification to the way that has been classically used to derive advanced mixing rules. This resulted in the formulation of EoS/ $a_{res}^{E,\gamma}$  mixing rules that were used in this thesis.

One may think that the solution to problem #2 is to define the system of two equations and two unknowns given by Eq. (8):

$$F(x) = \begin{pmatrix} a_{comb}^{E,EoS} - a_{comb}^{E,\gamma} \\ a_{res}^{E,EoS} - a_{res}^{E,\gamma} \end{pmatrix} = 0 \quad \text{with} \quad x = \begin{pmatrix} a_m \\ b_m \end{pmatrix} \quad (8)$$

Unfortunately, the problem described in Eq. (8) does not have solution. Indeed, no  $g^{E,\gamma}$  model contains a combinatorial term identical to the one provided by the EoS. Therefore, a sound starting point for advanced mixing rules could be:

$$a_{res}^{E,EoS} = a_{res}^{E,\gamma} \quad (9)$$

which is the starting point for the derivation of the EoS/ $a_{res}^{E,\gamma}$  mixing rules implemented for the extension of the  $tc$ -PR model to mixtures. The derivation of EoS/ $a_{res}^{E,\gamma}$  mixing rules is treated in detail in [Publication \[19\]](#). The resulting mixing rule for  $a_m/b_m$  seems particularly appropriate since the result is independent of the reference pressure (zero or infinite). It writes:

$$\begin{cases} b_m : \text{any mixing rule} \\ \frac{a_m}{b_m} = \sum_i^{n_c} z_i \frac{a_i}{b_i} + \frac{a_{res}^{E,\gamma}}{\Lambda_{EoS}} \quad \text{with} \quad \Lambda_{EoS} = \frac{1}{r_2 - r_1} \ln \left( \frac{1 - r_2}{1 - r_1} \right) \end{cases} \quad (10)$$

### **Reference database for mixtures**

In the last twenty years, hundreds of publications were devoted to the development of sophisticated models or to the improvement of already existing EoS [20]. Chemical engineering thermodynamics is thus a field under steady development and to assess the accuracy of a thermodynamic model or to cross-compare two models, it is necessary to confront model predictions with experimental data. Moreover, for the extension of the  $tc$ -PR EoS to mixtures using EoS/ $a_{res}^{E,\gamma}$  mixing rules, different strategies were tested and a reliable way of comparison was required.

For these reasons, [Publication \[21\]](#) was focused on the development of a high-quality reference database containing binary-system data for the cross-comparison of thermodynamic models and the assessment

of their accuracies. With such a database, it is possible to determine how well a thermodynamic model predicts the behavior of binary mixtures according to the associating character of their components. Indeed, a specific procedure for the calculation of the deviations between model calculations and experimental data was discussed in detail, as well as a methodology for grading a thermodynamic model was proposed. In total, 200 non-electrolytic binary mixtures were selected to cover all categories of mixtures. They were divided into 9 groups (characterized each by a so-called *binary association code*, BAC) according to the associating character of the two components, i.e., to their ability to be involved in a hydrogen bond. In addition, during the grading of a thermodynamic model, only four categories of binary systems are retained based on the type of association they exhibit.

In general, for each binary system of the database, ten properties were experimentally determined: liquid phase composition  $x$ , gas phase composition (or second liquid phase composition)  $y$ , three-phase pressure  $P_{LLV}$ , three-phase composition  $z_{LLV}$ , critical pressure  $P_c$ , critical composition  $x_c$ , azeotropic pressure  $P_{azeo}$ , azeotropic composition  $x_{azeo}$ , mixing enthalpy  $h^M$  and mixing heat capacity  $c_p^M$ .

The database developed in [Publication \[21\]](#) could be used to assess the impact of mixing-rules selection and the number of parameters included within. Models such as the Peng-Robinson (PR) EoS armed with classical mixing rules and temperature-dependent binary interaction parameters (BIPs), as well as the PC-SAFT EoS with classical mixing rules, no induced association scheme and no regressed BIPs have been graded following the proposed procedure, recently [\[21,22\]](#).

### **The $tc$ -PR-Wilson model**

In order to test the best approach to extend the  $tc$ -PR model to mixtures, it was decided to include three different  $a_{res}^{E,\gamma}$  models in the mixing rule for  $a_m/b_m$ . Such models were the residual part of the Wilson and UNIQUAC models and the  $a_{res}^{E,\gamma}$  NRTL model. The resulting models were called  $tc$ -PR-Wilson,  $tc$ -PR-UNIQUAC and  $tc$ -PR-NRTL, respectively. The implementation of such models is explained in [Publication \[19\]](#). The performance of the three resulting models was compared against the experimental data of the benchmark database, presented in [Publication \[21\]](#). Indeed, the binary interaction parameters for each model and for each of the 200 binary systems included in the database were fitted over available experimental data.

In the light of the obtained results, it is possible to conclude that the best choice to extend the  $tc$ -PR EoS to mixtures along with EoS/ $a_{res}^{E,\gamma}$  mixing rules is to use the residual part of the Wilson  $a_{res}^{E,\gamma}$  model, named  $tc$ -PR-Wilson. This conclusion is supported by the fact that the  $tc$ -PR-Wilson reaches the best results from the quantitative and qualitative standpoints. Nevertheless, improvements have to be made in terms of the behavior correlation of systems in which hydrogen bonds are broken without the possibility to form new ones, as well as in the reproduction of energetic properties for systems in which self-association does not take place. All the grading results, as well as the representation of some binary mixtures' behavior are summarized in [Publication \[19\]](#).

As stated before, in order to apply the  $tc$ -PR model to mixtures it is necessary to define mixing rules for  $a_m$ ,  $b_m$  and  $c_m$ . For the covolume of the mixture ( $b_m$ ), it has been applied the classical quadratic mixing rule with the generalized formulation of the combining rule proposed by Lorentz for  $b_{ij}$ , where the parameter  $s$  has been set to  $3/2$ . In addition, a linear MR has been chosen for the volume-translation

parameter:  $c_m(z) = \sum_i z_i \cdot c_i$ . To sum up, when applied to a mixture, the  $tc$ -PR EoS writes:



$$P(T, v, z) = \frac{RT}{v + c_m - b_m} - \frac{a_m(T, z)}{(v + c_m)(v + c_m + b_m) + b_m(v + c_m - b_m)}$$

$$\text{with: } \begin{cases} b_m = \sum_i^{n_c} \sum_j^{n_c} z_i z_j \left( \frac{b_i^{2/3} + b_j^{2/3}}{2} \right)^{3/2} & \text{and } c_m = \sum_i^{n_c} z_i \cdot c_i \\ a_m = b_m \left[ \sum_i^{n_c} z_i \frac{a_i}{b_i} + \frac{a_{res}^{E,\gamma}}{\Lambda_{PR}} \right] & \text{with } \Lambda_{PR} = -\sqrt{2}/2 \cdot \ln(1 + \sqrt{2}) \end{cases} \quad (11)$$

## 1.4 Applications

### Correlation of experimental data with high-quality thermodynamic models

Thanks to the proposed database in [Publication \[21\]](#), the benchmark of the PR EoS armed with two set of sophisticated mixing rules was possible. Such mixing rules were the classical VdW mixing rules with temperature-dependent binary interaction parameters, and advanced mixing rules combining the residual part of the Wilson activity coefficient. From such a benchmark it was concluded that both models are good enough to represent complex phase behavior.

This was further illustrated in [Publications \[23\]](#) and [\[24\]](#). In the first one, the phase behavior of the CO<sub>2</sub> (1) + cyclooctane (2) binary system was for the first time experimentally studied between 292.95 K and 373.55 K. In this temperature range, measurements made possible to conclude that the studied binary system probably exhibits a type V phase behavior in the classification scheme of Van Konynenburg and Scott (VKS). Despite the complexity of the phase behavior, the experimental data could be accurately correlated with the Peng-Robinson equation of state combined with sophisticated mixing rules that either involve temperature-dependent binary interaction parameters or that embed the residual part of the Wilson activity coefficient model.

Similarly, in [Publication \[24\]](#), the phase behavior of the CO<sub>2</sub> (1) + 2,3-dimethylbutane (2) binary mixture has been experimentally studied. For this system, experimental results reveal that the vapor-liquid critical locus is a continuous curve between the two pure compounds, meaning that the studied binary system exhibits a type I or II phase behavior in the VKS classification scheme. The experimental data can be very satisfactorily represented by the Peng-Robinson equation of state with mixing rules that embed a temperature-dependent binary interaction parameter.

### Working fluid selection for innovative energy conversion systems

One of the challenges of this thesis was to find the optimal working fluid for the CCHP cycle proposed by Briola [\[25\]](#). As stated in section 1.2, an approach considering thermodynamic, process-related, environmental, flammability and toxicity aspects in the selection process as well as performance assessment was developed in this thesis and presented in [Publication \[26\]](#). The key properties that should be properly predicted in order to ensure the consistency of the approach were: vapor pressure, density, enthalpy and entropy. This task was ensured by a thermodynamic model.

At this point, it was possible to capitalize the experience acquired with the *tc*-PR model for pure compounds and to implement it in a product-design methodology that made possible to screen about 60 000 species included in the DDB, the DIPPR and the NIST TDE 103b databases. The screening coupled with the performance evaluation have demonstrated that flammable fluids such as vinylacetylene or HFC-152 have a good potential for CCHP applications. In the case where highly constraining safety restrictions are imposed, HCFO-1233zd(E) could be an interesting candidate since it is non-flammable and non-toxic.

Another application in this field was the presentation of a predictive version of the Peng-Robinson EoS combined with sophisticated mixing rules that involve temperature-dependent binary interaction parameters [\[27\]](#) for the screening of mixtures for power and refrigeration cycles ([Book chapter \[28\]](#)).

Finally, all the results obtained from the study of cubic and SAFT-type EoS could be used in the future not only in energy-related applications but also in computer-aided process design.

## 1.5 References

- [1] E. Moine, A. Pina-Martinez, J.-N. Jaubert, B. Sirjean, R. Privat, *I*-PC-SAFT: an industrialized version of the volume-translated PC-SAFT equation of state for pure components, resulting from experience acquired all through the years on the parameterization of SAFT-type and cubic models, *Ind. Eng. Chem. Res.* 58 (2019) 20815–20827. <https://doi.org/10.1021/acs.iecr.9b04660>.
- [2] Y. Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent *tc*-PR and *tc*-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and super-critical domains, *Fluid Phase Equilibria.* 429 (2016) 301–312. <https://doi.org/10.1016/j.fluid.2016.09.003>.
- [3] A. Pina-Martinez, Y. Le Guennec, R. Privat, J.-N. Jaubert, P.M. Mathias, Analysis of the combinations of property data that are suitable for a safe estimation of consistent Twu  $\alpha$ -function parameters: updated parameter values for the translated-consistent *tc*-PR and *tc*-RK cubic equations of state, *J. Chem. Eng. Data.* 63 (2018) 3980–3988. <https://doi.org/10.1021/acs.jced.8b00640>.
- [4] N. Ramírez-Vélez, A. Pina-Martinez, J.-N. Jaubert, R. Privat, Parameterization of SAFT models: analysis of different parameter estimation strategies and application to the development of a comprehensive database of PC-SAFT molecular parameters, *J. Chem. Eng. Data.* 65 (2020) 5920–5932. <https://doi.org/10.1021/acs.jced.0c00792>.
- [5] A. Pina-Martinez, R. Privat, J.-N. Jaubert, D.-Y. Peng, Updated versions of the generalized Soave  $\alpha$ -function suitable for the Redlich-Kwong and Peng-Robinson equations of state, *Fluid Phase Equilibria.* 485 (2019) 264–269. <https://doi.org/10.1016/j.fluid.2018.12.007>.
- [6] A. Pina-Martinez, R. Privat, S. Lasala, G. Soave, J.-N. Jaubert, Search for the optimal expression of the volumetric dependence of the attractive contribution in cubic equations of state, *Fluid Phase Equilibria.* 522 (2020) 112750. <https://doi.org/10.1016/j.fluid.2020.112750>.
- [7] A. Pina-Martinez, R. Privat, J. Jaubert, Use of 300,000 pseudo-experimental data over 1800 pure fluids to assess the performance of four cubic equations of state: SRK, PR, *tc*-RK, and *tc*-PR, *AIChE J.* 68 (2022) e17518. <https://doi.org/10.1002/aic.17518>.
- [8] N. Ramírez-Vélez, R. Privat, A. Pina-Martinez, J. Jaubert, Assessing the performance of non-associating SAFT-type equations of state to reproduce vapor pressure, liquid density, enthalpy of vaporization, and liquid heat capacity data of 1800 pure fluids, *AIChE J.* 68 (2022) e17722. <https://doi.org/10.1002/aic.17722>.
- [9] J. Gross, G. Sadowski, Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules, *Ind. Eng. Chem. Res.* 40 (2001) 1244–1260. <https://doi.org/10.1021/ie0003887>.
- [10] J. Gross, G. Sadowski, Application of the perturbed-chain SAFT equation of state to associating systems, *Ind. Eng. Chem. Res.* 41 (2002) 5510–5515. <https://doi.org/10.1021/ie010954d>.
- [11] G.M. Kontogeorgis, P. Coutsikos, Thirty years with EoS/ $g^E$  models—what have we learned?, *Ind. Eng. Chem. Res.* 51 (2012) 4119–4142. <https://doi.org/10.1021/ie2015119>.
- [12] M.-J. Huron, J. Vidal, New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures, *Fluid Phase Equilibria.* 3 (1979) 255–271. [https://doi.org/10.1016/0378-3812\(79\)80001-1](https://doi.org/10.1016/0378-3812(79)80001-1).
- [13] M.L. Michelsen, A modified Huron-Vidal mixing rule for cubic equations of state, *Fluid Phase Equilibria.* 60 (1990) 213–219. [https://doi.org/10.1016/0378-3812\(90\)85053-D](https://doi.org/10.1016/0378-3812(90)85053-D).
- [14] S. Dahl, M.L. Michelsen, High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state, *AIChE J.* 36 (1990) 1829–1836. <https://doi.org/10.1002/aic.690361207>.
- [15] M.L. Michelsen, A method for incorporating excess Gibbs energy models in equations of state, *Fluid Phase Equilibria.* 60 (1990) 47–58. [https://doi.org/10.1016/0378-3812\(90\)85042-9](https://doi.org/10.1016/0378-3812(90)85042-9).
- [16] G.M. Kontogeorgis, G.K. Folas, *Thermodynamic models for industrial applications*, John Wiley & Sons, Ltd, Chichester, UK, 2010. <https://doi.org/10.1002/9780470747537>.
- [17] E. Voutsas, K. Magoulas, D. Tassios, Universal mixing rule for cubic equations of state applicable to symmetric and asymmetric systems: results with the Peng–Robinson equation of state, *Ind. Eng. Chem. Res.* 43 (2004) 6238–6246. <https://doi.org/10.1021/ie049580p>.
- [18] J. Ahlers, J. Gmehling, Development of an universal group contribution equation of state, *Fluid Phase Equilibria.* 191 (2001) 177–188. [https://doi.org/10.1016/S0378-3812\(01\)00626-4](https://doi.org/10.1016/S0378-3812(01)00626-4).
- [19] A. Pina-Martinez, R. Privat, I.K. Nikolaidis, I.G. Economou, J.-N. Jaubert, What is the optimal activity coefficient model to be combined with the *translated-consistent* Peng–Robinson equation of state through advanced mixing rules? Cross-comparison and grading of the Wilson, UNIQUAC, and NRTL  $a^E$  models against a benchmark database involving 200 binary systems, *Ind. Eng. Chem. Res.* 60 (2021) 17228–17247. <https://doi.org/10.1021/acs.iecr.1c03003>.
- [20] J.O. Valderrama, The state of the cubic equations of state, *Ind. Eng. Chem. Res.* 42 (2003) 1603–1618. <https://doi.org/10.1021/ie020447b>.
- [21] J.-N. Jaubert, Y. Le Guennec, A. Pina-Martinez, N. Ramirez-Velez, S. Lasala, B. Schmid, I.K. Nikolaidis, I.G. Economou, R. Privat, Benchmark database containing binary-system-high-quality-certified data for cross-comparing thermodynamic models and assessing their accuracy, *Ind. Eng. Chem. Res.* 59 (2020) 14981–15027. <https://doi.org/10.1021/acs.iecr.0c01734>.
- [22] I.K. Nikolaidis, R. Privat, J.-N. Jaubert, I.G. Economou, Assessment of the perturbed chain-statistical associating fluid theory equation of state against a benchmark database of high-quality binary-system data, *Ind. Eng. Chem. Res.* 60 (2021) 8935–8946. <https://doi.org/10.1021/acs.iecr.1c01234>.

- [23] S. Vitu, A. Pina-Martinez, R. Privat, M. Debaq, J.-L. Havet, J.-L. Daridon, J.-N. Jaubert, Experimental determination and modelling of high-pressure phase behavior for the binary system CO<sub>2</sub> + cyclooctane, *J. Supercrit. Fluids*. 174 (2021) 105249. <https://doi.org/10.1016/j.supflu.2021.105249>.
- [24] S. Zid, J.-P. Bazile, J.-L. Daridon, A. Pina-Martinez, J.-N. Jaubert, S. Vitu, Fluid phase equilibria for the CO<sub>2</sub> + 2,3-dimethylbutane binary system from 291.9 K to 373.1 K, *J. Supercrit. Fluids*. 179 (2022) 105387. <https://doi.org/10.1016/j.supflu.2021.105387>.
- [25] S. Briola, P. Di Marco, R. Gabbrielli, Thermodynamic sensitivity analysis of a novel trigeneration thermodynamic cycle with two-phase expanders and two-phase compressors, *Energy*. 127 (2017) 335–350. <https://doi.org/10.1016/j.energy.2017.03.135>.
- [26] A. Pina-Martinez, S. Lasala, R. Privat, V. Falk, J.-N. Jaubert, Design of promising working fluids for emergent combined cooling, heating, and power (CCHP) systems, *ACS Sustain. Chem. Eng.* 9 (2021) 11807–11824. <https://doi.org/10.1021/acssuschemeng.1c03362>.
- [27] J.-N. Jaubert, J.-W. Qian, S. Lasala, R. Privat, The impressive impact of including enthalpy and heat capacity of mixing data when parameterising equations of state. Application to the development of the *E*-PPR78 (Enhanced-Predictive-Peng-Robinson-78) model., *Fluid Phase Equilibria*. 560 (2022) 113456. <https://doi.org/10.1016/j.fluid.2022.113456>.
- [28] S. Lasala, A. Pina-Martinez, J.-N. Jaubert, A predictive equation of state to perform an extending screening of working fluids for power and refrigeration cycles, in: S. Lasala (Ed.), *Org. Rank. Cycles Waste Heat Recovery - Anal. Appl.*, IntechOpen, 2020. <https://doi.org/10.5772/intechopen.92173>.